Evaluate Wetland Systems for Treated Wastewater Performance to Meet Competing Effluent Water Quality Goals

WateReuse Research Foundation

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About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations.

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ACRONYMS

APAI	Alan Plummer Associates, Inc.
API	American Petroleum Institute
AWT	advanced wastewater treatment
BOD	biochemical oxygen demand
Br	bromide
BU	Baylor University
$CBOD_5$	carbonaceous biochemical oxygen demand
CCV	continuing calibration verfication
COD	chemical oxygen demand
DBP	disinfection by-product
DI	deionized
DO	dissolved oxygen
DOC	dissolved organic carbon
EDTA	ethylenediaminetetraacetic acid
ESI	electrospray interface
ET	evapotranspiration
FWS	free water surface
GLM	general linear model
GWSWWRF	George W. Shannon Wetlands Water Recycling Facility
HAA	haloaceticacid
HLB	hydrophilic-lipophilic balance
HLR	hydraulic loading rate
hr	hour
HRT	hydraulic retention time
IWA	International Water Association
LC-MS/MS	liquid chromatography/mass spectrometry/mass spectrometry
Li	lithium
LiBr	lithium bromide
mg/L	milligrams per liter
MGD	million gallons per day
MLRs	mass loading rates
mTorr	milliTorr
N	nitrogen
NaBr	sodium bromide
NADB	North American Treatment Wetland Database
NDMA	nitrosodimethylamine
ng/L	nanograms per liter
NH_4	ammonia nitrogen
NO_3	nitrate nitrogen
N2	nitrogen gas
P	phosphorus
PAC	Project Advisory Committee
PFD	plug flow with dispersion
psi	pounds per square inch
QAQC	quality assurance/quality control
RAC	Research Advisory Committee

SF	surface flow
SPE	solid-phase extraction
SPSS	SPSS Inc.
SRC	Syracuse Research Corporation
SSF	subsurface flow
TCEQ	Texas Commission on Environmental Quality
TDS	total dissolved solids
THM	trihalomethane
TIS	tanks-in-series
TN	total nitrogen
TP	total phosphorus
TRWD	Tarrant Regional Water District
TSS	total suspended solids
UC	University of California
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet
v/v	volume per volume
WDOCs	wastewater-derived organic compounds
WERF	Water Environment Research Foundation
WRF	WateReuse Research Foundation

FOREWORD

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse research topics including:

- Defining and addressing emerging contaminants
- Public perceptions of the benefits and risks of water reuse
- Management practices related to indirect potable reuse
- Groundwater recharge and aquifer storage and recovery
- Evaluation and methods for managing salinity and desalination
- Economics and marketing of water reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners include the Bureau of Reclamation, California State Water Resources Control Board, the California Energy Commission, Foundation subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and other funding relationships.

The WateReuse Research Foundation, as well as many other research, academic, and regulatory groups, recognizes the need to develop cost-effective tools to provide effective environmental protection. Although water reuse is a primary objective of the Foundation, benefits of this recycling option for wastewaters are dependent on a high standard for protection of environmental and human health. This wetland system evaluation project was contracted to review and summarize the current state-of-understanding of the use of constructed treatment wetlands for removal of a broad range of pollutants.

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EXECUTIVE SUMMARY

Development and use of advanced wastewater treatment technologies have greatly improved water quality of receiving waters over the past four decades. However, advances in analytical chemistry and molecular biology in the past decade have also indicated effects of trace level wastewater-derived organic compounds (WDOCs) on biota. Although multiple factors have been identified that may contribute to the observed WDOC effects on wildlife, potential for adverse ecological effects in effluent-dominated receiving waters raise questions about treated effluent used for augmentation of aquatic habitats and the safety of intentional and unintentional indirect potable water reuse.

Constructed wetlands are used to consistently and cost effectively reduce concentrations of conventional pollutants in reclaimed waters and can further reduce levels of certain WDOCs. A brief synopsis is provided regarding the current understanding of processes and performance of constructed treatment wetlands with a focus on their application for improving the quality of municipal effluents and especially reclaimed water intended for beneficial reuse. Existing data indicate that wetlands can effectively reduce both conventional pollutants as well as degradable and adsorbable trace organic contaminants.

Microcosm studies were utilized to identify key removal mechanisms for eight target analytes. Results indicated that bacteria treatment significantly influenced reduction of acetaminophen, atenolol and codeine, but not diltiazem and diazepam. Photolysis appeared to be an important mechanism for reduction of acetaminophen, codeine and diltiazem; but not as important for diazepam and atenolol. Although the presence of bacteria increased reduction of atenolol and diazepam, both molecules appeared relatively recalcitrant compared to acetaminophen, codeine, and diltiazem. Among all the compounds tested, diazepam was the most stable across the experimental treatment structure. Both photolysis and bacterial transformation appeared to be particularly important degradation pathways for acetaminophen.

A pilot-scale constructed wetland located at Pecan Creek Water Reclamation Plant in Denton, TX was spiked with both pharmaceuticals and steroids. Both lithium and bromide were used as tracers to determine hydraulic retention time of flows through the wetland system during the spiking events. The pilot-scale study involved testing both a cold season event and a warm season event. Each of these events provided information valuable to this research effort; however, operational issues involving regulation of the inlet flow resulted in the hydraulic retention time (HRT) during the cold season spiking study being much shorter than expected, which limited the amount of data developed during this event. The only steroid hormone detected in the wetland outflow samples during the cold season spiking event was ethinyl estradiol, which decreased from a concentration of approximately 20 ng/L 40 hours after spiking to less than 1 ng/L at 60 hours. On the basis of the lithium recovery (i.e., comparing the concentration of lithium detected at 40 hours with the maximum concentration detected in the subsequent study), it was concluded that the HRT was less than 24 hours during the cold-season study. However, the steroid hormone data for this study are consistent with removal of 17β-estradiol, testosterone, and progesterone. With the limited data developed from the cold season spiking event, it was difficult to determine if ethinyl

estradiol, which is the most recalcitrant of the steroid hormones, was removed during passage through the pilot-scale wetland.

Adjustments to the inflow to the pilot-scale wetland were made and several tracer studies conducted to confirm improvement in the HRT within the wetland prior to initiating the warm season spiking event. As a result, the warm season spiking study yielded results that provided insight into the removal of WDOCs in the wetland because the HRT was longer and samples were collected before, during, and after the pulse reached the outlet. Data on the concentration of the lithium tracer indicated that breakthrough of the spike started between 24 and 48 hours after spiking. The peak concentration of lithium was detected 74 hours after spiking. Lithium concentrations decreased by approximately 25% between the peak and the end of sample collection (i.e., 120 hours after spiking). All pharmaceutical concentrations in the outflow of the City of Denton wetland were reduced by the end of the study (at 120 hours), suggesting removal of these target analytes by this pilot-scale constructed wetland facility. Specifically, at the 120-hr sampling event, acetaminophen, atenolol, codeine, diazepam, diphenhydramine, diltiazem, gemfibrozil, and propranolol levels at the wetland outflow were 95.3%, 99%, 81.1%, 92.2%, 56.4%, 89.4%, 95.2%, and 81.4%, respectively, less than introduced concentrations in the wetland inflow at sample time 0.

Among the steroid hormones, ethinyl estradiol and 17β-estradiol were detected at concentrations up to approximately 6 ng/L after the spike. For comparison, municipal wastewater typically contains between 0.2 and 2 ng/L of 17β-estradiol and between 0.05 and 1 ng/L of ethinyl estradiol. The highest concentrations of both steroid hormones were detected 60 hours after spiking, which coincides with the highest concentrations of lithium measured in the wetland effluent. Furthermore, the concentration of ethinyl estradiol was always greater than that of 17β-estradiol, which is consistent with the resistance of ethinyl estradiol to biotransformation. The calculated removal rate for 17β-estradiol and ethinyl estradiol based on concentrations detected at the 120-hr sampling event indicated 99.9% removal.

Among the remaining steroid hormones, testosterone and progesterone were never detected and estrone (which was not spiked into the wetland) was consistently detected at concentrations between 5 and 10 ng/L, which is consistent with concentrations typically detected in municipal wastewater effluent. These data suggest that the wetland removed testosterone and progesterone but not estrone.

In addition to the pilot-scale wetland spiking studies, a performance assessment was conducted for a large-scale, 243-acre constructed wetland owned and operated by the Tarrant Regional Water District. This wetland system is operated primarily to remove or reduce conventional constituents. The assessment of 3.5 years of operating data for this wetland system confirmed that its performance is similar to the results reported for other wetlands. Operational data also indicated dense plant cover, shallow water depths, and good flow distribution are important for improved removal performance for nitrogen and phosphorus. Correlation of hydraulic and mass loading rates with wetland treatment area is also critical to achieving treatment objectives. Operational lessons learned at this large-scale constructed wetland are applicable to constructed wetland operations for treating WDOCs.

Research and analyses undertaken by this project supports continuing consideration of constructed wetlands as an option for providing polishing treatment to protect aquatic ecosystems and potable water supplies. The findings of the project indicate that constructed wetlands can be used to consistently and cost effectively reduce concentrations of

conventional pollutants remaining in reclaimed waters and can also further reduce levels of certain WDOCs. The research conducted for this project demonstrated potential efficiency for removal of WDOCs but also illustrated the highly individualistic properties that are important in these removal processes. Additional research is needed to better describe the effectiveness of constructed wetlands for polishing of individual trace organic compounds and for extrapolation to other unstudied compounds.

CHAPTER 1

INTRODUCTION

1.1 PROJECT BACKGROUND

Municipal wastewater effluent discharges impact water quality and the aquatic ecosystems of waterbodies into which they are discharged. This has been known for more than a century. The potential impact of conventional constituents (oxygen-demanding substances, total suspended solids (TSS), nitrogenous compounds, phosphorus compounds) have been the focus of developing wastewater treatment technologies for the past four decades, and technological advances have enabled effective removals and/or reductions in loadings to nonproblematic levels in most developed countries. Through employment of these advanced treatment technologies, we have greatly improved receiving water quality and come closer to realizing the Clean Water Act's objective of making our surface waters swimmable, fishable, and drinkable.

However, subtle changes are being seen in our fish, waterfowl, and wildlife in waters that receive a significant portion of their overall flow from wastewater treatment plants (Daughton and Ternes, 1999; Desbrow et al., 1998; Jobling et al., 1998; Routledge et al., 1998). Although multiple factors have been identified that may contribute to the observed effects on wildlife, these changes are especially troubling to utilities in water-stressed regions because wastewater effluent is increasingly being used for augmentation of aquatic habitats. Furthermore, adverse ecological effects in effluent-dominated receiving waters raise questions about the safety of intentional and unintentional indirect potable water reuse. In the last decade, significant advances have been made in our ability to detect trace levels of both synthetic and naturally occurring constituents (Sedlak et al., 2000). Our ability to quantify WDOCs has progressed to where parts-per-trillion levels are routinely identifiable. Coincident with our advances in analytical chemistry, improvements in molecular biology have facilitated major developments in aquatic toxicology. These advances have allowed us to document previously unknown effects of contaminants on aquatic organisms and have shown that the trace levels of contaminants in effluent can cause subtle impacts on biota.

The capability of identifying trace contaminants and the knowledge that these can cause measurable negative impacts leads to the pressing need to research and evaluate treatment technologies that can cost effectively remove these contaminants. Constructed wetlands provide one possible technology for achieving these goals. Wetlands engineered for wastewater treatment employ natural treatment mechanisms that improve water quality. These treatment mechanisms are largely driven by natural energies including sunlight, wind, rain, and the storage of potential energy in biomass (both plants and animals) and soils resulting in the transformation and degradation of pollutants that occur in conventional wastewaters into harmless byproducts or essential nutrients used for additional biological productivity. Through the capture of these natural energies, wetland systems typically use much less fossil fuel inputs than conventional wastewater treatment systems, thereby, substantially reducing the operating and maintenance costs associated with the treatment processes. A growing body of research data is indicating that constructed treatment wetlands may be effective for reducing the concentrations of a variety of WDOCs.

1.2 CONSTRUCTED WETLANDS AND WDOCs

Treatment wetlands are being used to improve the quality of wastewaters and stormwaters throughout the United States and the world. Whereas treatment wetland technology originated with the use of natural wetlands receiving contaminated waters, the focus of this report is the use of constructed wetlands to provide water quality benefits. Design information and operational performance data for constructed treatment wetlands have accumulated over the last four decades, and assessment of those data has led to subsequent design changes and improved performance. Environmental engineers and scientists have compiled and synthesized design and performance data from thousands of treatment wetland systems in order to elucidate design versus performance relationships. A brief synthesis of the current understanding of processes and performance of constructed treatment wetlands with a focus on their application for improving the quality of municipal effluents and especially reclaimed water intended for beneficial reuse is provided in this document.

Recent improvements in the sensitivity of analytical instruments have resulted in the detection of a variety of organic compounds in wastewater effluent and wastewater-receiving surface waters (Ternes, 1998; Kolpin et al., 2002). Some of these compounds (i.e., WDOCs) pose potential threats to aquatic organisms or downstream drinking water supplies. For example, steroid hormones in wastewater effluent have been linked to feminization of fish in effluent-dominated surface waters (Desbrow et al., 1998) and the potent carcinogen, nitrosodimethylamine (NDMA), is often present in municipal wastewater effluent at concentrations that are more than an order of magnitude higher than levels considered safe for drinking waters (Sedlak et al., 2005).

In response to concerns about the presence of WDOCs, utilities have adopted different approaches for removing or destroying trace concentrations of organic compounds after conventional biological wastewater treatment. The use of oxidants such as free chlorine (Pinkston and Sedlak, 2004; Westerhoff et al., 2005; Bedner and Maccrehan, 2006) or ozone (Huber et al., 2005) provides a convenient way of removing contaminants during wastewater disinfection. Alternatively, wastewater-derived contaminants can be removed by reverse osmosis or nanofiltration (Xu et al., 2005; Yoon et al., 2007). Although the use of chemical oxidation and membrane treatment processes can lower the concentration of WDOCs, neither method can remove all of the compounds present in wastewater effluent (Sedlak et al., 2005; Bellona et al., 2004; Mitch et al., 2003). Furthermore, concerns have been raised about the possible formation of toxic products from chemical oxidation of wastewater (Bedner et al., 2006), high costs associated with the disposal of membrane concentrates (Nghiem and Schafer, 2006) and the overall costs and energy use associated with advanced treatment processes (Jones et al., 2007).

Natural attenuation of chemical contaminants may provide an effective alternative to engineered unit processes for the removal of WDOCs. Both riverbank filtration (Heberer et al., 2004) and soil aquifer treatment (Drewes et al., 2002) have been used for more than three decades to remove WDOCs prior to indirect potable water reuse. However, many wastewater treatment plants are situated in locations that are not amenable to subsurface discharges of large volumes of water (e.g., they are located in areas with high water tables or impermeable soils). In these cases, constructed treatment wetlands offer an alternative means of achieving many of the same objectives while also obtaining the ancillary benefits provided by wetlands (e.g., wildlife habitat, nutrient removal, nature study). Despite the overall promise of treatment wetlands, our understanding of the fate of WDOCs in these systems is limited. Therefore, it is important that research be performed to increase the understanding of the performance of wetlands for removal of WDOCs.

1.3 CONSTRUCTED WETLANDS REFERENCES

A continuing series of publications have been devoted to summarizing and assessing the treatment wetland technology. Currently, the most detailed book that summarizes the design and performance of constructed wetlands for water quality improvement is the second edition of *Treatment Wetlands* (Kadlec and Wallace, 2009). This book offers constructed wetland performance and design guidance for most conventional pollutants of concern in municipal, industrial, and stormwater effluents. The most inclusive treatment wetland handbook that includes both performance information and descriptions of the ecological response of constructed wetlands is the first edition of *Treatment Wetlands* (Kadlec and Knight, 1996).

Another recent data compilation on smaller-scale constructed treatment wetlands is: *Small-Scale Constructed Wetland Treatment Systems: Feasibility, Design Criteria, and O&M Requirements* published by the Water Environment Research Foundation (WERF; Wallace and Knight, 2006). The WERF study compiled and assessed data from 1,640 small-scale constructed wetlands (defined as a design flow less than 2,000 m^3/d (528,000 gal/d) and a size less than 6 ha (14.8 ac)). Prior to the WERF study other technological assessments devoted to specific aspects of treatment wetlands were published.

A selection of additional relevant synthesis documents published in the last decade and applicable to the WRF Wetland System Evaluation Project includes:

- *Constructed Wetlands for Pollution Control Processes, Performance, Design, and Operation*, a worldwide synopsis of treatment wetland design and performance (International Water Association [IWA], 2000);
- *Constructed Wetlands Treatment of Municipal Wastewaters*, a constructed treatment wetland design handbook (U.S. Environmental Protection Agency [USEPA], 2000);
- *Free Water Surface Wetlands for Wastewater Treatment: A Technology Assessment*, a technology assessment for free water surface wetlands (USEPA, 1999);
- *Constructed Wetlands for Animal Waste Treatment*, a design manual for confined animal feeding operation treatment wetlands (Payne, 2002) and *Constructed Wetlands for Livestock Wastewater Management*, a database performance summary for these systems (CH2M HILL and Payne Engineering, 1997);
- *Use of Constructed Wetland Effluent Treatment Systems in the Pulp and Paper Industry*, a review of treatment wetlands used in the pulp and paper industry (Knight, 2004); and
- *The Use of Treatment Wetlands for Petroleum Industry Effluents*, a review of constructed wetland systems used to treat petroleum effluents (American Petroleum Institute [API], 1998).

In addition to these synthesis documents, there is a growing list of International Water Association (IWA) symposia proceedings that present peer-reviewed results of treatment wetland research projects worldwide:

- 1st International Conference on Wetland Systems for Water Pollution Control, Chattanooga, TN, 1988
- 2nd International Conference on Wetland Systems for Water Pollution Control, Cambridge, England, 1990
- 3rd International Conference on Wetland Systems for Water Pollution Control, Sydney, Australia, 1992

- 4th International Conference on Wetland Systems for Water Pollution Control, Guangzhou, China, May 1994
- 5th International Conference on Wetland Systems for Water Pollution Control, Vienna, Austria, September 1996
- 6th International Conference on Wetland Systems for Water Pollution Control, Aguas de Sao Pedro, Brazil, September/October 1998
- 7th International Conference on Wetland Systems for Water Pollution Control, Orlando, FL, November 2000
- 8th International Conference on Wetland Systems for Water Pollution Control, Dar es Salaam, Tanzania, September 2002
- 9th International Conference on Wetland Systems for Water Pollution Control, Avignon, France, September 2004
- 10th International Conference on Wetland Systems for Water Pollution Control, Lisbon, Portugal, September 2006
- 11th International Conference on Wetland Systems for Water Pollution Control, Indore, India, November 2008

CHAPTER 2

WETLAND SYSTEM EVALUATION PROJECT

2.1 PROJECT OBJECTIVES

The WateReuse Research Foundation (WRF) as well as many other research, academic, and regulatory groups recognize the need to develop cost-effective tools to provide effective environmental protection. Whereas reuse of reclaimed water is a primary objective of WRF, benefits of this recycling option for wastewaters are dependent on a high standard for protection of environmental and human health. The Wetland System Evaluation Project was contracted to review and summarize the current state-of-understanding of the use of constructed treatment wetlands for removal of a broad range of pollutants, including WDOCs.

The objective of the Wetland System Evaluation Project is to develop a design and performance matrix for known pollutants in surface-flow and subsurface-flow constructed wetland systems, including biochemical oxygen demand (BOD), total suspended solids (TSS), nutrients, pathogens, and WDOCs. This objective also includes the identification of specific chemicals to best represent or act as surrogates for various classes of pollutants and WDOCs. Although this project is not expected to answer all of the many questions related to the use of wetlands for water quality improvement, it is intended to provide an assessment of the current state of our knowledge about the effectiveness of these natural treatment systems to meet water quality goals.

The technology assessment presented in this document summarizes the current understanding of important processes and performance expectations relevant to wetlands designed for treatment of municipal wastewaters. Removal of conventional pollutants and a limited number of trace metals and organics are addressed. This review also summarizes previous research on the use of constructed treatment wetlands for the removal of wastewater-derived contaminants, identifies important factors affecting contaminant removal, and identifies research needed to develop more efficient and effective constructed wetland treatment systems. The Wetland System Evaluation Project was conducted to examine potential removal of selected hormones and pharmaceuticals through microcosm experiments and spiking studies of a pilot-scale constructed wetland. The microcosm studies were utilized to identify mechanisms associated with removal of the tested compounds. Performance of a large-scale constructed wetland was also evaluated from a perspective of identifying critical design and operating parameters affecting treatment performance.

2.2 RESEARCH PRINCIPAL TASKS

The Wetland System Evaluation Project included four principal tasks as follows:

1. A literature search on the fate of conventional pollutants and WDOCs through wetland systems and the impacts of design and operational parameters on the performance of constructed wetland treatment systems.
2. A research study to assess the fate of a spiked solution of pharmaceuticals, steroidal hormones, and personal care products within a set of bench-scale microcosms (20-gallon glass aquaria) adjacent to the pilot-scale wetland located at the Pecan Creek Water Reclamation Plant in Denton, Texas.

3. Monitoring the fate of a spiked solution of pharmaceuticals, steroidal hormones, and personal care products through a well-established pilot-scale wetland receiving effluent from the Pecan Creek Water Reclamation Plant.
4. Evaluation of an existing large-scale constructed wetland project database (Tarrant Regional Water District's Field-Scale Wetland near Corsicana, Texas) to validate the literature review and to model the fate of conventional constituents through a large, well-established wetland system.

2.3 RESEARCH APPROACH

The following describes the major components of the research approach:

2.3.1 Assemble Available Information

An extensive literature search and review was performed. The literature search included assembling information for constructed wetlands and for WDOCs. The constructed wetlands information is included in Chapters 3, 4, and 5. Chapter 6 presents information regarding WDOCs.

2.3.2 Conduct Microcosm Studies

A series of microcosm studies were performed to examine the treatment effectiveness under alternative experimental designs that involved testing with and without bacteria and with and without plants. The experimental units were seeded with eight different target analytes. Results of these studies are presented in Chapter 7.

2.3.3 Pilot-Scale Constructed Wetland Evaluation

A pilot-scale constructed wetland was operated to polish treated effluent from a wastewater treatment plant. The effluent was spiked with two different sets of analytes: pharmaceuticals and steroids. Both lithium and bromide were used as tracers to aid in the development of the hydraulic retention time of water flowing through the wetlands. Results of the pilot-scale evaluation is presented in Chapter 7.

2.3.4 Large-Scale Constructed Wetland Evaluation

An assessment was made of the performance of a large-scale constructed wetland that has been operating primarily to remove/reduce conventional constituents. The performance of this large-scale constructed wetland was examined in light of the performance of wetlands presented in the literature. Lessons learned from the operation of this wetland are applicable to operations of a constructed wetland applied to treating WDOCs. Chapter 7 presents information about the large-scale wetland.

2.4 DEVELOP CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations were prepared based on the findings of the various project tasks and are presented in Chapter 8.

2.5 IDENTIFY RESEARCH NEEDS

The knowledge gained through the current research performed for this project has helped to define specific issues for which further research should be performed. These identified research needs are presented in Chapter 9.

CHAPTER 3

CONSTRUCTED TREATMENT WETLANDS

3.1 INTRODUCTION

Two general types of constructed treatment wetlands have been widely used to treat municipal wastewater. These treatment wetland types are Surface Flow (SF) also called Free Water Surface (FWS), and Subsurface Flow (SSF) systems. SF treatment wetlands closely mimic natural marshes and can provide ancillary benefits for wildlife habitat in addition to their primary purpose of water quality purification. SSF wetlands are typically used to isolate incompletely treated industrial and domestic wastewaters from humans and wildlife and are often preferred in cold climate regions. Figure 3.1 provides a schematic illustration of these common treatment wetland types. Each wetland type is briefly described in this chapter.

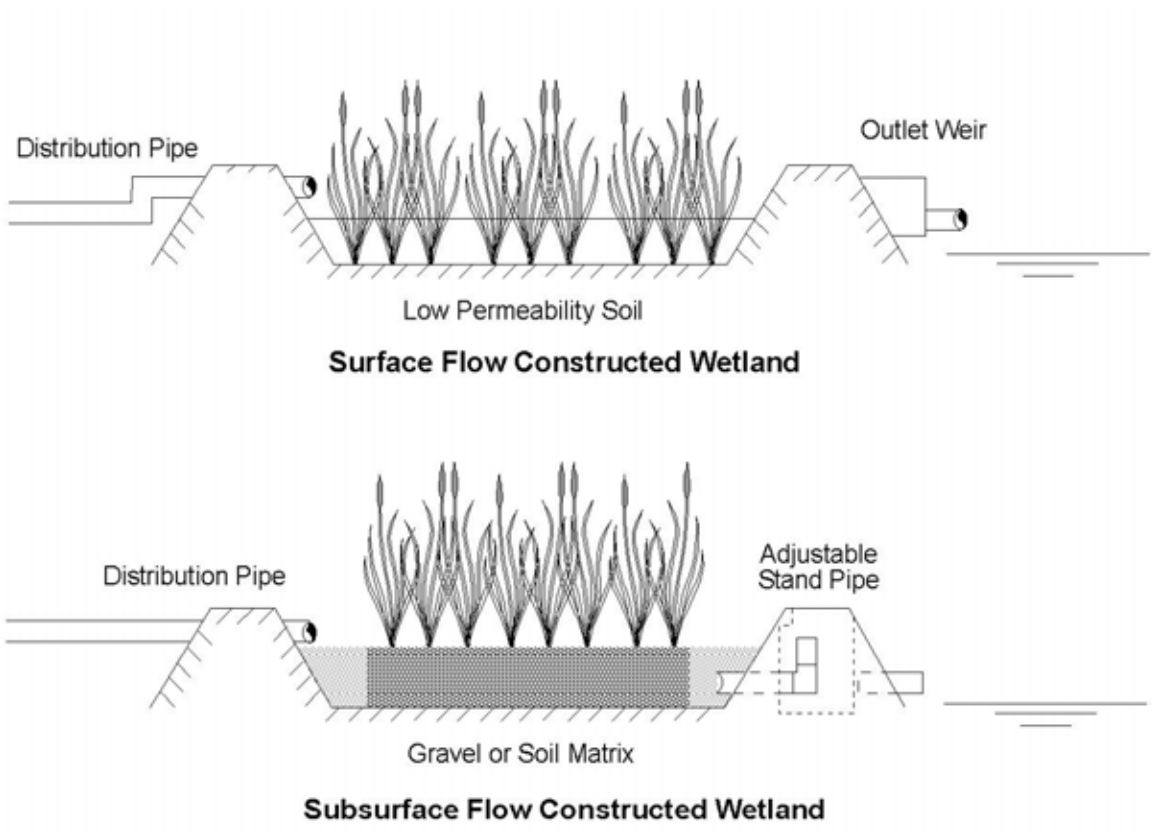


Figure 3.1. Major categories of constructed treatment wetlands. Adapted from Kadlec and Knight, *Treatment Wetlands*, CRC Press (Boca Raton, FL, 1996). Copyright 1995 by Taylor & Francis Group LLC. Reproduced with permission.

3.2 SURFACE FLOW (FREE WATER SURFACE) TREATMENT WETLANDS

3.2.1 General Properties of SF Treatment Wetlands

A constructed SF treatment wetland closely mimics a natural wetland system with regard to vegetation and hydrologic regime. Wastewater in a SF treatment wetland typically enters at one or more inlet point(s), flows over the surface of the soil and through a relatively dense emergent wetland plant community, and discharges at an outlet point. As the wastewater flows through a SF wetland, pollutants with concentrations that are elevated above normal wetland background concentrations are treated by the processes of sedimentation, filtration, oxidation, reduction, adsorption, and precipitation (USEPA, 2000). A decrease following a first-order or exponential curve in pollutant concentrations generally results as the water flows through the wetland (Figure 3.2). In some cases, water will flow into a SF treatment that does not contain a surface discharge. Instead, in these closed-water systems, water hydrates the wetland community and then exits the wetland through evaporation and infiltration to the underlying groundwater.

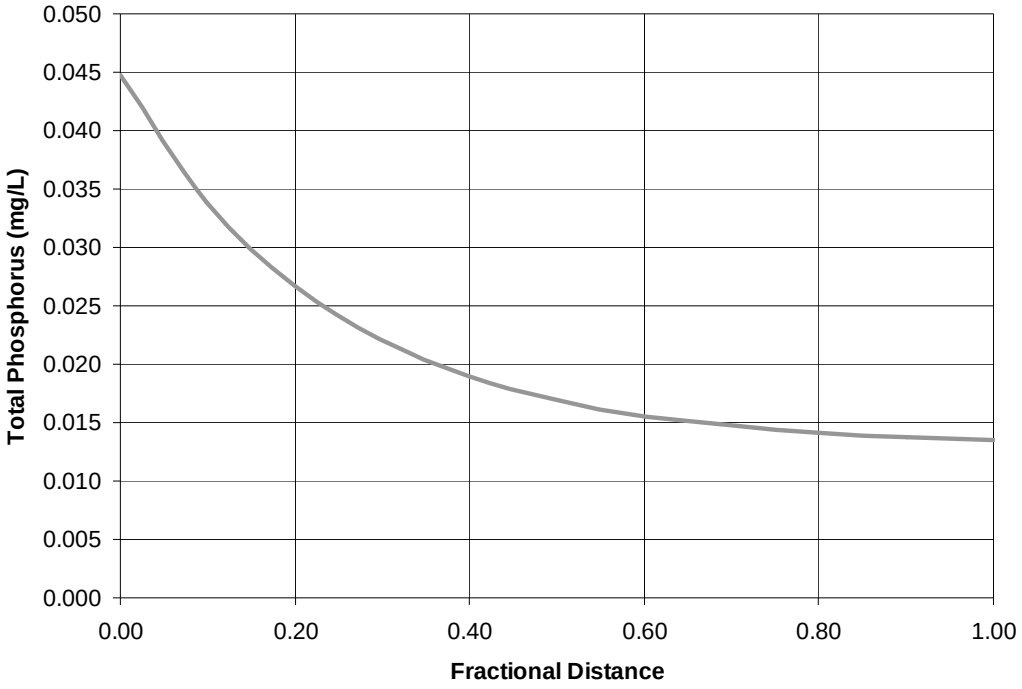


Figure 3.2. Example of pollutant concentration reduction through a constructed treatment wetland.

The most common applications for constructed SF treatment wetlands for municipal wastewater management in the United States are providing advanced secondary treatment (additional BOD reduction as well as nitrification/denitrification for effluents from facultative and aerated lagoons, trickling filter plants, and activated sludge systems) and final effluent polishing for advanced secondary and tertiary municipal effluents (Kadlec and Knight, 1996, Wallace and Knight, 2006). Constructed SF treatment wetlands are rarely used for primary or

secondary treatment of municipal wastewaters in the United States because of potential human exposure to pathogens and the relatively higher levels of ammonia, which can create highly reducing conditions that retard plant growth. Constructed SF treatment wetlands are best suited for temperate-to-warm climates because biological decomposition diminishes with decreasing water temperature and ice formation may impair or prevent winter operations (Wallace and Knight, 2006).

Constructed SF treatment wetlands typically consist of a shallow unlined or lined earth basin excavated into the soil or entirely surrounded by earthen embankments; inlet and outlet water control structures that control water depths within a limited range of depths (typically 15 to 60 cm); and a dense cover of rooted emergent herbaceous wetland plants adapted to growing in wetland conditions (e.g., cattails, bulrush, or comparable). Deeper wetland zones are often incorporated into constructed SF treatment wetlands to facilitate inlet distribution, outlet collection, and effective hydraulics within the SF wetland (Kadlec and Knight, 1996). These deep zones may or may not be dominated by floating and/or submerged aquatic plants such as duckweed, pond weed, filamentous algae, and so forth (IWA, 2000). Compared to SSF wetlands described in the following, constructed SF wetlands typically cost less to construct on a per-area and per-flow basis and provide greater flow control and less chance for hydraulic failure. Because constructed SF treatment wetlands mimic natural wetland communities, they often provide exceptional wildlife habitat and recreational opportunities (Knight et al., 2001). For instance, the Show Low/Pintail Lake wetlands in Arizona, the Arcata Marsh in northern California, and the Orlando Easterly and Green Cay wetlands in Florida are all highly popular hiking and birding locations.

3.2.2 Wetland Plants in Constructed SF Treatment Wetlands

Wetland plants are essential in SF treatment wetlands because they provide structure and a source of reduced carbon for the microbes that mediate most of the pollutant transformations that occur (IWA, 2000). The metabolism of these beneficial microbial communities is fueled by wetland plant litterfall and the resulting decomposition of organic plant material. Plants selected for SF treatment wetlands must be able to tolerate continuous flooding, low and often fluctuating oxygen levels, and often variable and elevated concentrations of pollutants. The particular plant species chosen for SF systems are of less importance than establishing a vigorous and productive stand of wetland vegetation (Wallace and Knight, 2006). The adapted wetland species that are most often used in SF constructed wetlands are persistent emergent plants such as cattails (*Typha* spp.), bulrushes (*Schoenoplectus* spp.), and common reed (*Phragmites australis*; Kadlec and Knight, 1996).

Constructed SF treatment wetlands function as land intensive and low energy biological treatment systems (Kadlec and Knight, 1996; USEPA, 2000). Although these treatment wetlands are somewhat self-sustaining, hydrologic and nutrient loading must be maintained within the tolerance levels of the wetland plant community (Wallace and Knight, 2006). A common misconception in designing SF treatment wetlands is that it is possible to increase water depth and resulting hydraulic retention time in order to increase treatment performance (USEPA, 2000). This effect has not been shown in actual performance data, indicating that SF wetland processes are primarily area-dependent and not volume dependent (IWA, 2000; Wallace and Knight, 2006). Also, increasing water depths greater than about 30 to 45 cm is detrimental to performance because of the intolerance of most wetland emergent plant species to excessive water depths and the resulting loss of vegetative cover and production of reduced carbon (Kadlec and Knight, 1996). Deeper open-water zones that do not colonize with emergent plants are often incorporated into the design of SF treatment wetlands, in spite of

their lower treatment performance per unit area, and are intended to improve hydraulics, promote sedimentation, and enhance wildlife habitat.

3.2.3 Removal Processes in SF Treatment Wetlands

Constructed SF treatment wetlands function as land-intensive biological treatment systems (Figure 3.3). Wetland water quality enhancement is correlated more with the wetland surface area than with wetland volume and hydraulic residence time. Wetland plant productivity and carbon production is directly correlated with the amount of incoming sunlight. Most microbial wetland processes occur in relation to the biomass of plants and the microbial populations at the water:soil interface. Inflow water containing particulate and dissolved pollutants slows and spreads through a large area of shallow water and emergent vegetation. Particulates (typically measured as TSS) tend to settle and are trapped because of lowered flow velocities and sheltering from wind. These particulates contain oxygen-demanding components, fixed forms of total nitrogen (TN) and total phosphorus (TP), and trace levels of metals and organics. These insoluble pollutants enter into and are subsequently transformed by the biogeochemical element cycles within the water column and surface soils of the wetland. At the same time, a fraction of the dissolved BOD, TN, TP, and trace elements are sorbed by soils and active microbial and plant populations throughout the wetland environment. These dissolved elements also enter the overall mineral cycles of the wetland ecosystem.

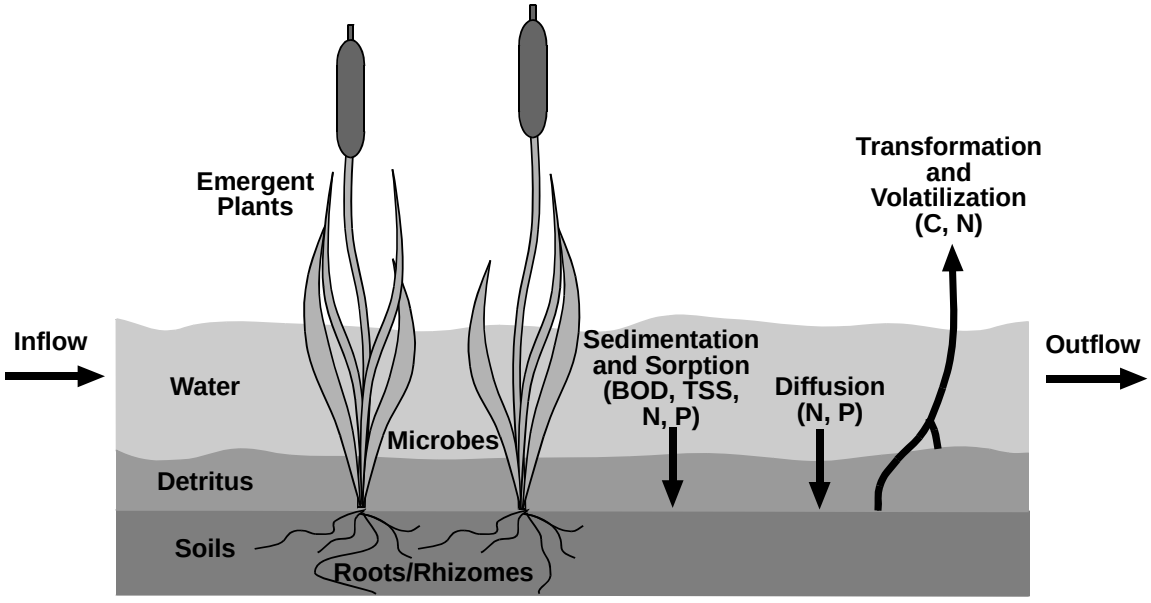


Figure 3.3. Wetland processes include sedimentation, chemical sorption, and microbial transformations of wastewater pollutants (adapted from ADEQ 1995).

SF treatment wetlands have some properties in common with facultative lagoons and also have some important structural and functional differences. Water column processes in deeper zones within treatment wetlands are nearly identical to ponds with a surface autotrophic zone dominated by planktonic or filamentous algae, or by floating or submerged aquatic macrophytes. Deeper zones tend to be dominated by anaerobic microbial processes in the

absence of light. However, shallow emergent macrophyte zones in treatment wetlands and aerobic lagoons may be quite dissimilar. Emergent wetland plants tend to cool and shade the water surface reducing algae growth and limiting water column processes that create dissolved oxygen. Net carbon production in emergent wetlands tends to be high compared to facultative ponds because of high gross primary production in the form of structural carbon accompanied by resistance to degradation and low organic carbon decomposition rates in the oxygen-deficient water column. This high carbon availability and the short diffusional gradients in shallow wetlands results in differences in biogeochemical cycling compared to ponds and lagoons.

During the process of elemental cycling within the wetland, chemical-free energy is extracted by heterotrophic biota (including detritivorous macroinvertebrates, bacteria, and fungi), and fixed carbon and nitrogen are lost to the atmosphere. A smaller portion of the phosphorus and other nonvolatile elements such as trace metals can be lost from the mineral cycle and buried in accreting sediments within the wetland. Wetlands are autotrophic ecosystems, and the additional fixed carbon and nitrogen from the atmosphere is processed simultaneously with the pollutants introduced from the wastewater source. The net effect of these complex processes is a general reduction of pollutant concentrations between the inlet and outlet of treatment wetlands. However, because of the internal autotrophic processes of the wetland, outflow pollutant concentrations seldom are zero, and, in some cases for some parameters, may exceed inflow concentrations. For example, high pretreatment levels in some wastewater reclamation facilities can achieve concentrations of TSS and BOD that are lower than normal treatment wetland background concentrations.

Incoming wastewater plant effluents containing particulates and dissolved pollutants enter the wetland and spread slowly throughout the wetland basin contacting the extensive surface area of the emergent plants and plant detritus (dead plant material). Particulates, often measured as TSS, tend to settle and become entrapped by the subaqueous plant biomass, submerged debris, and soil sediments (Wallace and Knight, 2006). Particulate organic matter and mineral solids (sand, silt, clay) are removed from the water column near the inflow point to the SF wetland. Gravitational settling of TSS is enhanced by the slow water velocity and to a smaller extent by the filtering and trapping effect of plant stems and leaves. Plant stems and leaves also reduce resuspension of settled particles by reducing the impact of wind mixing and wave action.

Replenishment of oxygen within the wetland environment—by atmospheric diffusion, wind and wave-induced mixing, and photosynthesis—is critical to fueling the aerobic component of the microbial population, whereas adjacent anaerobic zones, with low oxidation-reduction potentials caused by the high organic matter content of the wetland, support anaerobic microbial processes. The combination of these aerobic and anaerobic conditions within a SF wetland supports a relatively high rate of microbially induced degradation of organic and nitrogen compounds. These microbes consist of bacteria, fungi, algae, and other organisms and are responsible for the breakdown and consumption of organic matter, such as BOD in the influent wastewater, and uptake and transformation of nutrients, such as nitrogen (Wallace and Knight, 2006; USEPA, 2000; Kadlec and Knight, 1996).

Chemical transformations (oxidation-reduction, precipitation, etc.) are important removal mechanisms in SF treatment wetlands and are largely responsible for transformation and removal of dissolved forms of nitrogen (N), phosphorus (P), and trace metals. Molecules such as organic compounds can adsorb or bind to a substrate and then become microbially assimilated. Once assimilated the sediment sorption site becomes available for new

adsorption, resulting in a net removal of certain compounds. Some molecules adsorbed to sediment sorption sites are only partially assimilated by microbes or not assimilated at all. This can result in saturation of the available sorption sites and transformation of the molecules from one form to another (dissolved to adsorbed) without a net removal of the molecule.

Chemical removal of metals such as iron, copper, and nickel can occur in SF treatment wetlands by precipitation. Removal of these metals is often driven by hydroxide or sulfide precipitation within the wetlands and can secondarily remove other contaminants such as P that get bound to the precipitate.

Some molecules are partially or completely removed from SF wetlands by ultraviolet (UV) radiation from sunlight entering the water column. UV radiation can affect the viability of pathogens and other organisms and break apart some soluble organic molecules. Other molecules are removed from SF treatment wetlands by volatilization when those compounds partition to a gaseous state and exit the water column. This removal mechanism is important for nitrogen (through denitrification) and for carbon removal through the production of carbon dioxide and methane gas.

3.3 SUBSURFACE FLOW (SSF) TREATMENT WETLANDS

3.3.1 General Properties of SSF Treatment Wetlands

Constructed SSF wetlands are designed for water to flow below ground (subsurface) through a gravel and/or soil media bed. SSF wetlands can be designed for either horizontal or vertical flow through the media, depending on treatment goals. The three-dimensional treatment medium provided by the gravel/soil matrix colonized by aquatic microbial communities is effective for treatment processes such as anaerobic decomposition, filtration of particulates, and sorption. Treatment performance in SSF wetlands differs from SF wetlands because the wetland media in a SSF wetland provides a larger surface area for microbial growth and microbial biofilm (Wallace and Knight, 2006). The increased microbial density allows for a smaller SSF system footprint compared to SF systems and consequently a higher removal of BOD and trace organics on an area basis. However, increased substrate volume and effective microbial surface area in SSF treatment wetlands has not been found to significantly increase treatment performance for most other wastewater constituents such as TSS, TN, TP, coliforms, and trace metals. To a limited extent, wetland plants rooted in the gravel/soil media augment some pollutant treatment and removal mechanisms in SSF wetlands although this benefit appears to be small (IWA, 2000).

The majority of the wetland bed volume in SSF wetlands is occupied by the rooting medium (sand or gravel) and the roots, which typically occupy more than half of the total volume (USEPA, 1988). As a result, water flow is through the interstitial spaces in the media bed. The size of the medium determines the hydraulic conductivity of the bed. Compared to SF wetlands, horizontal flow SSF wetlands have a lower flow rate per unit of cross-sectional area, mainly because of the frictional losses that occur during subsurface flow (Darcy's law). Vertical flow SSF treatment wetlands are typically loaded with water intermittently to entrain atmospheric oxygen in the gravel/soil media and enhance aerobic microbial processes similar to a trickling filter. As the wastewater moves through the SSF wetland bed, some water is lost to evapotranspiration (ET) and some is gained during rainfall. Because most SSF wetlands are lined with an impermeable synthetic or clay liner, water loss through the bottom of the wetland is minimal (Wallace and Knight, 2006).

Constructed SSF wetlands typically are designed to treat primary or secondary municipal wastewaters that have been pretreated in septic or Imhoff tanks receiving raw domestic wastewaters from single-family homes or small clusters of homes. Constructed SSF treatment wetlands may be designed to discharge their effluents to the ground via a leachfield or may discharge to surface waters.

Constructed SSF wetlands are typically considered a low-cost method for treating a small volume waste stream. However, in comparison to SF wetlands, SSF treatment wetlands are more costly per unit area because they require underground drains and an engineered rooting medium during construction (Kadlec and Knight, 1996). This cost differential is typically not balanced by higher treatment performance per area and consequently SSF wetlands are not as cost-effective as SF treatment wetlands for many applications related to beneficial reuse of reclaimed waters. SSF constructed wetlands are primarily used for applications where the quality of wastewater to be treated is poor and has the potential to create nuisance conditions for humans and wildlife. SSF wetlands are also better insulated from climatic extremes than SF wetlands and are more frequently used in areas with colder climates and severe freezing conditions.

3.3.2 Wetland Plants in SSF Wetlands

Wetland plants are typically planted in SSF wetlands; however, their beneficial contributions to the wetland treatment system are less apparent than in SF treatment wetlands. In fact, comparison of pollutant removal performance of planted and unplanted SSF treatment systems found that plants typically provide only a small enhancement in pollutant removal capabilities (USEPA, 1999). Plants take up and assimilate macro- and micro-nutrients through their roots during active growth periods. However, plant uptake is a seasonal sequestration of the nutrients because most of these nutrients are returned to the wetland environment during biomass senescence.

It has been concluded that plants in SSF treatment wetlands may contribute to a relatively small performance boost by creating a larger and more diverse microbial community in the gravel matrix because of their ability to transfer some residual oxygen to the water column (although limited), the additional surface area for biofilm growth, and their introduction of fungi and symbiotic bacteria into the wetland reactor (Wallace and Knight, 2006). Plants that have significant root penetration into the bed media are likely to enhance treatment; however, the roots of most plants do not fully penetrate to the bottom of the media of SSF wetlands, so there is substantially more flow under the root zone than through it (USEPA, 1999). Plants add organic carbon to the surface of the gravel bed in a SSF treatment wetland during senescence, and this organic carbon likely provides some additional carbonaceous microbial fuel for BOD assimilation. Plant biomass production in SSF treatment wetlands is greatest in warm climates where growing seasons are long.

Planted SSF treatment wetlands may provide an aesthetic contribution to the landscape in some applications. Because wetland plants provide minimal removal performance in SSF wetlands, selection of plant species is best based on aesthetics, ease of propagation, and survivability in a relatively hostile substrate environment.

3.3.3 Removal Processes in SSF Wetlands

Horizontal and vertical flow SSF wetlands are highly effective at treating and removing TSS and BOD from the wastewater through the processes of flocculation, settling, and filtration of

suspended and large colloidal particles. The relatively low flow velocities and high media surface area in SSF wetlands facilitate the relatively high removal rates of TSS and BOD (USEPA, 1999).

Horizontal flow SSF treatment wetlands are generally entirely anaerobic unless supplied with supplemental aeration (Wallace and Knight, 2006). Vertical flow SSF treatment wetlands typically pulse between aerobic and anaerobic conditions depending on the point in the fill and drain cycle. During migration through a SSF wetland, the wastewater may come into contact with aerobic, anoxic, and anaerobic zones. Organic compounds are degraded aerobically and anaerobically by bacteria attached to plant roots and the high surface area media. In horizontal SSF wetlands, oxygen transport to the rhizosphere is negligible and oxygen diffusion from the atmosphere is limited by the gravel matrix and plant litter that restrict oxygen movement to the wastewater. Therefore, the predominant metabolic pathways for decomposition of organic compounds in horizontal SSF wetlands are anaerobic.

Nitrogen removal from SSF treatment wetlands is primarily by nitrification and denitrification—and to a lesser extent—volatilization, adsorption, and plant uptake (IWA, 2000). Organic nitrogen entering the SSF wetland will be mineralized, and the released ammonia may be available for plant uptake depending on the location of plant roots and the growth/dormancy cycle of the plants. However, net nitrogen removal by wetland plants is minor and considered only a seasonal sequestration of the nutrient. In vertical flow systems and in some lightly loaded horizontal flow SSF wetlands, ammonia nitrogen is oxidized to nitrate nitrogen by nitrifying bacteria in aerobic zones. Nitrates are, in turn, converted to nitrogen gas by denitrifying bacteria in anoxic zones. Incomplete nitrification can result from limited aerobic zones, which, in turn, suppresses denitrification and ultimately limits the removal of nitrogen, especially in heavily loaded horizontal flow SSF systems. For this reason, vertical flow SSF cells may precede horizontal flow SSF cells to provide a complete nitrogen removal process train. Denitrification is an important nitrogen removal mechanism in the largely anaerobic horizontal flow SSF wetlands and requires an adequate supply of organic carbon to fuel the microbially mediated process. Without augmentation, horizontal SSF wetlands may be carbon-limited because autotrophic production is limited to the bed surface.

Phosphorus removal in SSF wetlands primarily occurs by ligand exchange reactions (associated with the wetland media) in which phosphate displaces water or hydroxyl ions from the surface of iron and aluminum hydrous oxides. The gravel media in SSF treatment wetlands offers sorption, precipitation, and exchange sites for phosphatic molecules. Removal of metals such as iron, copper, and nickel can occur in SSF wetlands by precipitation and can secondarily remove other contaminants such as phosphorus that get bound to the precipitate. Phosphorus removal is also associated with accretion of phosphorus from decomposing plants (USEPA, 1999).

CHAPTER 4

TREATMENT PROCESSES AND POLLUTANT REMOVAL MECHANISMS

4.1 INTRODUCTION

An introduction to chemical, biological, microbial, and vegetative processes that are applicable to SF and SSF wetlands was provided in Chapter 3. This chapter describes the various treatment processes that are responsible for the removal of specific pollutants in constructed wetlands. Several physical factors strongly influence the effectiveness of the pollutant removal mechanisms described hereafter, the ability to correctly interpret performance data from operational systems, and the wetland design procedure. These physical factors include the wetland hydrologic regime, wetland hydraulic efficiency, and wetland thermal regime. These influencing factors are discussed first to provide a basis for understanding how removal rates and processes are modified.

4.2 WETLAND HYDROLOGY

The depth, duration, and frequency of inundation define the water regime of a wetland. Combined, these variables determine the storage volume in the wetland. The various inflows and storage volume determine the length of time that water spends in the wetland (hydraulic residence time), and thus the opportunity for interactions between waterborne substances and the wetland ecosystem.

4.2.1 Water Balance

Water may enter treatment wetlands via pumped (or gravity) inflows, streamflow, surface runoff, groundwater discharge, and precipitation (Figure 4.1). Water may exit treatment wetlands via streamflow, groundwater infiltration, lateral seepage, ET, and releases through an outlet control structure. For many treatment wetlands, groundwater exchanges and streamflows are negligible. ET occurs with strong diurnal and seasonal cycles, because it is driven by solar radiation and can be an important water loss pathway on a periodic basis. The overall dynamic water budget for a wetland follows:

$$Q_i - Q_o + Q_c - Q_b + Q_{sm} + (P - ET - I)A = \frac{dV}{dt} \qquad \text{(Equation 4.1)}$$

where:

A = wetland top surface area, square meters (m^2)

ET = evapotranspiration rate, meters per day (m/d)

I = infiltration to groundwater, m/d

P = precipitation rate, m/d

Q_b = bank loss rate, m^3/d

Q_c = catchment runoff rate, m^3/d

Q_i = input wastewater flow rate, m^3/d

Q_o = output wastewater flow rate, m^3/d

Q_{sm} = snowmelt rate, m^3/d

t = time, d

V = water storage in wetland, m^3

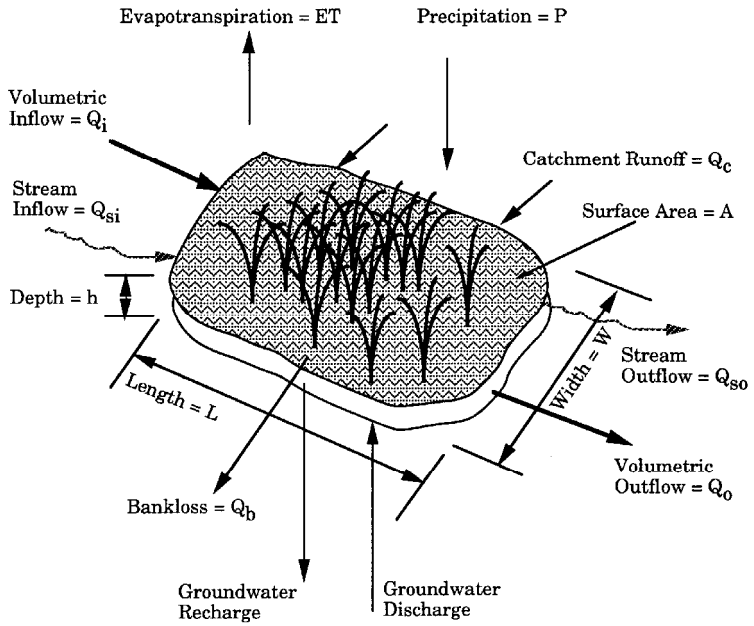


Figure 4.1. Components of overall wetland water mass balance. Adapted from Kadlec and Knight, *Treatment Wetlands*, CRC Press (Boca Raton, FL, 1996). Copyright 1995 by Taylor & Francis Group LLC. Reproduced with permission.

4.2.2 Hydraulic Loading Rate

The hydraulic loading rate (q) is the rainfall equivalent of the applied wastewater effluent flow and is calculated as the flow rate divided by the wetland area. It does not imply the physical distribution of water uniformly over the wetland surface (IWA, 2000).

$$q_i = Q_i/A \qquad \text{(Equation 4.2)}$$

where: q_i = inlet hydraulic loading rate, m/d

Q_i = inlet flow, m^3/d

A = wetland area, m^2

4.2.3 Water Depth

The mean water depth (h) calculation requires a detailed survey of the wetland bottom topography, combined with a survey of the water surface elevation. Water depth can be controlled by an outlet weir elevation, but for densely vegetated wetlands with relatively long flow paths, water depth is controlled by the frictional resistance to flow (head loss) over the wetland bottom and through the plants (Kadlec and Knight, 1996).

4.2.4 Void Fraction

The porosity (ε) of a wetland measures the void space (i.e. water volume only) that is not taken up by plant stems or substrate. For a SF wetland, the porosity will vary spatially because of vegetation pattern effects. It will also vary vertically, with lesser values near the bottom in the litter layer. For SSF wetlands, the porosity is more likely to be somewhat uniform. Mean values are typically greater than 0.95 for SF wetlands and about 0.30–0.40 for SSF wetlands (Kadlec and Knight, 1996; IWA, 2000).

4.2.5 Hydraulic Residence Time

The nominal hydraulic residence time (τ) is the ratio between flow rate Q and wetland water volume V and describes the amount of time that water spends in the wetland. The calculation of nominal residence time is often inaccurate because it combines the uncertainties in water depth and porosity.

In almost all cases, the mean hydraulic residence time (τ_m) is lower than the nominal hydraulic residence time because of the effects of hydraulic short circuits and poor flow distribution (Kadlec and Knight, 1996; Keller and Bays, 2001). For example, the nominal detention time for the Boggy Gut treatment wetland was estimated to be 19 days; however, the measured value was approximately 2 days (Knight and Ferda, 1989). Careful consideration of the site characteristics showed that this difference was due to large zones (both spatial and vertical) of wetland that were not in the flow path.

4.3 WETLAND HYDRAULICS

Common misconceptions regarding treatment wetlands are that they always operate as level pools and behave as plug-flow reactors. Observations of existing wetland systems have proven both of these concepts to be false for many typical operating conditions. The failure to account for flow versus depth relationships or hydraulic inefficiency may lead to permit violations, unplanned rehabilitation or expansion costs, and a general lack of confidence in the performance of treatment wetlands.

4.3.1 Frictional Losses

Flow in SF wetlands is analogous to flow in wide open channels. The depth of water at any point along the flow path is a function of the wetland bottom elevation, the outlet control elevation, the friction imposed by the wetland bottom and plant stems, and the horizontal velocity. For wetlands with relatively long flow paths and high flow rates, frictional effects can create a water surface profile that increases significantly with distance upstream from the outlet structure. In this case, water depths at the inlet can exceed the hydroperiod tolerances of the vegetation leading to a decrease in pollutant removal efficiency. Manning's equation is typically used for open channel hydraulics computations, but the equation is not valid for

densely vegetated wetlands that operate in the laminar to transitional flow regimes (as opposed to the turbulent flow regime assumed by Manning). Friction factors (Manning's n) referenced in open channel flow texts are lower than those measured in treatment wetlands. Variations on Manning's equation have been published specifically for wetlands (Kadlec and Knight, 1996; Kadlec, 2003; Bolster and Saiers, 2002; Jadhav and Buchberger, 1995).

Flow in SSF wetlands follows Darcy's Law for flow through porous media (Wallace and Knight, 2006). The water surface profile in the wetland bed is related to the hydraulic conductivity of the media, the bed slope, and the horizontal velocity. The active microbial biofilms that form on the surfaces of the bed media and in the pore spaces can lead to a decrease in hydraulic conductivity with time.

In either case, SF or SSF wetlands, negligence of frictional losses can lead to system failure.

4.3.2 Mixing

Numerous treatment wetland tracer studies have shown that the plug-flow condition does not occur (Kadlec and Knight, 1996; Kadlec, 1994; Stairs, 1993). Vertical velocity profiles, spatial variation in vegetation density, topographic heterogeneity, wind, and the location of inlet and outlet structures combine to force water molecules to take different paths through the wetland. Because this results in a distribution of residence times for water molecules in the wetland, pollutant removal calculations should be based on non-ideal process descriptions such as the tanks-in-series (TIS) and plug flow with dispersion (PFD) models (IWA, 2000).

As indicated earlier, tracer studies provide a method of measuring both the mean hydraulic residence time (τ_m) and the degree of mixing (the number of TIS, N). Wetlands cannot be designed, however, to yield a specific value of τ_m or N. These values vary with flow and with time as the spatial distribution of vegetation changes. Design approaches to maximize N and approach plug-flow conditions include the following:

- optimizing inflow distribution across the width of the wetland cell (Persson et al. 1999);
- maintaining even flow distribution by providing deep zones or other physical features to force flow redistribution at various points along the flow path (Lightbody et al. 2007);
- using collector canals or multiple outlet structures so that water does not channelize to a single outlet point;
- specifying grading tolerances that minimize topographic variation in the wetland; and
- requiring backfilling of existing ditches that fall within the wetland footprint that are oriented parallel to the direction of flow.

4.4 THERMAL EFFECTS IN WETLANDS

Some pollutant removal mechanisms are dependent on water temperature. Water temperature is determined by energy inputs and outputs. Inputs include solar radiation and energy entering the wetland with the inflow. Outputs include evapotranspiration and energy leaving with the wetland effluent. Energy exchanges between the ground and the water and between the water and air are reversible depending on the relative temperature differentials. Water in a wetland tends toward a balance point temperature that can be approximated by the ambient air temperature during nonfreezing conditions (Wallace and Knight, 2006). During freezing conditions, energy balance equations are required to determine the effects of insulating snow

and ice layers on the water temperature and pollutant removal performance. Wallace and Knight (2006) provide detail on thermal effects in both SF and SSF wetlands.

4.5 OXYGEN TRANSFER

Nutrient-enriched wastewater produces oxygen-limited wetland environments. Oxygen flow into and within the wetland occurs through oxygen diffusion into the water column, photosynthesis of submerged aquatic vegetation, photosynthesis of the algal population, and reaeration by rainfall. Oxygen diffusion from plant stems and leaves, down to the roots, and out to the rhizosphere is not a major treatment mechanism in wetlands (IWA, 2000; Wallace and Knight, 2006).

The dissolved oxygen (DO) concentration in SF wetlands is quite variable both spatially and temporally. DO concentration is typically highest at the water surface where oxygen diffusion is greatest, and it declines with increasing water depth (Wallace and Knight, 2006). As DO levels become depleted, anoxic conditions prevail at the sediment/water interface, and anaerobic conditions are measurable just below the sediment surface. This vertical DO stratification results in a wide range of redox concentrations spatially within the treatment wetland. Wide fluctuations in daily DO (and pH) occur in zones of open water where phytoplankton populations are high and diurnal algae photosynthesis is elevated. This temporal fluctuation can result in super-saturation of DO in the water column during the day and suppressed DO at night. Likewise, wind and wave-induced mixing can temporally distribute oxygen within the water column and increase the rate of atmospheric diffusion.

Insufficient oxygen supply is a common difficulty in SF treatment wetlands. When wetland systems are overloaded by oxygen-demanding constituents or are operated at excessive water depths, highly reduced conditions in the sediments can result in plant stress, plant mortality, and reduced removal efficiencies of BOD and ammonia nitrogen (IWA, 2000). In a nutrient-limited (oligotrophic) wetland, emergent wetland plants can tolerate deeper water conditions because of the higher concentration of DO in the water column. In the absence of high oxygen demand, DO diffuses into the sediment layer and produces less anoxic (higher redox potential) conditions. In comparison, higher oxygen demand from nutrient-enriched wastewater results in a depletion of DO in the water column. The nutrient loadings increase plant biomass production, which, in turn, increases the amount of decaying plant material in the detritus layer. These two effects create a highly anaerobic sediment layer. The oxygen gradient between the root tissue and sediments is greater in enriched wetlands than in nutrient-limited wetlands, leading to increased oxygen losses from the root tissue of wetland plants in highly enriched wetlands. Wetland plants will attempt to mediate this oxygen loss by rooting in the uppermost sediments where the least reducing conditions are present. Therefore, emergent wetland macrophytes in highly enriched wetlands are subjected to greater oxygen stress and, consequently, tolerate less flooding—typically less than half the water depth for the same species in an oligotrophic wetland environment (Wallace and Knight, 2006).

4.6 ORGANIC MATTER DEGRADATION

Wastewater contains a wide range of organic carbon compounds and other oxygen-demanding substances that range from being easily degradable to highly refractory (Wallace and Knight, 2006). Two laboratory tests are routinely used to quantify the amount and type of organic matter in wastewaters:

- 5-day Carbonaceous Biochemical Oxygen Demand ($CBOD_5$)—measures oxygen demands resulting from the microbial breakdown of carbon-based compounds. If a nitrification inhibitor is not used during the test, the results may include the oxygen demands from microbial breakdown of nitrogenous compounds as well (BOD_5).
- Chemical Oxygen Demand (COD)—measures the oxygen demands resulting from chemical oxidation of organic compounds.

Because there is a range of degradability, the removal rate for BOD decreases as water moves from the wetland inlet to outlet (Wallace and Knight, 2006). BOD can be produced in a wetland through internal carbon cycling (**Figure 4.2**), resulting in a non-zero background concentration (Kadlec and Knight, 1996).

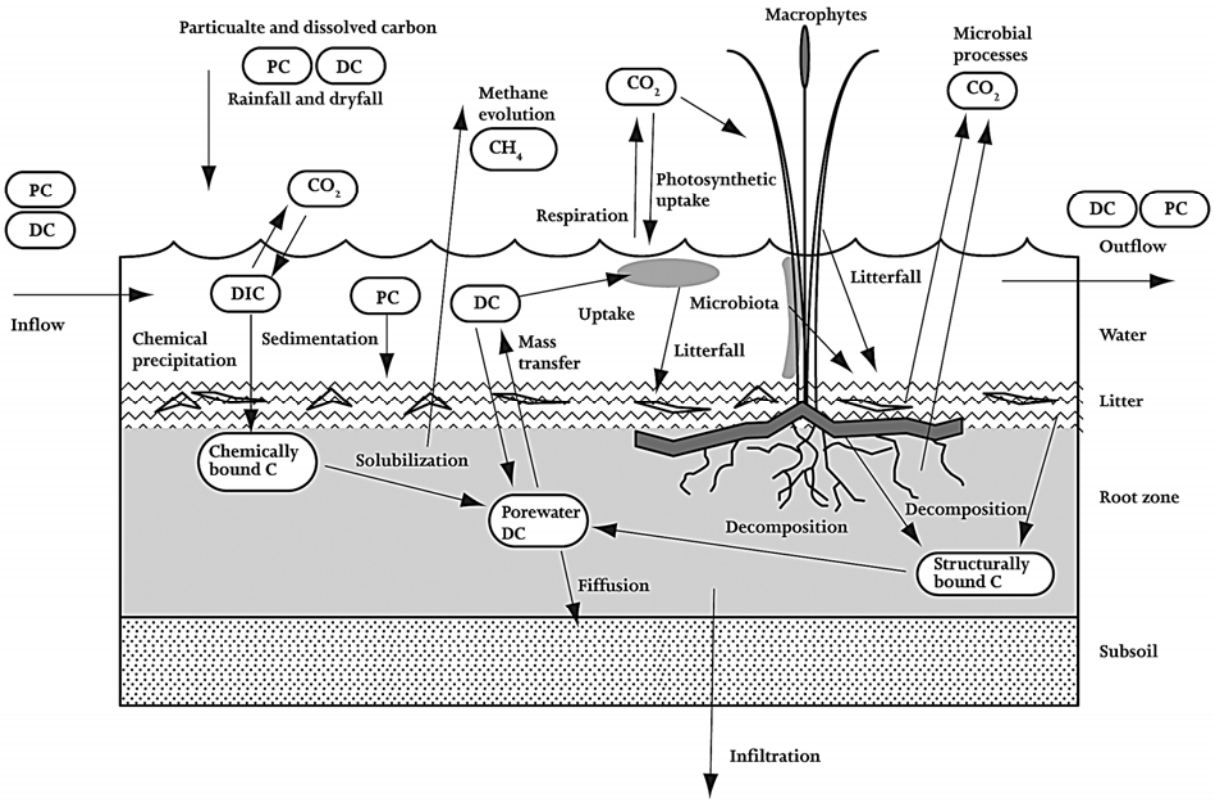


Figure 4.2. Carbon cycling in SF wetlands. Adapted from Kadlec and Knight, Treatment Wetlands, CRC Press (Boca Raton, FL, 1996). Copyright 1995 by Taylor & Francis Group LLC. Reproduced with permission.

Both aerobic and anaerobic decomposition occur in wetlands and the dominant pathway depends on the oxygen transfer rate and organic matter loads. Aerobic heterotrophic (use of organic carbon rather than carbon dioxide for growth) microbes convert soluble organic matter to carbon dioxide and water through the following reaction:

$$(CH_2O) + O_2 \longrightarrow CO_2 + H_2O$$

where (CH_2O) represents soluble organic matter.

Anaerobic degradation requires multiple steps and is carried out by facultative or obligate anaerobic heterotrophs. The first step involves the breakdown of sugars to fatty acids:

$$C_6H_{12}O_6 \longrightarrow 3\ CH_3COOH + H_2$$

In the second step anaerobic methane-forming bacteria convert the fatty acids to methane:

$$CH_3COOH + 4\ H_2 \longrightarrow 2\ CH_4 + 2\ H_2O$$

4.7 SUSPENDED SOLIDS REMOVAL

Suspended solids removal mechanisms that occur in constructed treatment wetlands include sedimentation, aggregation, and interception. These processes are facilitated by the relatively slow horizontal velocities, the high number of plant stems in SF wetlands, and the surface area of bed media in SSF wetlands.

Large diameter and/or dense particles are normally removed from the water column in the inlet region of the wetland. The efficiency of discrete particle settling is related to the size distribution (and therefore settling velocity distribution) of solids in the wetland. Particle settling velocities can be measured or estimated using Stoke's law (Kadlec and Knight, 1996). If the time required for a given particle to settle (maximum value is the water depth divided by the settling velocity) is lower than that particle's residence time in the wetland (length of flow path divided by the horizontal velocity), then the particle would be expected to be removed. As particle sizes and densities decrease, longer residence times are required for removal.

Some particles combine into larger particles through the process of aggregation (also called flocculation). Aggregation is a function of the strength of attractive forces, which are defined by surface chemistry and the countering strength of shear forces created by mixing and turbulence. Without the addition of chemicals or polymers, there are no design approaches that can be taken to increase particle attractive forces. Fortunately, bed media (in SSF wetlands) and plant detritus (in SF wetlands) serve to reduce shear forces, resulting in some degree of aggregation and enhanced settling performance.

Very small particles such as bacteria, some algal solids, and colloids often do not aggregate enough to be removed within the residence time of the wetland. However, these particles can be removed by impacting plant stems or bed media or being trapped in the biofilm growing on wetland bed media (in SSF systems) and emergent wetland plants/detritus (in SF wetlands).

In addition to the various processes that reduce suspended solids concentrations, there are mechanisms in wetlands that generate solids. These include algal production in areas where there is minimal nutrient and light competition from macrophytes, wind-related resuspension of sediments, and bioturbation from fish, mammals, and birds.

4.8 NITROGEN TRANSFORMATION

Nitrogen can exist in many different forms (organic matter, ammonia, nitrite, nitrate, or nitrogen gas) in a wetland depending on the oxidation/reduction (redox) conditions in the wetland, which is a result of oxygen transfer rate as well as internal and external organic matter loadings (Wallace and Knight, 2006). Almost all the nitrogen in untreated municipal wastewater is either organic nitrogen or ammonia. A net removal requires that nitrogen be driven through the nitrogen cycle (Figure 4.3) and be converted to nitrogen gas. The dominant sequential processes are as follows:

- Mineralization (ammonification)—aerobic or anaerobic conversion of organic nitrogen to ammonia.
- Nitrification—two-step biological oxidation of ammonia to nitrite and then to nitrate. The nitrification rate is limited by the availability of dissolved oxygen. Approximately 4.3 grams of oxygen are required to nitrify one gram of ammonia (Kadlec and Knight, 1996).

$$NH_4^+ + 1.5O_2 \longrightarrow NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + 0.5O_2 \longrightarrow NO_3^-$$

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$$

- Denitrification—biological conversion of nitrate to nitrogen gas, which diffuses from the water column to the atmosphere. Denitrification requires anaerobic conditions as the nitrate ion is used as an electron acceptor. Denitrification requires a 1.1 mass ratio of available carbon to nitrogen (Kadlec and Knight, 1996). Except under extreme nitrate loadings, the necessary dissolved carbon supply can typically be provided by the biomass in the wetland.

$$6(CH_2O) + 4NO_3^- \longrightarrow 6CO_2 + 2N_2 + 6H_2O$$

The rate of nitrogen transformation processes increase in proportion to the water temperature (IWA, 2000).

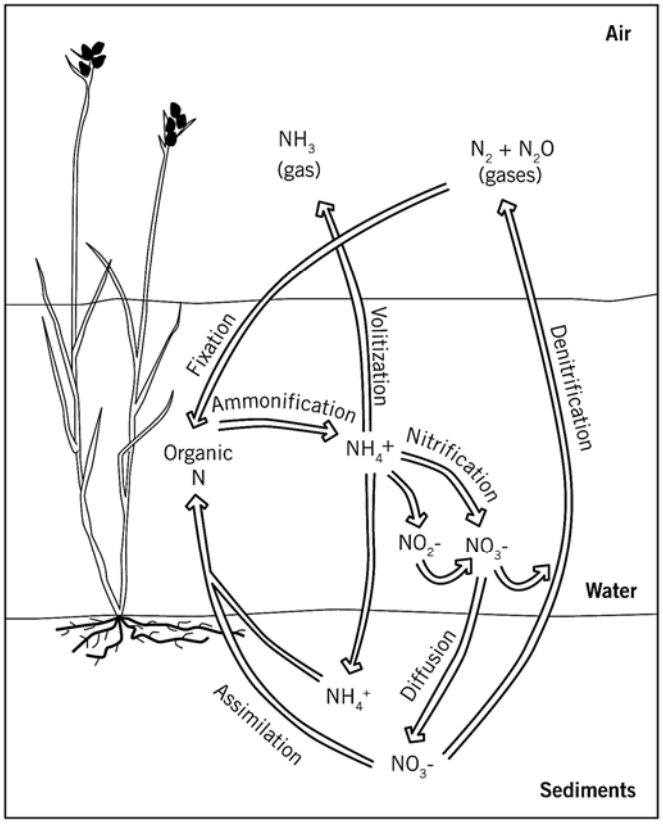


Figure 4.3. Nitrogen cycling in SF wetlands. Adapted from Kadlec and Knight, *Treatment Wetlands*, CRC Press (Boca Raton, FL, 1996). Copyright 1995 by Taylor & Francis Group LLC. Reproduced with permission.

4.9 PHOSPHORUS CYCLING

One mechanism for phosphorus removal is sorption onto exchange sites in the wetland sediments. Under typical wastewater loading rates, this storage compartment is rapidly filled (Kadlec and Knight, 1996).

Sustainable removal is by the accumulation of phosphorus into accreted bottom sediments (Figure 4.4). Plant biomass takes up phosphorus from the water column, but when the plant dies and decomposes, some of the phosphorus is returned to the water column, whereas the fraction that is associated with nondegradable material is retained (IWA, 2000).

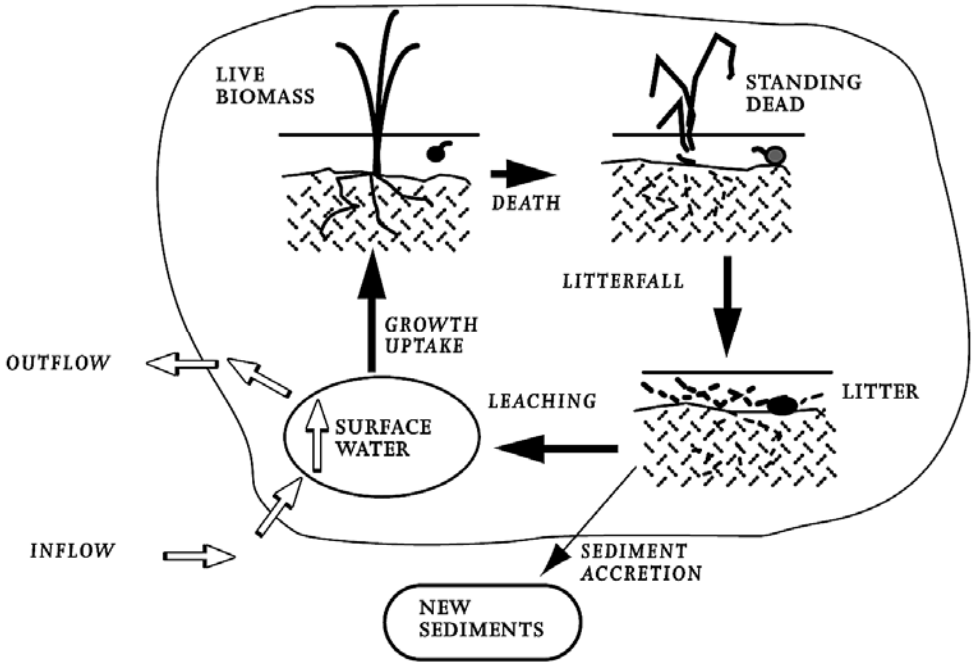


Figure 4.4. Phosphorus cycling in SF wetlands. Adapted from Kadlec and Knight, *Treatment Wetlands*, CRC Press (Boca Raton, FL, 1996). Copyright 1995 by Taylor & Francis Group LLC. Reproduced with permission.

4.10 PATHOGEN REDUCTION

Bacteria, viruses, protozoa, and helminths that occur in municipal effluents are removed in wetlands through the processes of sorption to organic matter, predation, filtration, photo-deactivation by exposure to ultraviolet light, sedimentation, oxidation, and exposure to plant-produced biocides (Wallace and Knight, 2006). Wetland environments are hostile to non-adapted microscopic organisms. Most human pathogens are poorly evolved to withstand the ambient temperatures existing in wetlands, serve as food for the adapted wetland fauna, and are physically trapped through sedimentation because of the long hydraulic and solids residence time in most treatment wetlands. Wetlands provide habitat for warm-blooded animals that contribute pathogens (e.g., waterfowl and other birds and mammals) and resulting background fecal coliform populations are typically in the range of 50 to 2,000 colonies per 100 mL (Kadlec and Knight, 1996).

4.11 METALS SEQUESTRATION

Unlike organic carbon, nitrogen, and pathogens, there is no process that completely removes metals from the wetland environment. Wetlands do, however, remove metals from the water column so that lower concentrations are discharged to the receiving system. Metal removal in constructed wetlands is a storage process, involving accretion of new sediments, chemical precipitation, or ion exchange to wetland substrate. Biological processes are of secondary importance (Kadlec and Wallace, 2009). Metals that enter the wetland in particulate form are trapped via the same processes responsible for TSS reduction. Dissolved metals are sequestered through adsorption and cation exchange processes with organic matter and clay sediments. Ion exchange is a saturable mechanism, and the wetland will lose removal capability after all exchange sites are filled and if additional sediments are not provided by accretion. Reduced iron can be microbially oxidized by *Thiobacillus ferrooxidans* and then

precipitated as an iron oxyhydroxide (IWA, 2000). Microbial sulfate reduction converts sulfate ions to sulfide, which forms almost irreversible bonds with metal ions. Metal sulfides are relatively dense and settle to the sediment surface. Plant and microbial uptake is also a mechanism for metals removal, but the metals may be returned to the water column if the organic material decomposes. In plants, metals preferentially accumulate in roots, not in the above-ground tissues (Kadlec and Knight, 1996).

4.12 REMOVAL OF TRACE ORGANICS

Wetlands effectively reduce the concentrations of many hydrocarbons and hydrocarbon classes. Classes that are typically reduced in wetlands include: fuels, oils, aliphatic and aromatic hydrocarbons, halogenated hydrocarbons (e.g., PCB, DDT, and DCB), oxygenated hydrocarbons (acids, alcohols, glycol, phenols, starches, and sugars), volatile organic compounds (e.g., TCE, DCE, and BTX), herbicides, and insecticides (Kadlec and Knight, 1996). Dominant removal mechanisms for hydrocarbons and other volatile substances include volatilization, photochemical oxidation, sedimentation, sorption, and biological degradation (Kadlec and Wallace, 2009). Additional information about the removal of some classes of trace organics are provided in Section 6 of this report.

4.13 POTENTIAL EFFECTS ON WILDLIFE USING TREATMENT WETLANDS

During the review of new and existing discharge permits to water quality wetlands, environmental agency staff must assess the potential for harmful environmental effects. The potential receptors of most interest are typically the vertebrate inhabitants of the wetlands, including fish, amphibians, reptiles, birds, and, to a lesser extent, mammals. These organisms tend to be more highly visible to people than their invertebrate neighbors, and concern for their fate is highest in the public's priorities.

Wilhelm et al. (1989) describe the planning and design of the city of Show Low, Arizona, treatment wetlands, one of the earliest intentional multi-use constructed treatment wetlands in the United States. This system was observed to have very high waterfowl and other wildlife usage. Following the early observations at Show Low, a number of authors have described the ancillary wildlife and human use benefits resulting from treatment wetlands (Sather, 1989; Feierabend, 1989; Knight, 1992, 1997).

The USEPA conducted a pilot study of wildlife usage and habitat functions of constructed water quality wetlands during the summer of 1992. The USEPA used a consistent rapid-assessment protocol at six constructed surface flow wetlands (including two in Florida, two in Mississippi, and two in the southwestern U.S.) to evaluate their habitat structure and function and the possibility of environmental hazards (McAllister, 1992, 1993a, 1993b). No detrimental effects to wildlife that colonize constructed water quality wetlands were documented by that study. The USEPA subsequently published a detailed description of the water quality and wildlife habitat benefits of 17 constructed wetlands for water quality polishing throughout the United States (USEPA, 1993).

As a follow-up to these pilot studies, in 1996 the USEPA funded an inventory and analysis of all available existing data on the habitat values of constructed and natural wetlands receiving municipal and industrial wastewaters and stormwaters. This project was titled the Environmental Technology Initiative program and resulted in the creation of an electronic database of habitat, wildlife, human use, and ecological risk data from North American water

quality wetlands. This database was appended to the previously existing North American Treatment Wetland Database (NADB; Knight et al., 1993) to form the NADB Version 2 (CH2M HILL, 1998; Knight et al., 2001). This data summary currently provides the best source available to identify benefits or hazards to wildlife using enhancement wetlands and can be obtained at: www.wetlandsolutionsinc.com.

The NADB Version 2 contains habitat and related data for 109 water quality wetland sites, 168 separate systems, and 386 individual cells from 31 states or provinces in the U.S. and Canada. Eighty-five percent of the sites are constructed wetlands; the rest are natural wetlands. A total of 29,960 data records related to wildlife, toxics, and human uses are included in the NADB Version 2. Contaminant data from constructed wetlands receiving trace concentrations of heavy metals and organic pollutants are available in the NADB Version 2 for sediments and biological tissues. Table 4.1 lists representative U.S. water quality wetland sites where wildlife habitat creation and human use are principal project objectives.

Although the use of wetlands to improve the quality of wastewaters is considered an important goal, it is also important to balance the benefits of meeting that goal with the avoidance of harm to those organisms that will ultimately reside in the living treatment system. The information gathered for the NADB Version 2 indicates that biological changes can occur in response to discharges of treated effluents. These changes cover the spectrum from obvious to subtle. Many of the changes that have been noted favor one group of species over another. The most common changes result in an increase of wetland structure and function at an ecosystem level rather than a reduction in normal wetland functions.

There is currently no evidence that highly treated wastewater effluents cause increased risks for vertebrates in water quality wetlands. This lack of evidence does not prove that there are no effects, but it indicates that most wetland water quality projects can be permitted without special requirements other than reasonable caution. Greater caution should be exercised when project wastewaters are known or suspected to contain unusually elevated concentrations of heavy metals, trace organics, un-ionized ammonia, or other chemicals that are likely to be acutely or chronically toxic to aquatic and wetland biota.

Table 4.1. Representative Constructed Water Quality Wetlands in the NADB Version 2 That Include WildlifeHabitat and/or Human Use as Principal Objectives

Site Name and Location	Wet Area (ha)	Source of Wastewater	Wildlife Habitat	Human Use
Arcata, CA	15.2	MUN	X	X
Beltway 8 (Harris County), TX	89.0	STW	X	X
Des Plaines, IL	10.1	OTH	X	X
DuPont (Victoria), TX	21.4	IND	X	X
Hayward, CA	58.7	MUN	X	X
Hemet/San Jacinto, CA	14.2	MUN	X	
Hillsboro, OR	35.7	MUN	X	X
Incline Village, NV	173.3	MUN	X	X
Indian River County, FL	75.3	MUN	X	X
Iron Bridge (Orlando), FL	494.0	MUN	X	X
Mt.View Sanitary District, CA	37.0	MUN	X	X
Olentangy (Columbus), OH	2.0	OTH	X	X
Phinizy Swamp (Augusta), GA	162.0	MUN	X	X
Pinetop/Lakeside, AZ	51.0	MUN	X	X
Santa Rosa, CA	4.1	MUN	X	
Show Low, AZ	54.2	MUN	X	X
Sweetwater (Tucson), AZ	7.0	MUN	X	X
Tres Rios, AZ	4.2	MUN	X	X
Wakodahatchee (Palm Beach County), FL	21.0	MUN	X	X

Note. MUN = municipal, STW = stormwater, IND = industrial, OTH = other.

CHAPTER 5

WETLAND PERFORMANCE SUMMARY

5.1 INTRODUCTION

For most parameters of concern, treatment wetland performance is highly dependent on both the inflow concentration and the hydraulic loading rate (the product of these is the inflow mass loading rate). Performance for some parameters such as BOD, TSS, and fecal coliforms can be approximated in some cases with linear regressions that are dependent only on the inflow concentration. For nitrogen and phosphorus, better correlations are found if the hydraulic loading rate is also included. In much of the literature, wetland performance is expressed in terms of the concentration reduction efficiency; however, these values are not adequate for use as design criteria as they lead practitioners to incorrectly presume that concentration reduction efficiency is independent of either the inflow concentration or the inflow mass loading rate.

Previous efforts (Knight et al., 1993; Kadlec and Knight, 1996; CH2M HILL, 1998; IWA, 2000; Wallace and Knight, 2006; Kadlec and Wallace, 2009) have compiled performance data from a wide range of treatment wetlands that receive municipal wastewaters. No attempt was made for the current effort to recompile or update wetland system databases. Undoubtedly, there are relevant data points that fall outside the ranges presented in the following, but the information summarized provides a solid overview of municipal wastewater treatment wetland performance. In addition to the regressions and loading plots reproduced in the following, there are numerous literature sources that provide removal rate constant calibrations that can be used with first-order design equations. As this document is not a design manual and is intended only to summarize treatment wetland types, processes, and performance, neither the models nor the ranges of removal rate constants are presented.

The following conventions are used herein:

C_i = inflow concentration, mg/L

C_o = outflow concentration, mg/L

q = hydraulic loading rate, cm/d

L_i = inflow mass loading rate, kg/ha/d

L_o = outflow mass loading rate, kg/ha/d

Major removal mechanisms in treatment wetlands for conventional parameters may be classified into physical, chemical, or biological processes with specific contaminants affected by multiple removal mechanisms either simultaneously or sequentially. Major removal mechanisms for conventional water quality parameters in FWS wetlands are summarized in Table 5.1 with further discussion provided in the following sections.

Table 5.1. Removal Mechanisms for Conventional Water Quality Parameters

Parameters	**Physical**	**Chemical**	**Biological**	**Comments**
Suspended Solids	***Sedimentation (discrete and flocculent); Filtration/ interception***	Not applicable	Microbial degradation	Wetland systems are very efficient at removal of suspended solids but also produce suspended solids (e.g. phytoplankton, plant detritus). Wind mixing, bioturbation, gas lift, etc. may also result in resuspension of settled solids.
Biological Oxygen Demand	Sedimentation	UV radiation	***Microbial degradation***	Sedimentation of organic solids facilitates microbial degradation through increased retention time of solids within the wetland.
Chemical Oxygen Demand	Sedimentation	UV radiation; adsorption	***Microbial degradation***	Adsorption of organic compounds increases retention time beyond that of the hydraulic retention time (HRT) to facilitate microbial degradation.
Metals (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn)	Sedimentation	***Precipitation***; adsorption; ion exchange	Microbial uptake; plant uptake	Chemical precipitation results in formation of insoluble (or slightly soluble) compounds. Secondary removal of other contaminants (such as P) may result, if bound to the precipitate.
Petroleum Hydrocarbons (fuels, oil and grease, alcohols, BTEX, TPH)	***Volatilization***	UV radiation; adsorption	***Microbial degradation***; plant uptake	Volatility increases with temperature (e.g. when sunlight heats the water column) so volatilization may be a significant removal mechanism during summer. Adsorption increases retention time beyond that of HRT to facilitate microbial degradation.

Source: Wallace and Knight (2006)

Note. Significant removal mechanisms are italicized and bolded**.**

Table 5.1. Removal Mechanisms for Conventional Water Quality Parameters (cont.)

Parameters	**Physical**	**Chemical**	**Biological**	**Comments**
Synthetic Hydrocarbons (PAHs, chlorinated and nonchlorinated solvents, pesticides, herbicides, insecticides)	Sedimentation; volatilization	Adsorption; UV radiation	***Microbial degradation***; plant uptake	Volatility increases with temperature (e.g. when sunlight heats the water column) so volatilization may be a significant removal mechanism during summer. Adsorption increases retention time beyond that of HRT to facilitate microbial degradation.
Nitrogenous Compounds (Organic N, NH_3, NH^{4+}, NO_3^-, NO_2^-)	Sedimentation	Adsorption, volatilization (ammonia)	***Microbial uptake and transformation***; plant uptake	Biofilms on emergent plants and litter layer uptake soluble pollutants from the water column; cycling of nutrients through microbe life cycle results in accretion and burial within wetland sediments.
Inorganic and Organic Phosphorus	Sedimentation	***Precipitation; adsorption***	Microbial uptake; plant uptake	Precipitation and adsorption to sediments play major role; but biofilms (as described earlier) result in long-term storage through accretion and burial within wetland sediments.
Pathogens (bacteria, viruses, protozoa, helminthes)	***Sedimentation***	UV radiation	***Die-off***; microbial predation	Human pathogens expire rapidly within a wetland system, but wildlife inputs of coliform bacteria and other pathogens have to be considered.

Source: Wallace and Knight (2006)

Note. Significant removal mechanisms are italicized and bolded**.**

5.2 BIOLOGICAL OXYGEN DEMAND

Wetlands are capable of producing very low BOD concentrations (< 5 mg/L) when receiving wastewater of secondary quality or better. Consistent performance in SF wetlands requires the maintenance of a relatively dense emergent marsh community. SF wetlands can become a source of BOD if operated at depths that limit vegetation growth or if the vegetation is severely damaged by storm events or herbivory. In these instances, algal production dominates, and the BOD discharged from the wetland consists of algal solids rather than the wastewater-related organic matter that entered the system.

Kadlec and Knight (1996) provide regressions for BOD removal by SF and SSF wetlands:

SF	SSF
$C_o = 0.173*C_i + 4.70$	$C_o = 0.33*C_i + 1.4$
$r^2 = 0.62$; N = 440	$r^2 = 0.48$; N = 100
$0.27 < q < 25.4$ cm/d	$1.9 < q < 11.4$ cm/d
$10 < C_i < 680$ mg/L	$1 < C_i < 57$ mg/L
$0.5 < C_o < 227$ mg/L	$1 < C_o < 36$ mg/L

Brix (1994) reported the following regression for BOD removal in Danish soil-based SSF wetlands:

$C_o = 0.11*C_i + 1.87$

$r^2 = 0.74$; N = 73

$0.8 < q < 22$ cm/d

$1 < C_i < 330$ mg/L

$1 < C_o < 50$ mg/L

For SSF systems in the Czech Republic, Vymazal (1998) reported the following concentration and mass loading regressions for BOD removal:

$C_o = 0.099*C_i + 3.24$	$L_o = 0.13*L_i + 0.27$
$r^2 = 0.33$; N = 39	$r^2 = 0.57$; N = 34
$0.6 < q < 14.2$ cm/d	$0.6 < q < 14.2$ cm/d
$5.8 < C_i < 328$ mg/L	$2.6 < L_i < 99.6$ kg/ha/d
$1.3 < C_o < 51$ mg/L	$0.32 < L_o < 21.7$ kg/ha/d

Figure 5.1 shows the relationship between BOD mass loading rate and outflow concentration for SF wetlands in the North American Database Version 2.

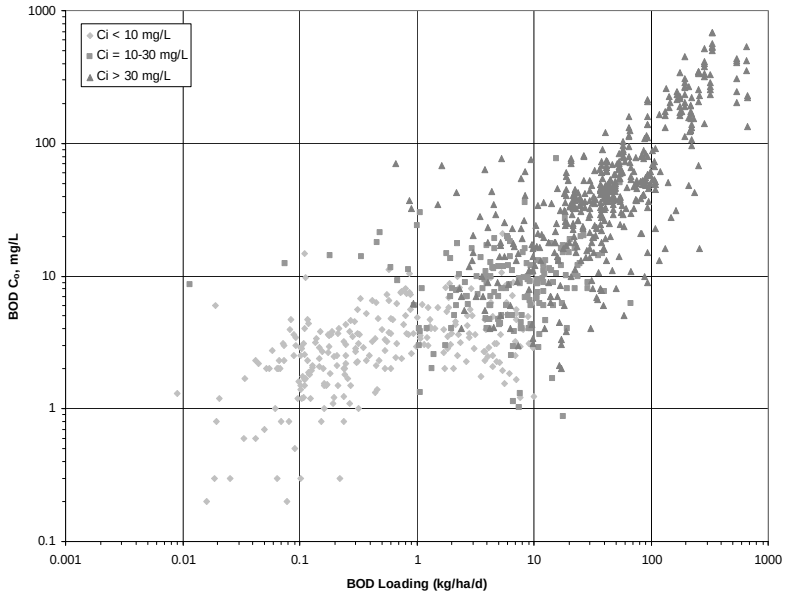


Figure 5.1. SF wetland loading chart for BOD (data from NADB, CH2M HILL, 1998).

5.3 TOTAL SUSPENDED SOLIDS

Like BOD, densely vegetated wetlands perform extremely well for TSS removal. Wetland effluent TSS concentrations below 5 mg/L (annual average basis) can be achieved even for very high inflow concentrations and mass loading rates. TSS export can be an issue in SF wetlands that have large open water areas, particularly if they are located near outflow structures.

Kadlec and Knight (1996) provide a regression for TSS removal by SF wetlands:

$C_o = 1.125 * C_i^{0.58}$

$r^2 = 0.38$; N = 460

$1 < C_i < 800$ mg/L

$0.5 < C_o < 200$ mg/L

Brix (1994) reported the following regression for TSS removal in Danish soil-based SSF wetlands:

$C_o = 0.09 * C_i + 4.7$

$r^2 = 0.67$; N = 77

$0 < C_i < 330$ mg/L

$0 < C_o < 60$ mg/L

For SSF systems in the Czech Republic, Vymazal (1998) reported the following concentration and mass loading regressions for TSS removal:

$C_o = 0.021*C_i + 9.17$	$L_o = 0.083*L_i + 1.18$
$r^2 = 0.018$; N = 37	$r^2 = 0.64$; N = 30
$0.6 < q < 14.2$ cm/d	$0.6 < q < 14.2$ cm/d
$13 < C_i < 179$ mg/L	$3.7 < L_i < 123$ kg/ha/d
$1.7 < C_o < 30$ mg/L	$0.45 < L_o < 15.4$ kg/ha/d

Figure 5.2 shows the relationship between TSS mass loading rate and outflow concentration for SF wetlands in the North American Database Version 2.

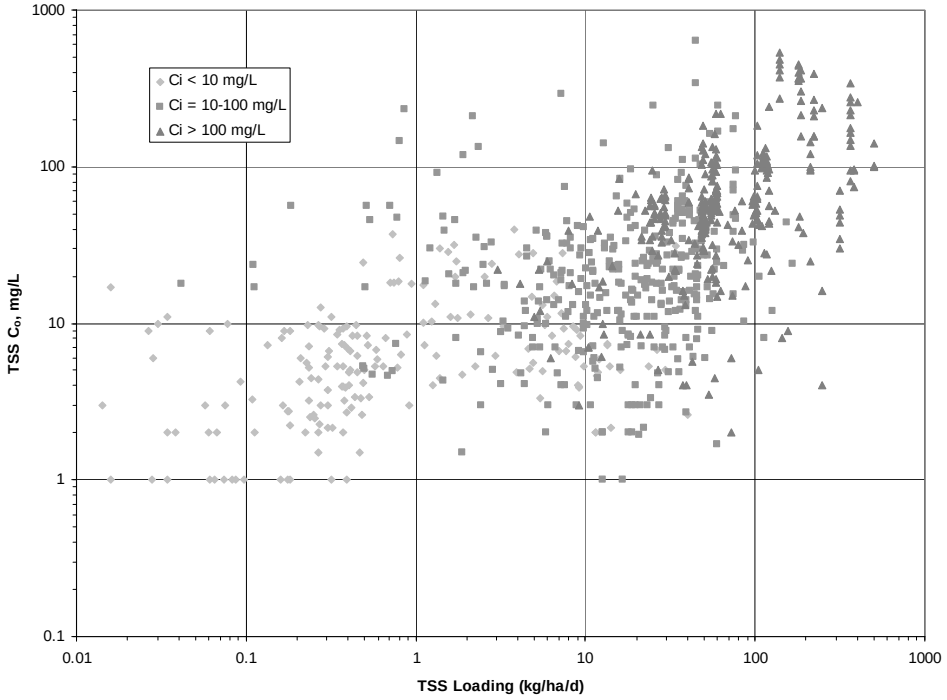


Figure 5.2. SF wetland loading chart for TSS (data from NADB, CH2M HILL, 1998).

5.4 NITROGEN

Total nitrogen removal in wetlands is strongly influenced by the relative fractions of organic nitrogen, NH_4 and NO_3. Wetlands have a background TN concentration of 1 to 2 mg/L (Kadlec and Knight, 1996) which consists entirely of organic nitrogen. The background organic nitrogen fraction is illustrated by the cluster of points at loading rates less than 1 kg/ha/d in Figure 5.3 Inorganic nitrogen (NH_4 and NO_3) can theoretically be completely removed in a sufficiently sized, well-functioning treatment wetland. The asymptotic effect of the irreducible background concentration is not exhibited in the plots for NH_4 (Figure 5.4) or NO_3 (Figure 5.5).

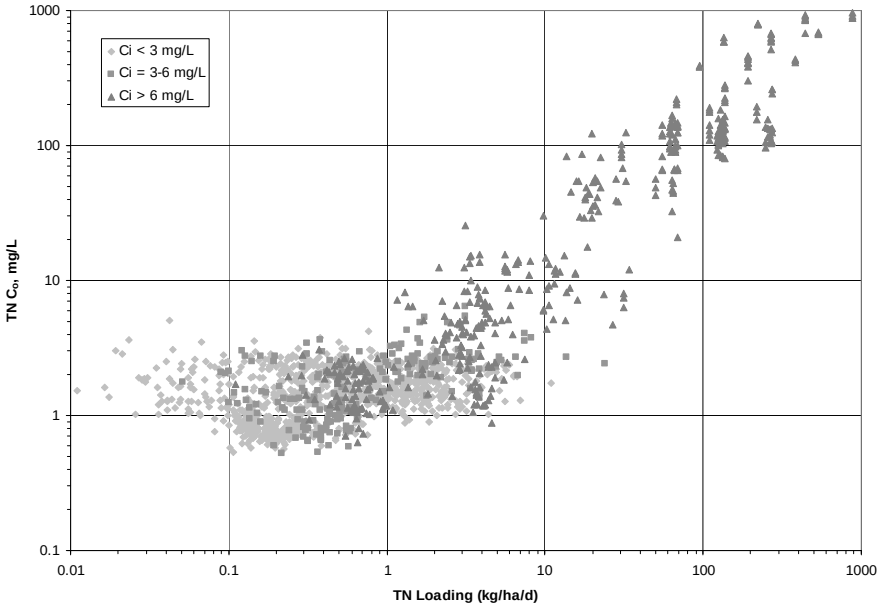


Figure 5.3. SF wetland loading chart for TN (data from NADB, CH2M HILL, 1998).

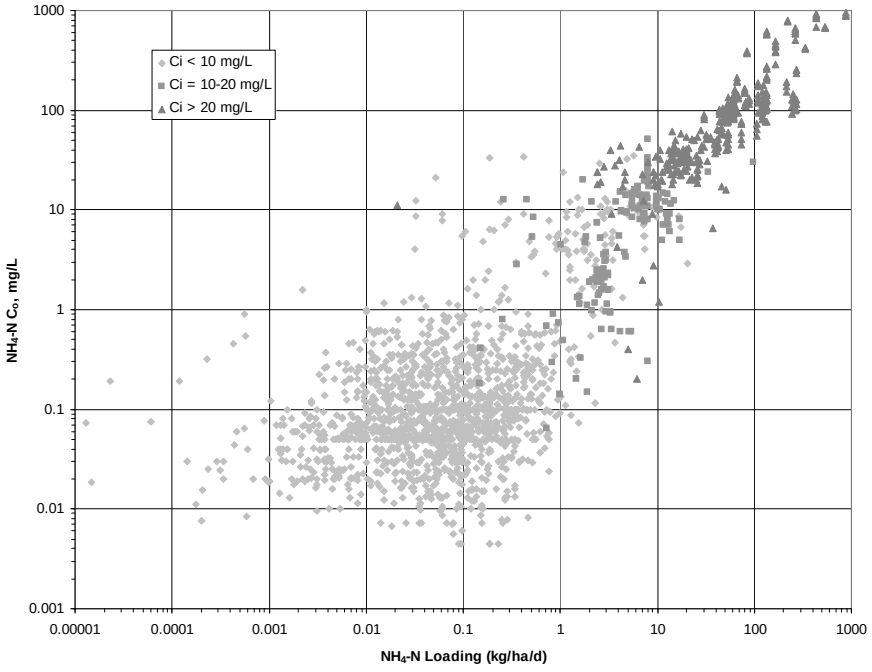


Figure 5.4. SF wetland loading chart for NH_4 (data from NADB, CH2M HILL, 1998).

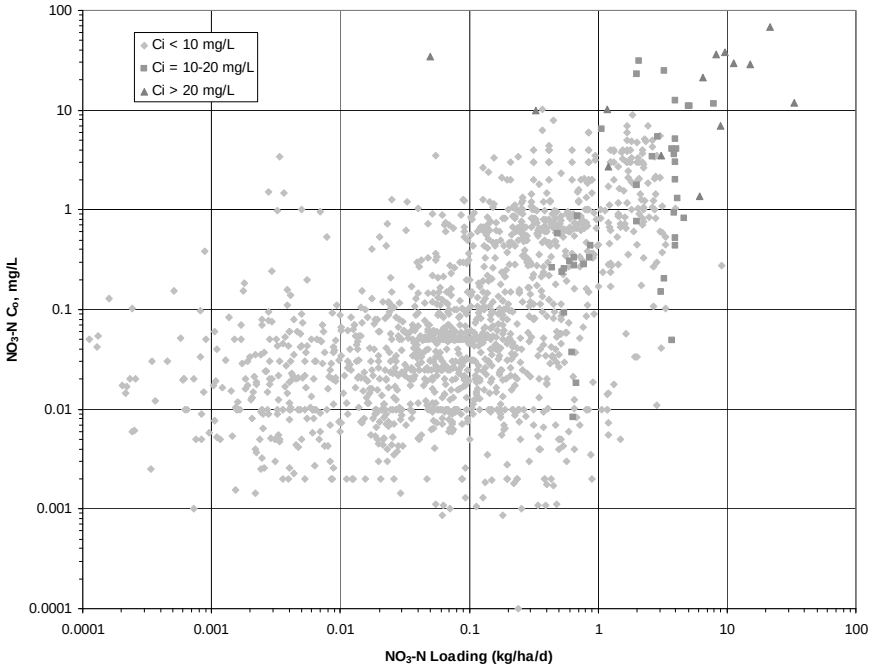


Figure 5.5. SF wetland loading chart for NO_3 (data from NADB, CH2M HILL, 1998).

Regression equations that summarize performance for TN, organic nitrogen, NH_4, and NO_3 are provided in the following.

5.4.1 Total Nitrogen

Kadlec and Knight (1996) provide regressions for TN removal by SF and SSF wetlands:

SF	SSF
$C_o = 0.409*C_i + 0.122*q$	$C_o = 0.46*C_i + 0.124*q + 2.6$
$r^2 = 0.48$; N = 408	$r^2 = 0.45$; N = 135
$0.2 < q < 28.6$ cm/d	$0.7 < q < 48.5$ cm/d
$2.0 < C_i < 39.9$ mg/L	$5.1 < C_i < 58.6$ mg/L
$0.4 < C_o < 29.1$ mg/L	$2.3 < C_o < 37.5$ mg/L

Brix (1994) reported the following regression for TN removal in Danish soil-based SSF wetlands:

$C_o = 0.52*C_i + 3.1$

$r^2 = 0.63$; N = 58

$0.8 < q < 22$ cm/d

$4 < C_i < 142$ mg/L

$5 < C_o < 69$ mg/L

For SSF systems in the Czech Republic, Vymazal (1998) reported the following concentration and mass loading regressions for TN removal:

$C_o = 0.42*C_i + 7.68$	$L_o = 0.68*L_i + 0.27$
$r^2 = 0.72$; N = 25	$r^2 = 0.96$; N = 24
$1.7 < q < 14.2$ cm/d	$1.7 < q < 14.2$ cm/d
$16.4 < C_i < 933$ mg/L	$3.97 < L_i < 51.9$ kg/ha/d
$10.7 < C_o < 49$ mg/L	$3.67 < L_o < 36.4$ kg/ha/d

5.4.2 Organic Nitrogen

Kadlec and Knight (1996) provide regressions for organic nitrogen removal by SF and SSF wetlands:

SF	SSF
$C_o = 1.00*C_i^{0.476}$	$C_o = 0.1*C_i + 1.0$
$r^2 = 0.52$; N = 243	$r^2 = 0.07$; N = 89
$0.2 < q < 27.4$ cm/d	$0.7 < q < 48.5$ cm/d
$0.09 < C_i < 19.9$ mg/L	$0.6 < C_i < 21.8$ mg/L
$0.16 < C_o < 15.5$ mg/L	$0.1 < C_o < 11.1$ mg/L

For SSF systems in the Czech Republic, Vymazal (1998) reported the following concentration and mass loading regressions for organic nitrogen removal:

$C_o = 0.23*C_i + 1.39$	$L_o = 0.49*L_i + 7.56$
$r^2 = 0.39$; N = 14	$r^2 = 0.72$; N = 13
$1.7 < q < 14.2$ cm/d	$1.7 < q < 14.2$ cm/d
$0.9 < C_i < 18$ mg/L	$0.60 < L_i < 8.47$ kg/ha/d
$0.55 < C_o < 5.5$ mg/L	$0.24 < L_o < 5.75$ kg/ha/d

5.4.3 Ammonia

Kadlec and Knight (1996) provide regressions for NH_4 removal by SF and SSF wetlands:

SF	SSF
$C_o = 0.336*C_i^{0.728}*q^{0.456}$	$C_o = 0.46*C_i + 3.3$
$r^2 = 0.44$; N = 542	$r^2 = 0.63$; N = 92
$0.1 < q < 33.3$ cm/d	$0.7 < q < 48.5$ cm/d
$0.04 < C_i < 58.5$ mg/L	$0.1 < C_i < 43.8$ mg/L
$0.01 < C_o < 58.4$ mg/L	$0.1 < C_o < 26.6$ mg/L

For SSF systems in the Czech Republic, Vymazal (1998) reported the following concentration and mass loading regressions for NH_4 removal:

$C_o = 0.42*C_i + 4.37$	$L_o = 0.81*L_i - 72.86$
$r^2 = 0.65$; N = 26	$r^2 = 0.86$; N = 26
$1.7 < q < 14.2$ cm/d	$1.7 < q < 14.2$ cm/d
$3.4 < C_i < 66$ mg/L	$2.27 < L_i < 23.8$ kg/ha/d
$1.7 < C_o < 37$ mg/L	$1.45 < L_o < 22.1$ kg/ha/d

5.4.4 Nitrate

Kadlec and Knight (1996) provide regressions for NO_3 removal by SF and SSF wetlands:

SF	SSF
$C_o = 0.093*C_i^{0.474}*q^{0.745}$	$C_o = 0.62*C_i$
$r^2 = 0.35$; N = 553	$r^2 = 0.80$; N = 95
$0.2 < q < 27.4$ cm/d	$0.7 < q < 48.5$ cm/d
$0.01 < C_i < 24.5$ mg/L	$0.01 < C_i < 27.0$ mg/L
$0.01 < C_o < 21.7$ mg/L	$0.01 < C_o < 21.0$ mg/L

For SSF systems in the Czech Republic, Vymazal (1998) reported the following concentration and mass loading regressions for NO_3 removal:

$C_o = 0.55*C_i + 3.10$	$L_o = 0.28*L_i + 47.25$
$r^2 = 0.41$; N = 16	$r^2 = 0.26$; N = 14
$1.7 < q < 14.2$ cm/d	$1.7 < q < 14.2$ cm/d
$0.79 < C_i < 22$ mg/L	$0.18 < L_i < 31.3$ kg/ha/d
$0.7 < C_o < 16$ mg/L	$0.15 < L_o < 22.7$ kg/ha/d

5.5 Phosphorus

As indicated in Chapter 4, phosphorus removal is sustainable in wetlands, but at lower rates than most other conventional wastewater parameters. Phosphorus removal requirements frequently control the size of wetlands needed for a particular wastewater source.

Kadlec and Knight (1996) provide a regression for TP removal by SF wetlands:

$C_o = 0.195*q^{0.53}*C_i^{0.91}$

$r^2 = 0.77$; N = 373

$0.1 < q < 33$ cm/d

$0.02 < C_i < 20$ mg/L

$0.009 < C_o < 20$ mg/L

Brix (1994) reported the following regression for TP removal in Danish soil-based SSF wetlands:

$C_o = 0.65*Ci + 0.71$

$r^2 = 0.75$; N = 61

$0.8 < q < 22$ cm/d

$0.5 < C_i < 19$ mg/L

$0.1 < C_o < 14$ mg/L

For SSF systems in the Czech Republic, Vymazal (1998) reported the following concentration and mass loading regressions for TP removal:

$C_o = 0.26*C_i + 1.52$	$L_o = 0.67*L_i - 9.03$
$r^2 = 0.23$; N = 27	$r^2 = 0.58$; N = 24
$1.7 < q < 14.2$ cm/d	$1.7 < q < 14.2$ cm/d
$0.77 < C_i < 14.3$ mg/L	$28 < L_i < 307$ kg/ha/d
$0.4 < C_o < 8.4$ mg/L	$11.4 < L_o < 175$ kg/ha/d

Figure 5.6 shows the relationship between TP mass loading rate and outflow concentration for SF wetlands in the North American Database Version 2 (CH2M HILL, 1998). This plot indicates that very low phosphorus concentrations can be achieved at loading rates less than 1 kg/ha/d. At loading rates exceeding 100 kg/ha/d, Kadlec (1999) reported that there is insignificant concentration reduction between wetland inflows and outflows.

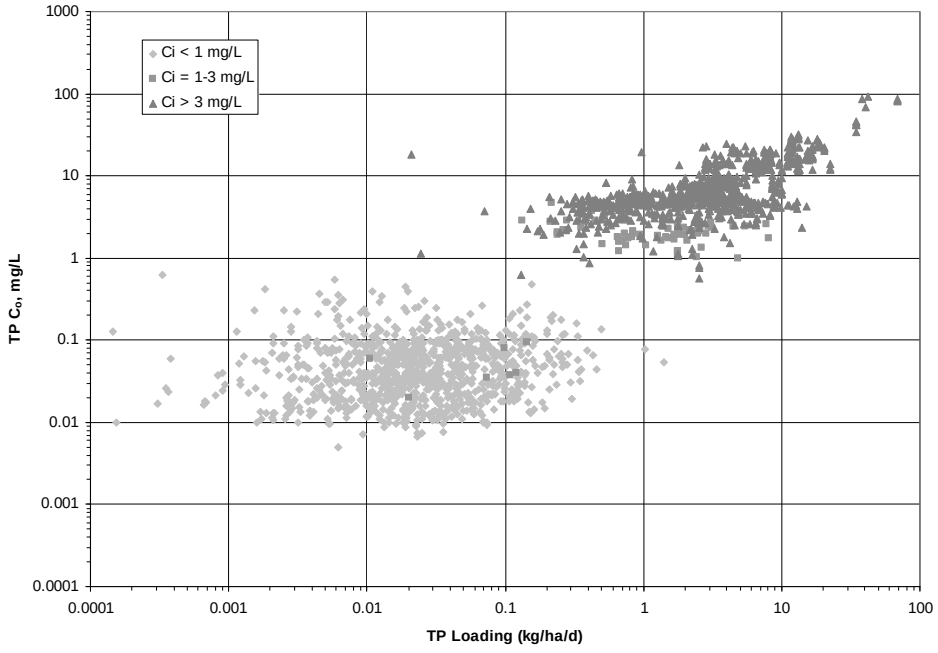


Figure 5.6. SF wetland loading chart for TP (data from NADB, CH2M HILL, 1998).

5.6 PATHOGENS

Because wetlands are a harsh environment for pathogens, removal rates are often high. Pathogen concentrations are typically reduced by two to three orders of magnitude at residence times of three to five days. In many instances, permit standards for pathogens are met between the conventional wastewater treatment plant process units (chlorine contact, ultraviolet, or ozone) and the wetland units. In these cases where the wetland influent pathogen concentrations are low, the wetlands can become a source for regulated parameters such as fecal coliforms. These coliforms, however, are from wildlife rather than humans. When wetland water is to be reused, secondary disinfection may be required.

Figure 5.7 shows the general relationship between inflow and outflow fecal coliform concentrations.

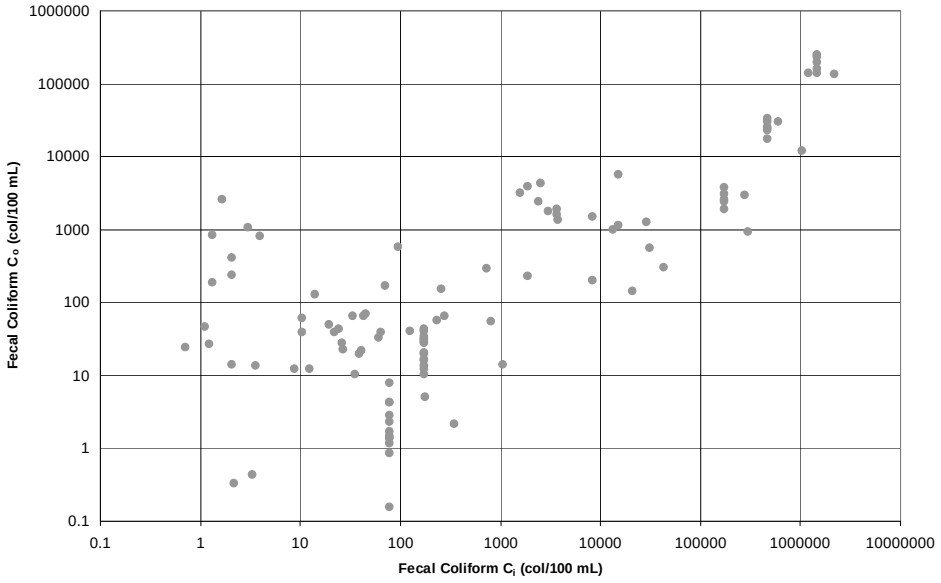


Figure 5.7. SF wetland loading chart for fecal coliforms (data from NADB, CH2M HILL, 1998).

5.7 TRACE METALS

Data for trace metal removal in wetlands are sparser than data for conventional wastewater parameters. There have been, however, many studies that indicate that most trace metals can be reliably removed in both SF and SSF wetlands. Published removal rates (Kadlec and Knight, 1996) are wide, ranging from about 10 to more than 90% (concentration and mass basis) but performance is highly correlated with mass loading rate and inflow concentration. Estimated first-order removal rates for a variety of potentially toxic trace metals such as copper, cadmium, lead, silver, and zinc in constructed wetlands are similar to observed rates for nutrients such as nitrogen and phosphorus (Kadlec and Wallace, 2009). Some metals that are present at elevated concentrations in soils may increase in concentration between the wetland inlet and outlet. Iron and potassium are two examples. Any conservative metals and

salts that are present at elevated concentrations may exhibit this behavior and concentration increases may be exacerbated in arid climates where evapotranspiration exceeds water inputs.

5.8 TRACE ORGANICS

Removal data for organic contaminants are as sparse as for metals, but there are similar ranges of efficiency reported in the literature (Kadlec and Knight, 1996). Much of what is available for organics is from outside the realm of municipal wastewater treatment wetlands, but the data are applicable regardless of wetland type or water source. Almost all trace organics would be lumped into BOD or COD measurements, and there would generally be a measurable decline in concentration and load as water passes through a treatment wetland.

Starting in the 1980s, scientists began studying the removal of moderately hydrophobic organic pesticides in wetlands. With few exceptions, removal occurs when dissolved contaminants partition on to plant surfaces or litter. Because sorption is a physical removal process, contaminants are not permanently removed unless biotransformation occurs after sorption. For example, atrazine (log K_{ow}=2.56) was slightly retarded as it passed through a constructed wetland; however, it was not detected in sediment and plant samples taken from a wetland cell that had been amended with the herbicide, suggesting that any atrazine retained in the wetland was transformed after adsorption (Alvord and Kadlec, 1995). Several organophosphorus insecticides (e.g., chlorpyrifos, azinophos-methyl, prothiofos) were completely attentuated in constructed wetland during dry weather when residence times were longer and loading that was due to agricultural runoff was lower (Moore et al,. 2002). However, these same compounds were detected in wetland effluents during wet weather (Schulz and Peall, 2001) presumably because of insufficient time for sorption and biotransformation.

More recently, scientists have begun studying the removal of more polar contaminants. Wetlands also can be very effective at removing low molecular weight species such as chlorinated disinfection by-products (DBPs), with observed decreases in trihalomethanes (THMs) and haloaceticacids (HAAs) ranging from 67 to 97% over a residence time of approximately 3 days (Rostad et al., 2000). Although the mechanisms responsible for removal are unknown, caffeine and ethylenediaminetetraacetic acid (EDTA) also were attentuated in wetlands (Barber et al., 2001).

Most of the available studies on the fate of WDOCs in engineered wetlands have relied on focused monitoring of contaminant concentrations in the influent and effluent of wetland systems. Such empirical studies are problematic because concentrations of contaminants in wastewater effluent at an individual treatment plant can vary in order of magnitude over periods of a few days (Kolodziej et al., 2003; Ternes, 1998). As a result, it may be impossible to detect modest removals of contaminants within a wetland system. In an attempt to circumvent some of these problems, a study of steriod hormone removals in a pilot-scale engineered treatment wetland was conducted (Gray and Sedlak, 2005). As part of the study, a pulse of approximately 100 ng/L of steroid hormones (i.e., about 50 times higher than the concentrations typically present in wastewater effluent) was added to the wetland along with a lithium chloride tracer. By monitoring the recovery of the hormones and the lithium tracer at the exit of the wetland, a removal of approximately 35% of the steroid hormones was documented during the 3-day hydraulic residence time. Further discussion regarding research efforts to determine removal effectiveness of WDOCs in constructed wetland treatment systems is presented in Chapter 6.

CHAPTER 6

WASTEWATER-DERIVED ORGANIC COMPOUNDS (WDOCs)

6.1 INTRODUCTION

With continued advancements in detection capabilities and technology, several hundred different organic compounds have been detected in wastewater effluent (Snyder et al., 2003). Although the potential ecological and human health impacts of the trace concentrations of these compounds have not been determined, at higher concentrations some of these compounds have been shown to have deleterious effects on aquatic ecosystems. The most studied effect is feminization of male fish in surface waters that receive significant amounts of wastewater effluent (Desbrow et al., 1998; Jobling et al., 1998). Available data indicate that synthetic estrogens such as 17ά-ethinyl estradiol and endogenous estrogens (17β-estradiol and estrone) are responsible for the observed effects (Desbrow et al., 1998; Huang and Sedlak, 2001; Routledge et al., 1998). However, degradation products of popular alkylphenol detergents (e.g., nonylphenol) also can cause feminization of fish (Jobling and Sumpter, 1993; Sheahan et al., 2002) as can temperature fluctuations during development (Nakamura et al., 1998; Devlin and Nagahana, 2002).

Increasing evidence suggest that WDOCs even at trace concentrations may be capable of causing other adverse impacts on aquatic organisms. For example, many species of fish use steroid hormones as pheromones to identify fertile mates and time reproduction. Several natural (e.g., testosterone) and manmade hormones (e.g., medroxyprogesterone) are present in wastewater effluent at or above concentrations that elicit pheromonal responses in fish (Kolodziej et al., 2003). In addition, compounds including the beta-blocker propranolol (Huggett et al., 2002) and the antibiotic triclosan (Reiss et al., 2002) may be present at concentrations near or above levels at which adverse impacts have been reported.

Compared to our knowledge of the potential impacts of WDOCs on aquatic organisms, we know little about potential adverse impacts of human exposure to the low levels of WDOCs in wastewater effluents. Following the reports of widespread occurrence of WDOCs in surface waters, water utilities expressed interest in low-cost approaches for removing WDOCs from wastewater in systems where indirect potable water reuse is practiced (Snyder et al., 2003) Because most of the WDOCs are removed during drinking water treatment and those compounds that have been detected have usually been present at concentrations below thresholds for health effects, human health concerns usually is not the main motivation for examining WDOC removal in constructed treatment wetlands. However, considerable effort is being directed at research on human health effects of low-level exposure to WDOCs, and concerns about human exposure could become more important in the future.

6.2 REMOVAL OF WASTEWATER-DERIVED ORGANIC COMPOUNDS IN PILOT- AND LARGE-SCALE WETLANDS

The removal of contaminants in treatment wetlands is typically quantified by measuring the concentrations of the contaminant in the influent and effluent of a pilot- or large-scale system. These data are used along with the calculated mean hydraulic retention time (HRT) to calculate rate constants for contaminant removal assuming plug flow and first-order kinetics.

The mean HRT is the mean depth divided by the mean hydraulic loading rate (HLR). The mean HLR is used directly in the estimation of first-order area-based rate constants, K (m/yr) (Kadlec and Knight, 1996). Although flow mixing dynamics for most wetland systems fall between 1.5 and 8 tanks-in-series (TIS), global k values calculated using the plug flow assumption may be more conservative because of the use of the more efficient model resulting in a more conservative design. Alternatively, the TIS variation of the model may be used to calculate rate constants with a conservative estimate of number of tanks for systems where tracer study data is not available

$$\ln\left(\frac{C_{in}}{C_{out}}\right)=\frac{k}{q}$$

where:

C_{out} = average outlet concentration (ng/L)

C_{in} = average inlet concentration (ng/L)

q = average hydraulic loading rate (m/yr)

Estimation of rate constants for contaminant removal in large-scale treatment systems may be complicated by variability in inlet concentrations arising from fluctuations in contaminant concentrations in wastewater effluent. This potential problem is most pronounced for trace contaminants such as WDOCs and generally less of an issue with conventional pollutants such as BOD, TSS, and nutrients. Hydraulic inefficiencies as a result of short-circuiting and variations in plant densities and distributions occur in all constructed wetlands and require data to be interpreted and wetland system design to consider non-ideal flow patterns when predicting removal rates based on simple first-order models (Kadlec, 2000). Procedures for estimating seasonal and stochastic variability are explained in Kadlec and Wallace (2009). Quantitative measurements of wetland performance must be assessed in the context of the specific system in which the data were collected.

Studies of the removal of WDOCs indicate that many compounds are removed to an appreciable extent in constructed treatment wetlands, with overall removals up to around 90% for certain compounds (see Table 6.1). When investigators have attempted to quantify the removal of trace contaminants by monitoring concentrations entering and leaving wetlands, estimates have had large uncertainties because of fluctuations in the concentrations of contaminants entering the wetlands. As a result, it has often been difficult to determine if any removal has occurred (Kolodziej et al., 2003; Gross et al., 2004; Rostad et al., 2000; Waltman et al., 2006). In contrast, studies in which WDOCs were added to the inflow of the wetland have provided more precise data on contaminant removal (Gray and Sedlak, 2005; Matamoros and Bayona, 2006). However, such studies have only been performed on pilot-scale treatment wetlands, which possibly have more operational control enabling minimization of short-circuiting.

Despite the uncertainties in the quality of the data, it is evident that many wastewater-derived trace contaminants are removed in treatment wetlands and that the compounds removed to the greatest extent are those that are also readily removed in wastewater treatment plants. For example, compounds that are difficult to remove in conventional wastewater treatment plants (e.g., carbamazepine, gemfibrozil) also are difficult to remove in constructed treatment

Table 6.1. Removal of Wastewater-Derived Organic Compounds in Constructed Treatment Wetlands

Contaminant	Removal (%)	Ref.	HRT (d)	K* (m/yr)	Wetland type	Comment
Alkylphenols	75±72	(1)	2.5	130	Full, surface	Flow data from (2)
A+CAPnEC	8±48	(1)	2.5	8.1	Full, surface	Flow data from (2)
Bromoacetic acid	27	(3)	3.5	19	Full, surface	Flow data from (4), average of HS1 & CS2 sites
Caffeine	97	(5)		50	Pilot, subsurface	Influent similar to raw sewage
Chloroform	80	(3)	3.5	86	Full, surface	Flow data from (4), average of HS1 & CS2 sites
Dichloroacetic acid	87	(3)	3.5	110	Full, surface	Flow data from (4), average of HS1 & CS2 sites
17β-estradiol	36	(6)	3.5	29	Pilot, surface	
Estrone	ND	(7)	6.5		Full, surface	Significant variability in influent
Ethinyl estradiol	44	(6)	3.5	29	Pilot, surface	
Galaxolide	52	(5)		18	Pilot, subsurface	Influent similar to raw sewage
Gemfibrozil	58±103	(1)	2.5	84	Full, surface	Flow data from (2)
Ibuprofen	47±37	(1)	2.5	62	Full, surface	Flow data from (2)
Ibuprofen	87	(5)		19	Pilot, subsurface	Influent similar to raw sewage
Naproxen	85			28	Pilot, subsurface	Influent similar to raw sewage
Testosterone	ND	(7)	6.5		Full, surface	Significant variability in influent
Triclosan	68	(8)	4.3	14	Pilot, surface	Flow data from (9)

*Calculated based on plug-flow, first-order kinetics.

Source:

(1) Gross, B.; Montgomery-Brown, J.; Naumann, A.; Reinhard, M. Occurrence and fate of pharmaceuticals and alkylphenol ethoxylate metabolites in an effluent-dominated river and wetland. *Environmental Toxicology and Chemistry* **2004**, *23*, 2074–2083.

(2) Lin, A. Y. C.; Debroux, J. F.; Cunningham, J. A.; Reinhard, M. Comparison of rhodamine WT and bromide in the determination of hydraulic characteristics of constructed wetlands. *Ecological Engineering* **2003**, *20*, 75–88.

(3) Rostad, C. E.; Martin, B. S.; Barber, L. B.; Leenheer, J. A.; Daniel, S. R. Effect of a constructed wetland on disinfection byproducts: Removal processes and production of precursors. *Environmental Science & Technology* **2000**, *34*, 2703–2710.

(4) Keefe, S. H.; Barber, L. B.; Runkel, R. L.; Ryan, J. N.; McKnight, D. M.; Wass, R. D. Conservative and reactive solute transport in constructed wetlands. *Water Resources Research* **2004**, *40*.

(5) Matamoros, V.; Bayona, J. M. Elimination of pharmaceuticals and personal care products in subsurface flow constructed wetlands. *Environmental Science & Technology* **2006**, *40*, 5811–5816.

(6) Gray, J. L.; Sedlak, D. L. The fate of estrogenic hormones in an engineered treatment wetland with dense macrophytes. *Water Environment Research* **2005**, *77*, 24–31.

(7) Kolodziej, E. P.; Gray, J. L.; Sedlak, D. L. Quantification of steroid hormones with pheromonal properties in municipal wastewater effluent. *Environmental Toxicology and Chemistry* **2003**, *22*, 2622–2629.

(8) Waltman, E. L.; Venables, B. J.; Waller, W. Z. Triclosan in a North Texas wastewater treatment plant and the influent and effluent of an experimental constructed wetland. *Environmental Toxicology and Chemistry* **2006**, *25*, 367–372.

(9) Hemming, J. M.; Waller, W. T.; Chow, M. C.; Denslow, N. D.; Venables, B. Assessment of the estrogenicity and toxicity of a domestic wastewater effluent flowing through a constructed wetland system using biomarkers in male fathead minnows (Pimephales promelas Rafinesque, 1820). *Environmental Toxicology and Chemistry* **2001**, *20*, 2268–2275.

wetlands, whereas those compounds that are readily removed in wastewater treatment plants (e.g., caffeine, ibuprofen) are removed efficiently in engineered treatment wetlands. The effectiveness for removal of compounds by conventional wastewater treatment plants and by constructed wetlands appears to achieve similar results. However, further research is needed to define removal effectiveness of constructed wetlands designed and operated to maximize treatment performance relative to WDOCs. Gaining additional understanding about the effects of the longer hydraulic retention times associated with wetlands and whether there are additional removal mechanisms that occur in the wetlands is of interest.

6.3 MECHANISMS OF ORGANIC COMPOUND REMOVAL IN TREATMENT WETLANDS

As a result of the complex nature of pilot- and large-scale wetlands and the limited number of previous studies in which removals were determined with high precision, it is difficult to predict the fate of many wastewater-derived trace contaminants in constructed treatment wetlands or to optimize wetland design for trace contaminant removal. To gain insight into the factors controlling trace contaminant removal in constructed treatment wetlands, it is helpful to consider previous studies on the fate of organic compounds in natural wetland systems and in wetlands designed for treatment of agricultural and industrial runoff. Through analysis of data from field and laboratory studies in these similar systems, it may be possible to identify specific mechanisms through which wastewater-derived contaminants are removed and to develop a better understanding of how constructed treatment wetlands function with respect to the removal of WDOCs.

6.3.1 Removal of Organic Compounds by Partitioning to Plants and Sediments

Sorption to plant surfaces and wetland sediments can decrease the concentration of wastewater-derived contaminants as water passes through treatment wetlands. Compounds that do not undergo transformation after sorption may accumulate in plants and sediments (Gobas *et al*,. 1991), posing a potential long-term risk for sediment-dwelling organisms and their consumers. Recalcitrant WDOCs present in sewage, such as polybrominated diphenyl ethers, are removed efficiently in municipal wastewater treatment plants (North, 2004). As a result, the accumulation of these compounds in biosolids produced by municipal wastewater treatment plants has been an area of substantial research interest (Stevens et al., 2003). Although the concentrations of these compounds in wastewater effluent entering constructed treatment wetlands is much lower than the concentrations in raw sewage, additional research is needed to assess the accumulation of persistent organic compounds in the sediments of these treatment wetlands.

Once equilibrium partitioning is reached, contaminants can be removed from wetlands by burial in sediments and plant harvesting. Because rates of sediment burial in treatment wetlands are slow and harvesting of plants is uncommon in treatment wetlands (Kadlec and Knight, 1996), sorption will only be an important removal mechanism if it is irreversible or if it is accompanied by a transformation reaction. For contaminants that undergo transformation, sorption can result in contaminant removal by increasing the residence time of the contaminant in the wetland and by providing an environment conducive to transformation reactions.

To predict the effect of sorption on the residence time of WDOCs in an engineered constructed wetland, it is necessary to quantify the phase partitioning between water, plants,

and sediments. For ideal plug-flow conditions, the impact of sorption on the hydraulic residence time can be predicted with a retardation factor, R_f (28):

$$R_f = 1 + \frac{m_s}{m_w} = 1 + Kr_{s/w}$$ [equation 6.1]

where

m_s = mass of solute associated with solid phase (i.e., plants and sediment)

m_w = mass of solute in dissolved phase

K = distribution coefficient (i.e., $\frac{c_s}{c_w}$)

$r_{s/w}$ = solid/water ratio (kg solid/L water)

Partitioning of organic compounds between water and sediments has been studied extensively, and numerous approaches are available to predict distribution coefficients. For organic compounds, partitioning is usually described by linear (Karickhoff et al., 1979) or Freundlich (Xing and Pignatello, 1996) isotherms:

$$C_s = K_d C_w$$ [equation 6.2]

$$C_s = K_f C_w^{\,n}$$ [equation 6.3]

In a mature constructed treatment wetland, the sediment that comes in contact with the water normally consists of organic detritus derived from the decay of wetland plants (Kadlec and Knight, 1996). Therefore, partitioning of the compound to the partially degraded plant material will be governed by many of the same factors that affect partitioning to the roots, shoots, and leaves of intact plants. Organic carbon-normalized distribution coefficients for aged detritus may be higher than those measured for fresh sediments, because organic matter polarity decreases as labile compounds, such as carbohydrates, are degraded (Alvord and Kadlec, 1995).

Partitioning of organic compounds to intact plants can be considered as a two-step process, where compounds associate with the external portion of the plant, followed by uptake into the plant. In most cases, the external surface of the plant is populated by a biofilm that includes organisms that can transform organic compounds (Kang and Goulder, 1996). As a result, sorption may bring the contaminant into the region where biotransformation occurs.

After the contaminant enters the plant, it can undergo one of two possible fates. For recalcitrant hydrophobic compounds, the contaminant is likely to associate with the lipid phase (e.g., waxy cuticle) of the plant (Gobas et al., 1991) where it is sequestered. Alternatively, compounds may undergo enzymatic transformation reactions followed by conversion of the products into bound residues, which are stored in the cell wall of the plant (Sandermann, 1992). Aquatic macrophytes are capable of transforming numerous organic

compounds including chlorophenols (Roy and Hanninen, 1994), trinitrotoluene (Bhadra et al., 1999), organophosphate pesticides (Gao et al., 2000a), and DDT (Gao et al., 2000b). However, such transformation reactions have not been demonstrated to have an appreciable effect on the removal of WDOCs under conditions encountered in treatment wetlands.

In many constructed treatment wetlands that receive wastewater effluent, the predominant species of macrophytes are cattails (*Typha* spp.), bulrush (*Schoenoplectus* (*Scirpus*) spp.) and duckweed (Lemnaceae). Using typical values for biomass in cattail and bulrush wetlands (Kadlec and Knight, 1996) and the previously described linear partitioning model (Equation 6.2), we predict that only relatively hydrophobic compounds will be associated with wetland plants to an appreciable extent under the conditions encountered in constructed treatment wetlands. As a result, retardation factors are less than 10 for compounds with octanol/water partition coefficients less than 10^3. For more hydrophobic compounds, partitioning to plant surfaces will become increasingly important giving contaminants ample time to undergo transformation or uptake.

Field studies in which partitioning between water and plants have been measured are consistent with the relationship depicted in Figure 6.1 for compounds that are removed by hydrophobic partitioning. For example, in a wetland designed for treatment of agricultural runoff, partitioning of the hydrophilic organophosphate pesticide, azinphos-methyl (log K_{ow} = 2.75 (SRC, 2007)), onto sediments was relatively unimportant, with less than 10% of the total mass detected on the plants and detritus. For chlorpyrifos (log K_{ow} = 4.8) in a similar wetland system, partitioning to plant surfaces resulted in the removal of 20–40% of the pesticide (Moore et al., 2002).

Attempts to predict sorption of hydrophilic compounds from octanol/water partition coefficients are likely to underestimate the partitioning, especially in the presence of mineral surfaces (Tolls, 2001), because many of the functional groups undergo specific interactions with mineral surfaces or organic matter-coated surfaces. For example, only about 30% of the injected mass of the moderately hydrophobic tracer, rhodamine WT, was recovered from a large-scale constructed wetland system (Lin et al., 2003). On the basis of sorption experiments and bromide tracer studies, Lin *et al.* (2003) concluded that the compound was lost through irreversible sorption on plant surfaces and organic detritus through specific interactions and not hydrophobic partitioning. Incomplete recovery of rhodamine WT also was reported in a constructed treatment wetland with a lower density of macrophytes (Keefe et al., 2004). Although the potential for contaminant removal by specific interactions with surfaces in wetlands has been documented, additional research is needed to assess the potential importance of such interactions on the loss of polar WDOCs.

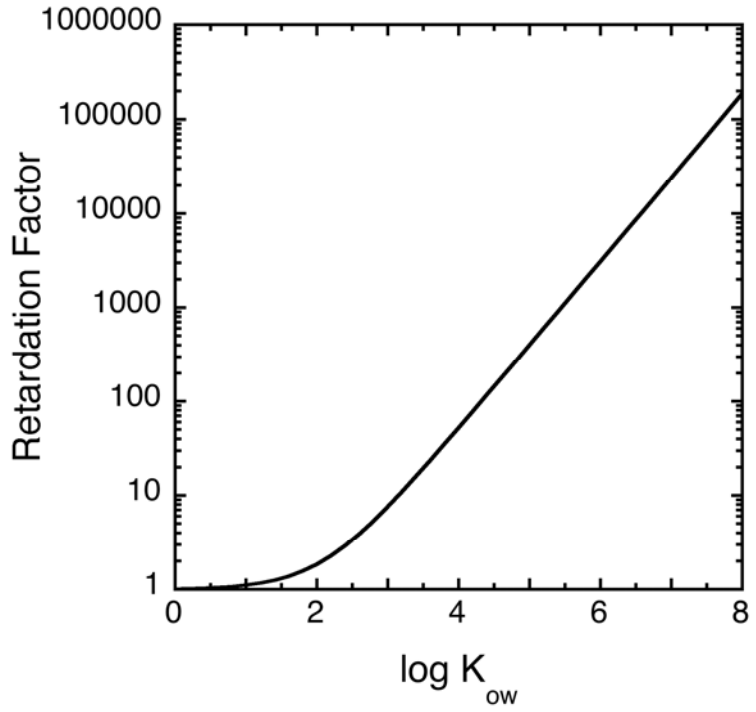


Figure 6.1: Relationship between octanol/water partition coefficient and retardation factor for compounds under conditions expected in a constructed treatment wetland (i.e., 10 gm/L or organic surfaces available for partitioning).

6.3.2 Removal of Organic Compounds by Biotransformation

In wastewater treatment plants, effluent-impacted surface waters and constructed treatment wetlands, the microbial community derives most of its energy from the metabolism of labile organic carbon (i.e., biodegradable organic compounds). The concentrations of WDOCs are usually about four to six orders of magnitude lower than that of the labile organic compounds (i.e., typical concentrations of labile organic carbon are several mg/L, whereas trace organic compounds are usually present at concentrations ranging between 1 and 100 ng/L). As a result, the biotransformation of contaminants is likely to be strongly affected by the nature of the labile organic carbon. In other words, the microbial activity and community structure is likely to be controlled by the metabolism of labile organic carbon, and transformation of WDOCs occurs because the bacteria that metabolize the contaminants are supported by the community that processes the labile organic carbon. In wastewater treatment plants, the labile organic carbon consists of biopolymers produced by organisms in the treatment system and other organic compounds present in sewage. In surface waters and in treatment wetlands, the labile organic carbon includes compounds in the wastewater effluent (e.g., biopolymers) and decaying plant material. As a result, the main factors leading to differences in biotransformation rates in wastewater treatment plants, surface waters, and constructed wetlands are the nature and amount of labile organic carbon and the electron acceptors. There would also be a difference in rates expected because the wetland receives effluent that has already passed through a treatment process. The easier-to-remove fractions of various organic compounds will have already been reduced leaving the more recalcitrant forms for reduction

by the constructed wetland. Consequently, rates in the constructed wetland would be expected to be lower, but the exiting concentrations may also be lower.

To assess the biotransformation of WDOCs in effluent-impacted surface waters, researchers have conducted microcosm studies by spiking samples with low concentrations of contaminants (i.e., typically 0.1-10 μg/L) and incubating unfiltered river water for days to weeks (Jurgens et al., 2002; Fono et al., 2006; Lin et al., 2006; Ying and Kookana, 2003). Biotransformation rates are estimated by comparing rates of loss to sterilized controls exposed to identical conditions. Such studies provide an approximation of biotransformation kinetics in river waters that may be useful to understanding biotransformation in aerobic, open water sections of wetlands. However, extrapolation of such results to conditions in wetlands must be done with caution because the bacteria on the suspended particles in surface waters may be quite different from those attached to biofilms in wetlands. Furthermore, microcosm studies that extend beyond a few days are often not representative of conditions expected in surface water or wetlands because the labile organic matter in wastewater effluent is normally metabolized after about one week and the microbial community in a surface water microcosm will change substantially after all of the labile organic carbon is metabolized.

Despite these limitations, results from surface water microcosms indicate that biotransformation rates are affected by the initial concentration of labile organic carbon. For example, Jürgens et al. (2002) reported faster rates of biotransformation of 17β-estradiol in surface water microcosms for samples collected during summer, when higher densities of algae were present. Attempts to decrease the concentration of labile organic carbon by diluting wastewater effluent or to increase the concentration of labile organic carbon by adding labile organic carbon from plant extracts showed a positive correlation between labile organic carbon content and biotransformation of trace concentrations of common WDOCs, such as naproxen, atenolol, and bisphenol A (Lim et al., 2008).

The biotransformation of WDOCs in treatment wetlands will be different from that observed in surface waters because most of the biomass in wetlands is attached to wetland plants and sediments (Kadlec and Knight, 1996). The microbial community structure and transport of solutes into the biofilms is likely to play an important role in biotransformation rates. In addition, available evidence suggests that the community composition and morphology of aerobic biofilms is affected by exposure to relatively low concentrations of WDOCs. For example, changes in a lotic biofilm were observed relative to controls following exposure to 10 μg/L of caffeine, carbamazepine, furosemide, ibuprofen, or triclosan (Lawrence et al., 2005; Lawrence et al., 2007). Although it is possible to conduct microcosm studies to assess the biotransformation of wastewater-derived contaminants by lotic biofilms with rotating annular reactors (Winkler et al., 2001), attempts to simulate biofilms in treatment wetlands will be complicated because the biofilm structures are likely to be affected by the surfaces (i.e., wetland plants) that are a source of labile organic carbon. Additional research is needed to assess the effects of WDOCs on biofilm community structure and functions in treatment wetlands.

In addition to labile organic carbon, ammonia can serve as a source of energy for microbial communities. Ammonia can be present in wastewater as un-ionized ammonia (NH_3) or ionized ammonia (ammonium ion) (NH_4^+) with the ionized form of ammonia predominant in most wetland systems (Kadlec and Knight, 1996). Ammonia nitrogen can be readily utilized as a nutrient form of nitrogen by most wetland plant species as well as autotropic bacteria species. High concentrations (>2 mg/L) can also be toxic to many forms of aquatic life

including fish and insect species important for natural control of vectors. Very high concentrations (>100 mg/L) can be toxic even to many wetland plant species that utilize ammonia as a nutrient source at lower concentrations. Transformation of nitrogen species within wetland systems is presented in detail in Chapter 4, Section 4.8. Available data from studies of municipal wastewater treatment plants suggests that nitrifying bacteria may be capable of transforming compounds that are not degraded effectively by aerobic bacteria, such as ethinyl estradiol (Joss et al., 2004; Vader et al., 2000; Yi and Harper, 2007) and trimethoprim (Batt et al., 2006; Perez et al., 2005). The role of nitrifying bacteria in the removal of trace organic compounds in wastewater treatment plants is currently unknown and merits further study.

A key difference between surface waters and constructed treatment wetlands is the nature of the terminal electron acceptor. With the exception of open pond areas and a thin layer below the air/water interface, wetland waters do not contain appreciable concentrations of DO. Under most conditions, the terminal electron acceptor in treatment wetlands will be nitrate. Studies on the biotransformation of WDOCs in bank filtration systems (Massmann et al., 2006) and in surface water microcosms (Ying and Kookana, 2003) suggest that biotransformation is faster in the presence of oxygen. Experiments conducted in a pilot-scale subsurface wetland indicated better removal of labile pharmaceutical compounds in shallow parts of the wetland that were assumed to have higher redox potentials (Matamoros et al., 2005), implying that biotransformation is faster while nitrate remains in the system. In SF (or FWS) wetlands, biotransformation of pesticides occurs at a relatively fast rate when straw is used as a substrate and nitrate serves as the terminal electron acceptor (Aslan and Turkman, 2005). Therefore, it is possible that biotransformation of WDOCs will occur under denitrifying conditions in wetlands. Additional research is needed to evaluate the potential for transformation of WDOCs in denitrification systems.

6.3.3 Removal of Organic Compounds by Photolysis

In a densely vegetated, constructed treatment wetland, most sunlight is absorbed by emergent macrophytes and plants floating on the water surface. As a result, photolysis is usually not considered as an important loss mechanism for organic compounds in treatment wetlands. However, some treatment wetlands have considerable open water areas that are designed into the system to facilitate flow distribution, mixing, and treatment function, as well as to enhance wildlife habitat (Kadlec and Knight, 1996; Gearheart et al., 1999; USEPA, 2000). Furthermore, it might be possible to design constructed treatment wetlands with shallow, open water areas or hybrid systems combining marsh areas with emergent vegetation and open water pond areas with sufficient depth of water to inhibit emergent plants if it provided advantages with respect to treatment (e.g., removal of trace organic contaminants). However, open water areas whether shallow or deep would need to be kept clear of floating vegetation to enable penetration of sunlight through the water column. The potential importance of photolysis to contaminant fate in wetland systems should be considered during design.

Many WDOCs undergo photolysis in the presence of sunlight (Boreen et al., 2003) with half-lives ranging from minutes to weeks under typical conditions encountered near the air–water interface. To predict the rate of photolysis in an engineered constructed wetland system, it is necessary to consider the attenuation of sunlight with depth. Under conditions typically encountered in wastewater effluent, the intensity of light decreases by about an order of magnitude over the first 50 cm (Fono et al. 2006). Thus, photolysis rates in engineered wetlands will depend on water depth. The relatively high rates of photolysis reported when

samples are exposed to light in reactors with short light path lengths in the laboratory will only be observed in the top few centimeters of the water column.

For compounds undergoing direct photolysis, it is possible to predict removal rates as a function of water depth using spectral data from the compound and chromophores present in the water, experimental data on the direct photolysis quantum yield, and sunlight intensity data (Zepp and Cline, 1977). Because wastewater effluent and water in constructed treatment wetlands usually contains high concentrations of compounds that absorb light (i.e., chromophores) in the spectral range that is most important for direct sunlight photolysis (i.e., 295–330 nm), direct photolysis is only likely to be significant for compounds that are particularly susceptible to direct photolysis such as NDMA, FeEDTA, and diclofenac (Buser et al., 1998).

For compounds undergoing indirect photolysis, transformation rates can be estimated using models that have been calibrated for production of reactive oxygen species and other photo-produced species and rate constants for reactions of the transients with the compound of interest (Lam et al., 2003). In general, estimates of indirect photolysis rates have less precision than those for direct photolysis because the input data are more difficult to obtain with a high degree of precision. For example, studies on indirect photolysis of the herbicide alachlor in wetlands suggest that indirect photolysis reactions mediated by hydroxyl radical are the most important mechanisms of phototransformation of the compound, with half-lives ranging from about 1 to 20 days under near surface conditions (Miller and Chin, 2005). The rate of hydroxyl radical production will depend strongly on the concentration of nitrate, which undergoes direct photolysis to produce hydroxyl radical (Zepp et al., 1987). Thus, the elevated concentrations of nitrate often entering constructed treatment wetlands could enhance the rate of indirect photolysis of wastewater-derived contaminants.

CHAPTER 7

RESEARCH STUDIES

7.1 EXPERIMENTAL APPROACH

The experimental approach to examine potential removal of select hormones and pharmaceuticals by constructed wetlands involves the performance of microcosm experiments, the operation and testing of a pilot-scale wetland system, and the assessment of the performance of a large-scale constructed wetland. The microcosm and pilot-scale constructed wetland studies included testing for removal of selected hormones and pharmaceuticals. The large-scale constructed wetland was evaluated from a perspective of identifying critical design and operating parameters that should be considered in providing a constructed wetland that would perform effectively.

7.1.1 Microcosm Study for WDOCs Removal

The microcosm study involved the use of twelve 75L clean glass experimental units as shown in Figure 7.1. Bacteria and plants were the two primary experimental factors evaluated in this study using a 2^2 factorial design; Table 7.1 presents all treatments applied to microcosms. Further description of the experimental methods is included in Appendix A. Bacterial transformation was experimentally manipulated at two levels: "no bacteria" and "bacteria." In addition, replicate microcosms contained Nanopure water or effluent with dissolved organic matter from cattail extract. These additional microcosms, in addition to those two microcosms containing "no plants" and "no bacteria" allowed for exploration of the importance of direct and indirect photolysis transformation of the study compounds. For example, Arnold and McNeill (2007) specifically review the importance of photolysis transformation processes for pharmaceuticals. Adsorption to plant material was also manipulated at two levels: "no plants" and "plants." The microcosm units were set up adjacent to the City of Denton's pilot-scale constructed wetland located at the city's Pecan Creek Water Reclamation Plant (PCWRP). The treated effluent for the PCWRP was used in the microcosm studies. The experiments involved spiking the treatment water with several target analytes including acetaminophen, codeine, diphenhydramine, diltiazem, diazepam, 17β-estradiol, 17α-ethinyl estradiol, and testosterone.

Table 7.1. Treatment Letters and Corresponding Treatment Types

Treatment Letter	Treatment Type Description
A	2 microcosms with no plants, no bacteria (due to sodium azide treatment)
B	2 microcosms with plants, no bacteria (due to sodium azide treatment)
C	2 microcosms with no plants, bacteria (due to NO sodium azide treatment)
D	2 microcosms with plants, bacteria (due to NO sodium azide treatment)
E	2 microcosms with plants in DI water
F	2 microcosms with plants, bacteria (due to NO sodium azide treatment) and DOC extract

7.1.2 Pilot-Scale Wetland Study for WDOCs Removal

The pilot-scale constructed wetland is located at the PCWRP and received effluent from that treatment plant. The wetland was constructed in fall 1992. A diagram of the pilot-scale wetland is presented in Figure 7.2. Specifically, this wetland included four main channels with varying depths; additional characteristics of the wetland are documented in Hemming et al. (2002). The testing process involved spiking with two different sets of analytes: pharmaceuticals and steroids.

There were two spiking events—one during January 2008 (cold season event) and a second during the October 2008 (warm season event). The cold-season tracer studies showed a HRT of just 36 to 42 hours. During the warm season spiking event, the HRT was adjusted to 65 to 70 hours by reducing the inflow into the wetlands. A description of the experimental methods for the pilot-scale wetland spiking studies is included in Appendix B.

a)

b)

4	6
10	9
1	12
7	8
3	2
5	11

Figure 7.1. (a) Arrangement of glass microcosms adjacent to the City of Denton wetland; (b) experimental numbers assigned to microcosms using a random number generator.

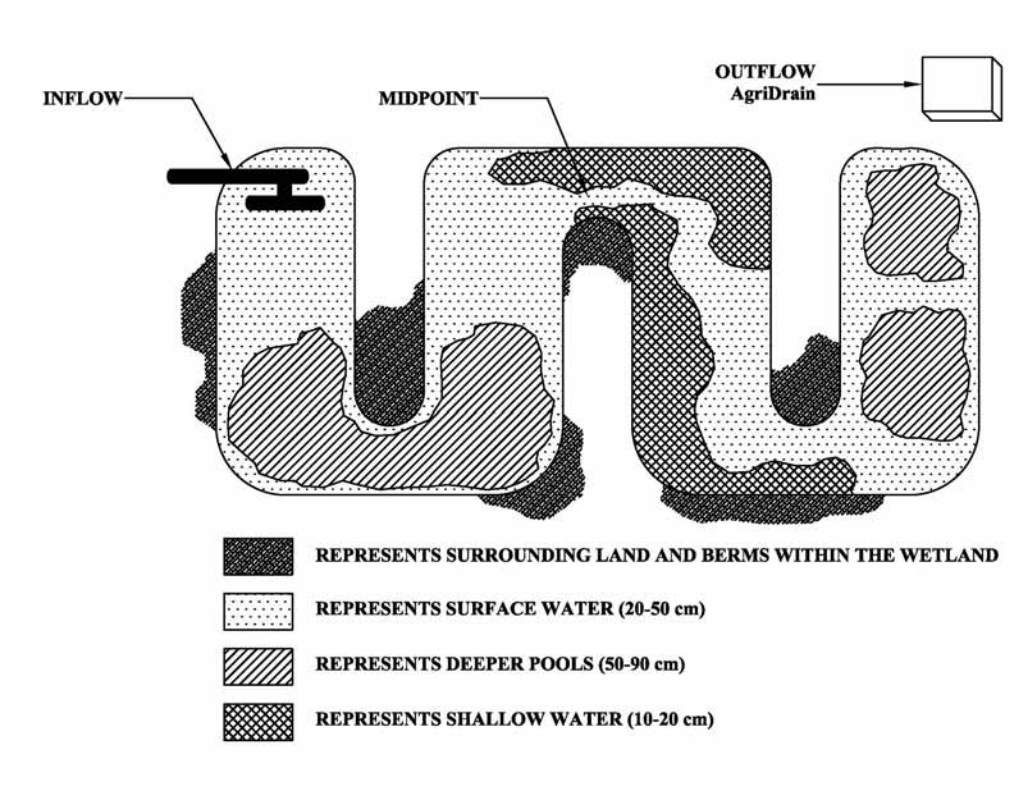


Figure 7.2. Diagram of the City of Denton constructed wetland flow path and approximate depths.

7.1.3 Large-Scale Constructed Wetland System

As indicated in Chapters 3, 4, and 5, constructed wetlands have demonstrated the ability to provide effective removal of conventional constituents. This research project has included an assessment of a large-scale constructed wetland system to develop information relevant to extrapolating the performance observed during the microcosm and pilot-scale constructed wetland to a large-scale wetland. Although data for WDOCs are not available for the large-scale constructed wetland, the treatment effectiveness data for conventional constituents and the design and operational considerations associated with that facility are of significant value.

The large-scale constructed wetland system known as the George W. Shannon Wetlands Water Recycling Facility (GWSWWRF) field-scale wetland is owned and operated by the Tarrant Regional Water District (TRWD). The GWSWWRP field-scale wetland located in Texas at the Richland-Chambers Reservoir started with the design, construction, and eight-year operation of a 2.5-acre pilot-scale constructed wetland, which allowed the performance evaluation of extensive research and testing. The results of TRWD's eight-year pilot-scale study enabled the design of a 243-acre field-scale constructed wetland to perform further research regarding the treatment expectations of the wetland system and verification of the performance capabilities documented during the eight-year pilot-scale study. The field-scale constructed wetland has been in operation since June 2003. Figure 7.3 presents an aerial photo of the field-scale wetland. A detailed description of the GWSWWRF is included in Appendix D.

Figure 7.3. Aerial photograph of the Tarrant Regional Water District's field-scale constructed wetland.

7.1.4 Analytical Methods

The analytical methods established for this project were critical in order to develop reliable data involving compounds measured at extremely low concentrations. The correct sample collection and preservation procedures were very important. The processing and testing of samples involved solid-phase extraction (SPE) and liquid chromatography/mass spectrometry/mass spectrometry (LC-MS/MS) analysis. Details of the analytical methods are presented in Appendix C.

7.1.5 Statistical Analyses

Differences in target analyte reduction data from microcosm experimental treatment were determined using a general linear model (GLM) approach for the factorial design (SPSS, Inc.).

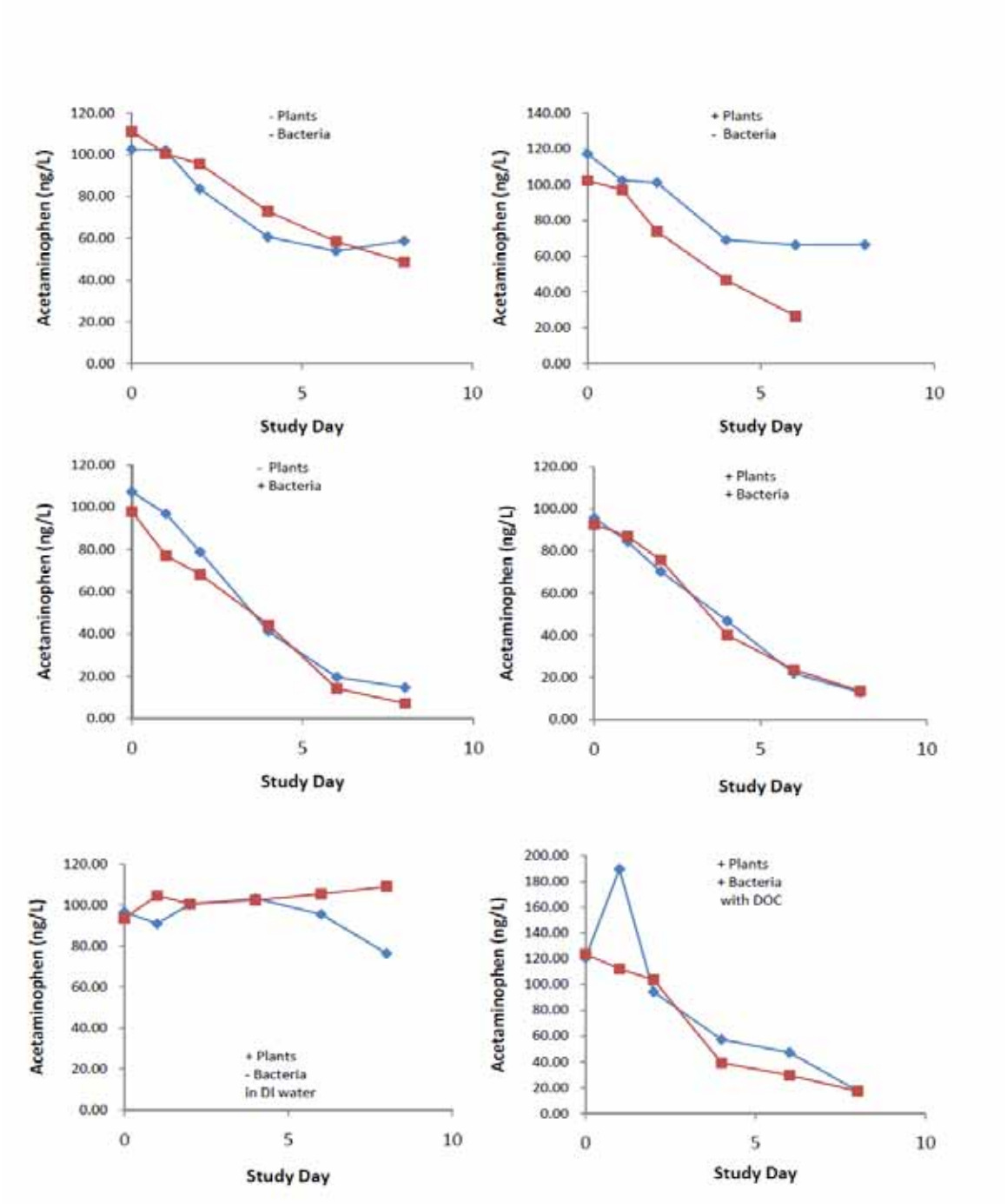
7.2 STUDY RESULTS

The following section presents the findings of the microcosm study, the pilot-scale wetland study, and the assessment of the large constructed wetland system.

7.2.1 Microcosm Study

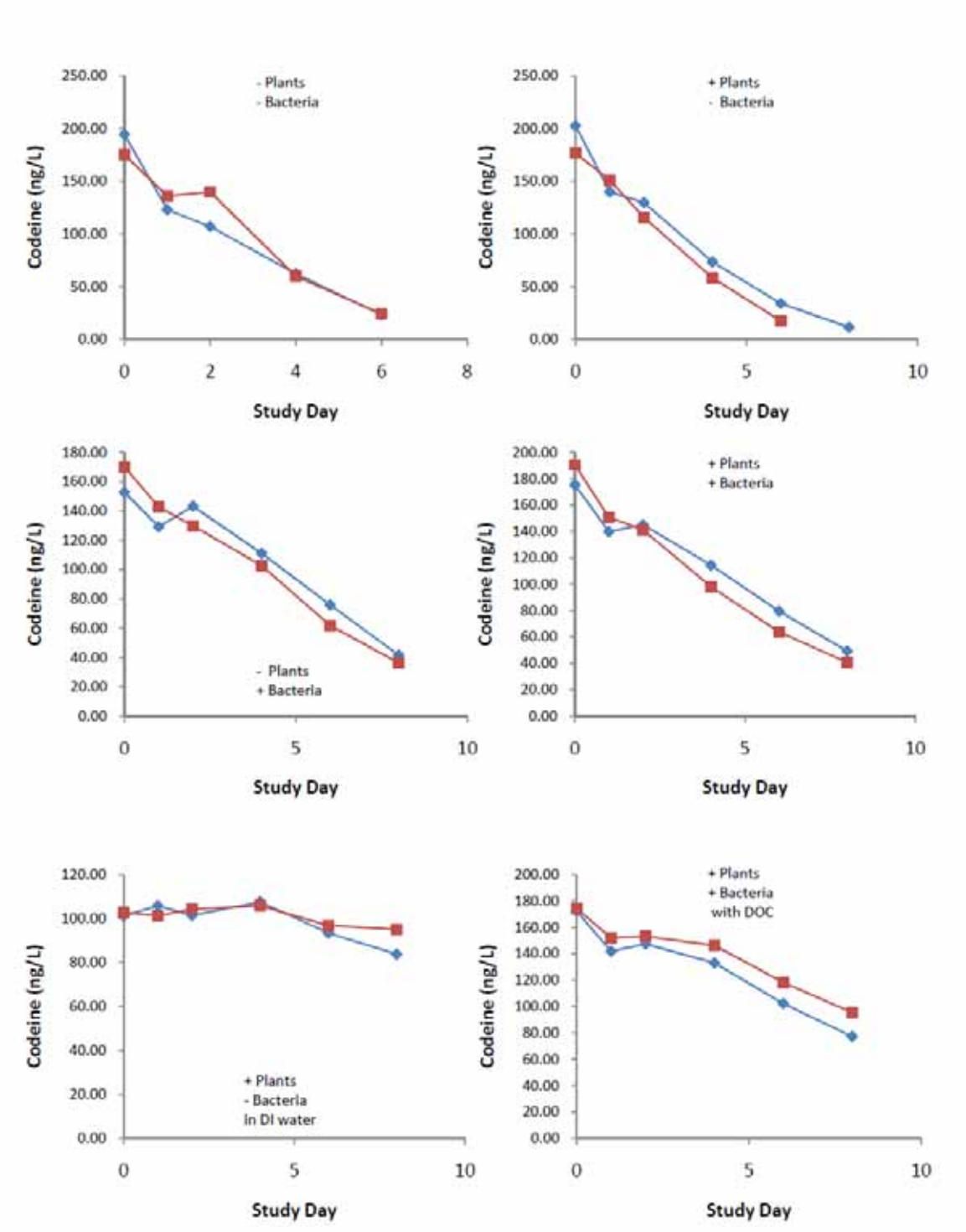
The microcosm studies conducted at the City of Denton's PCWRP indicated differential removal among target pharmaceuticals, apparently by different transformation process. Figures 7.4a-7.4f present concentration data through the microcosm study period for acetaminophen, codeine, diphenhydramine, diltiazem, diazepam, and atenolol, respectively. Steroid results, as summarized in Lim (2008a), are presented in Figures 7.5a–7.5d for estradiol, ethinyl estradiol, testosterone, and progesterone, respectively.

Specifically, the effect of plant adsorption and bacterial treatments, and combinations thereof, on pharmaceutical degradation was tested using a cross-classified 2^2 factorial design. Bacteria treatment was observed to significantly influence reduction of acetaminophen ($p = 0.017$), atenolol ($p = 0.003$) and codeine ($p = 0.006$), but not diltiazem ($p = 0.253$) and diazepam ($p = 0.156$). Figures 7.5a–7.5e present bivariate interaction plots for acetaminophen, atenolol, codeine, diazepam, and diltiazem, respectively.



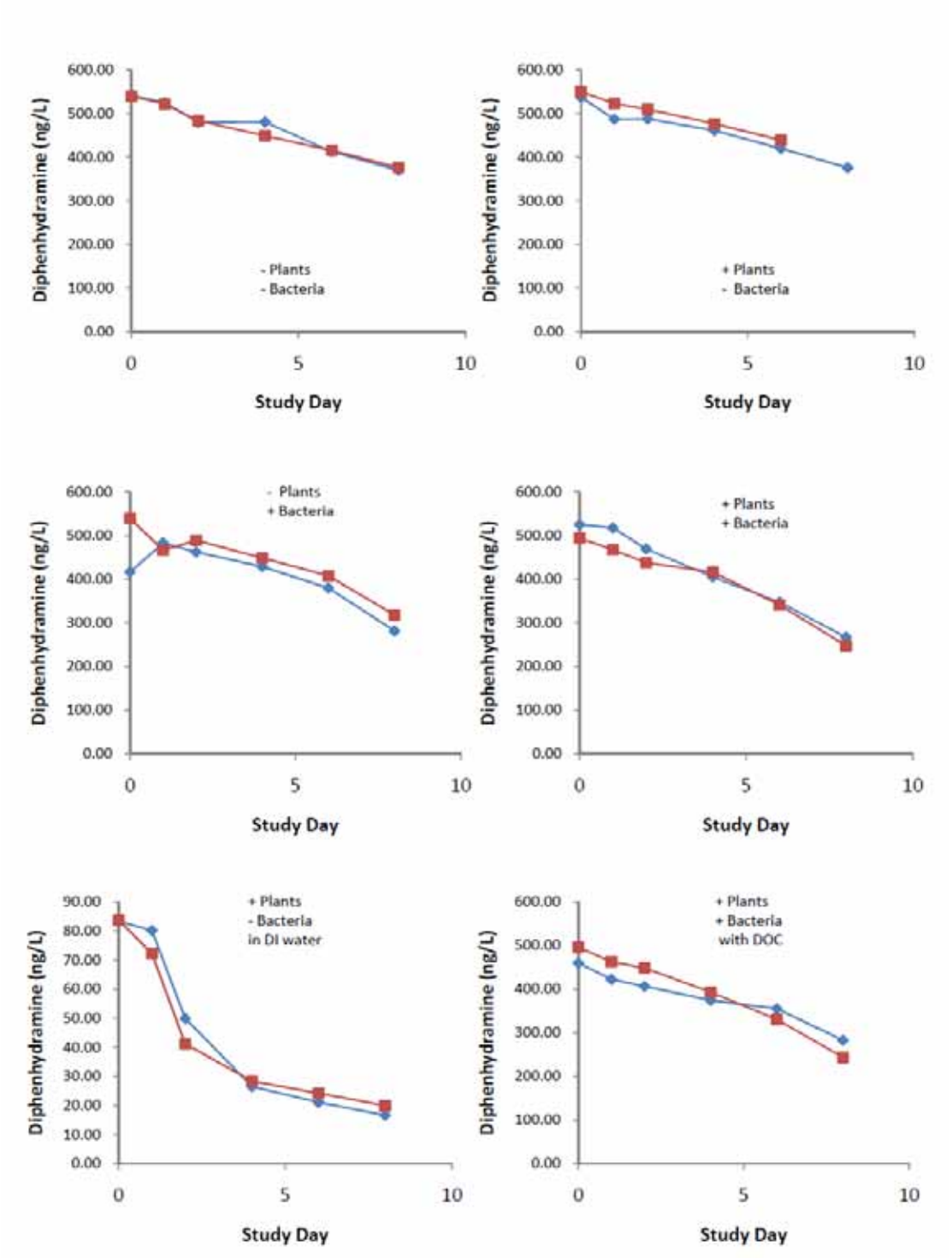
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent / present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure water.

Figure 7.4a. Acetaminophen concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



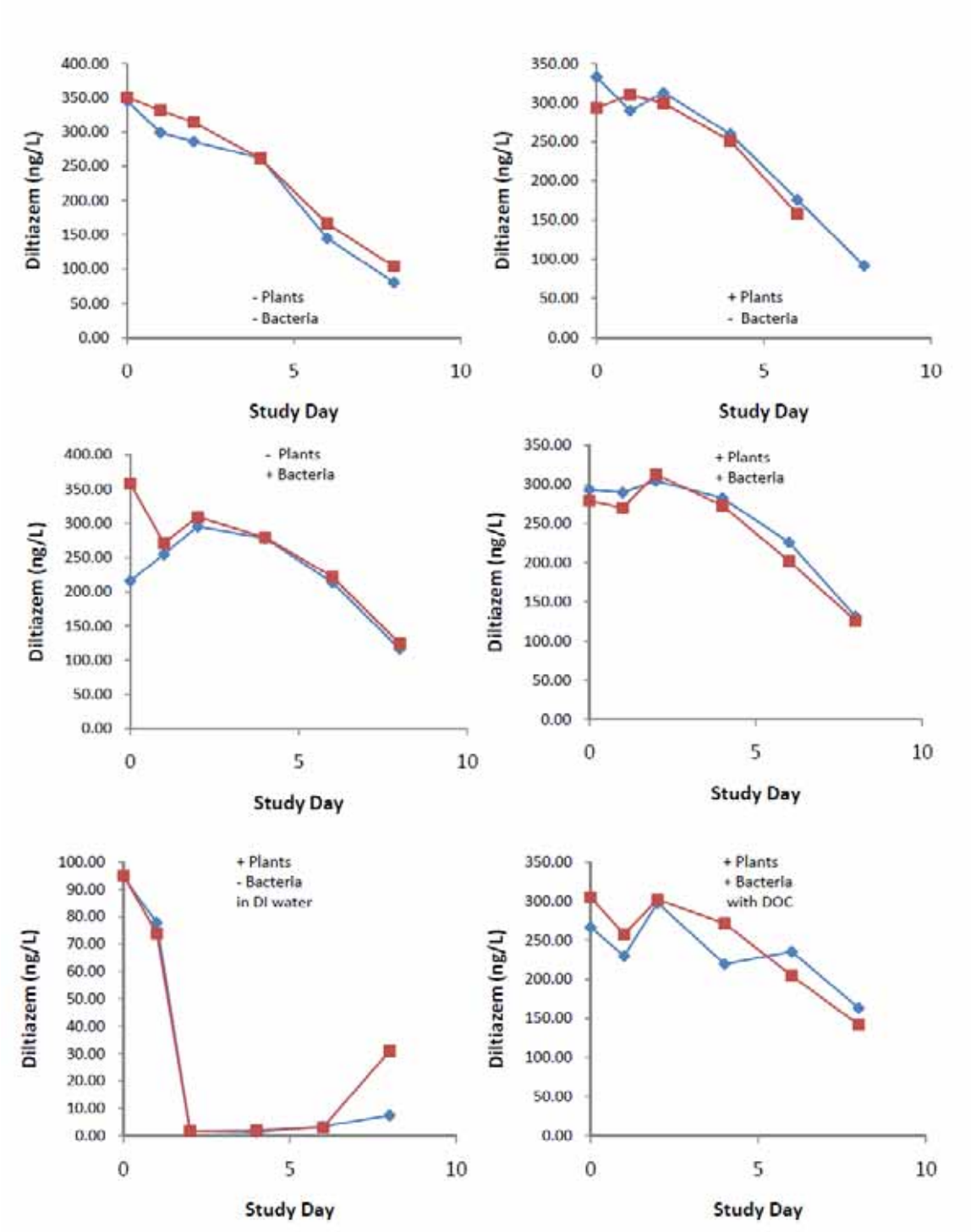
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent / present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure

Figure 7.4b. Codeine concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



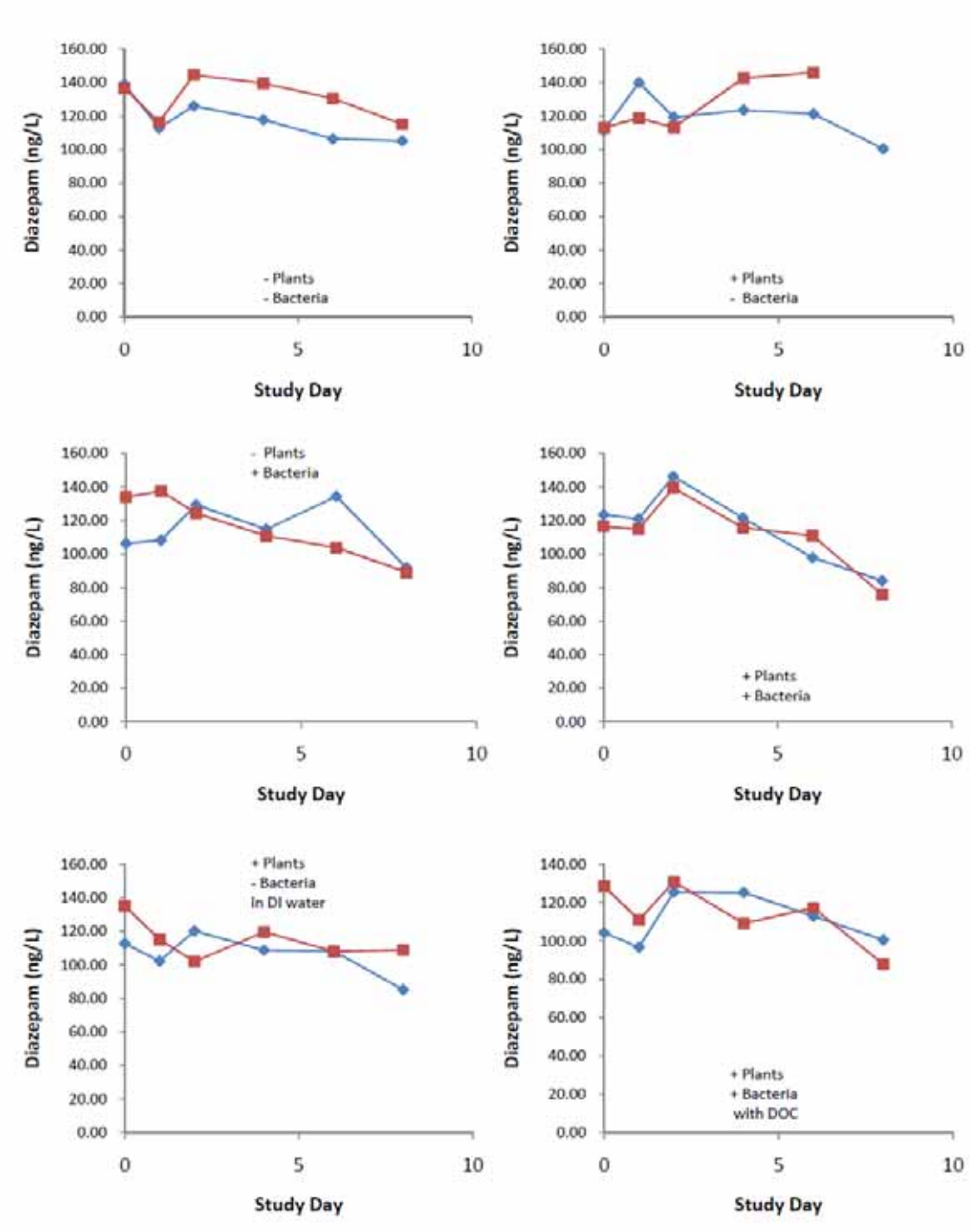
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent/present; –/+ Bacteria = sodium azide present / absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure water.

Figure 7.4c. Diphenhydramine concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



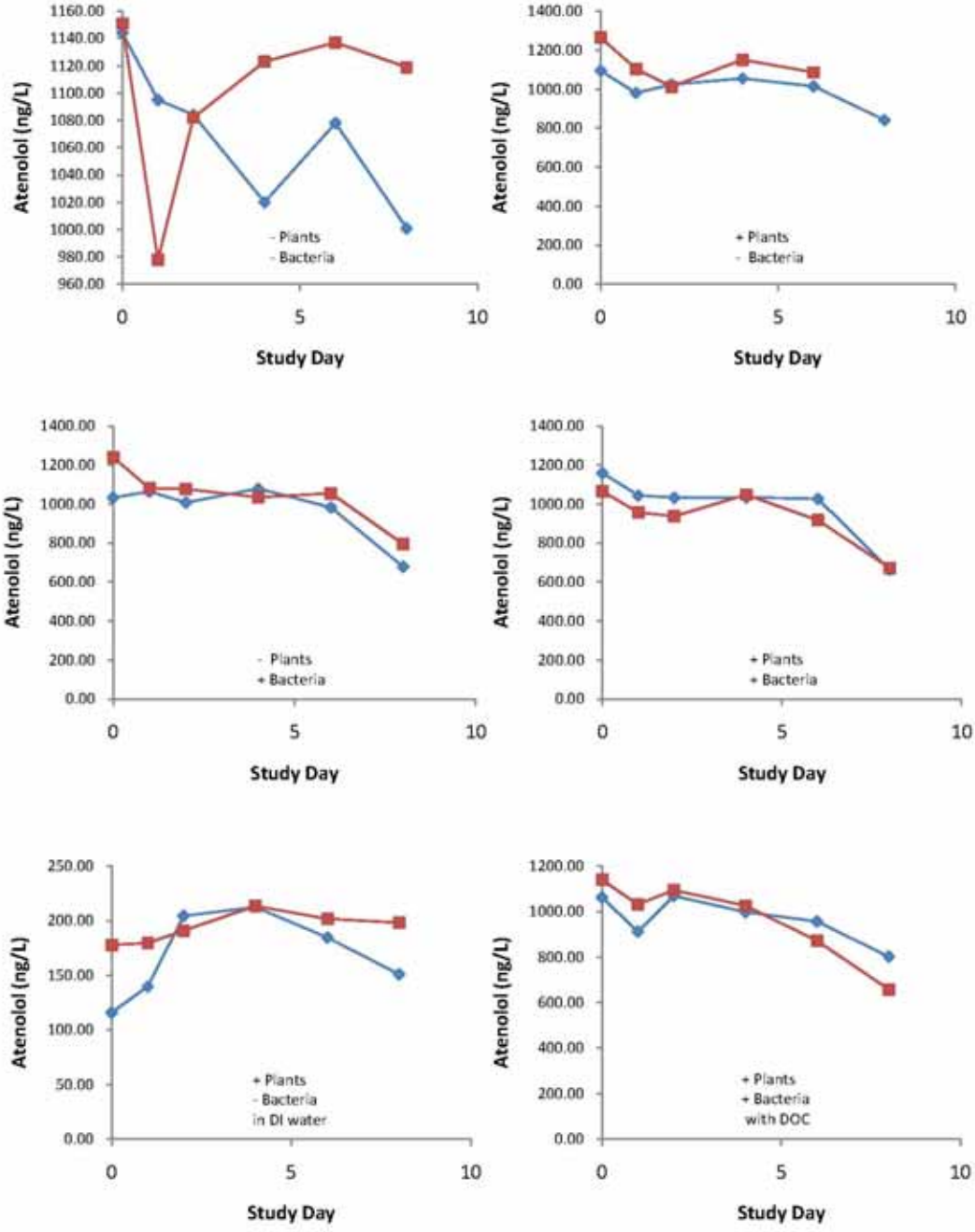
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent / present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure water.

Figure 7.4d. Diltiazem concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



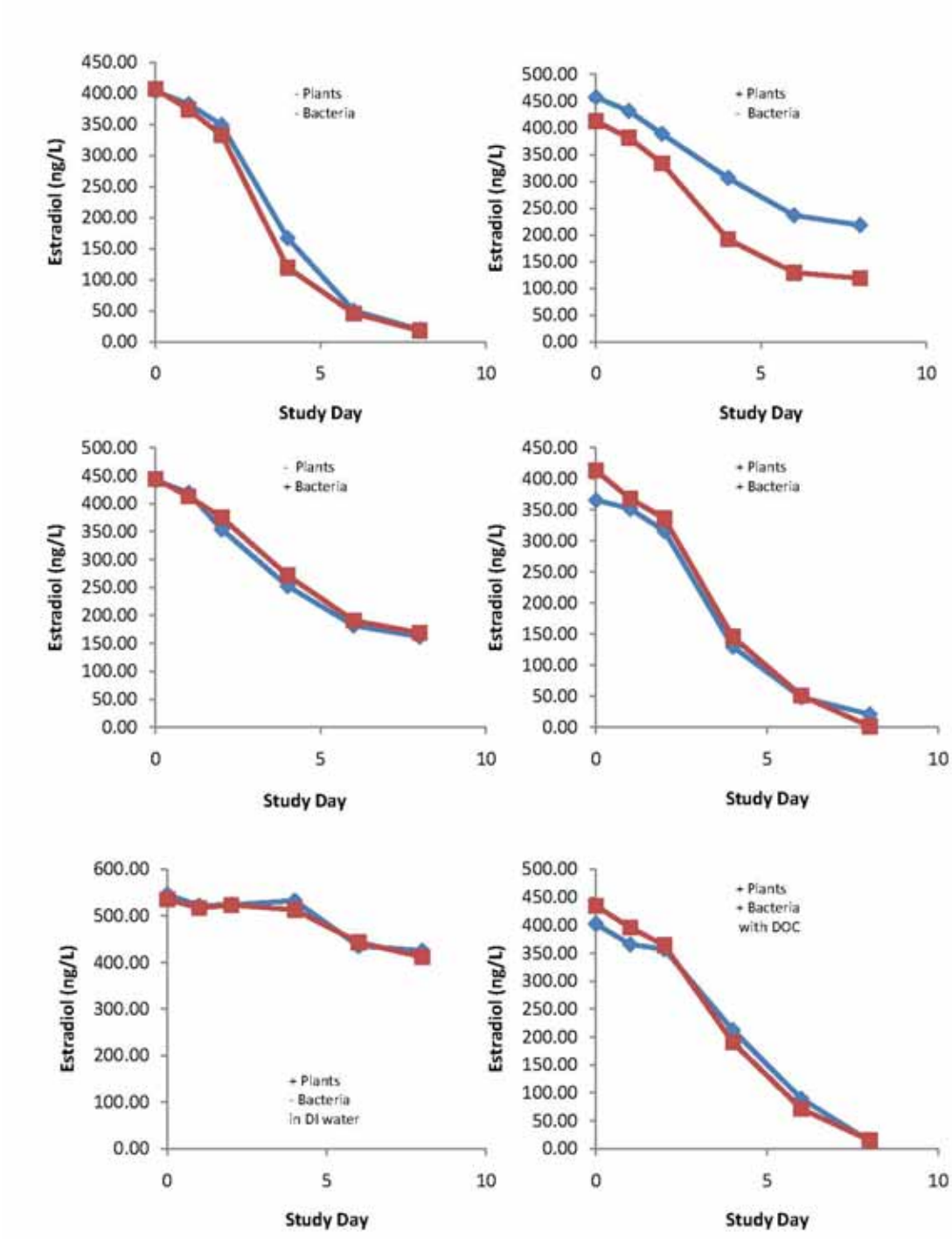
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent / present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure

Figure 7.4e. Diazepam concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



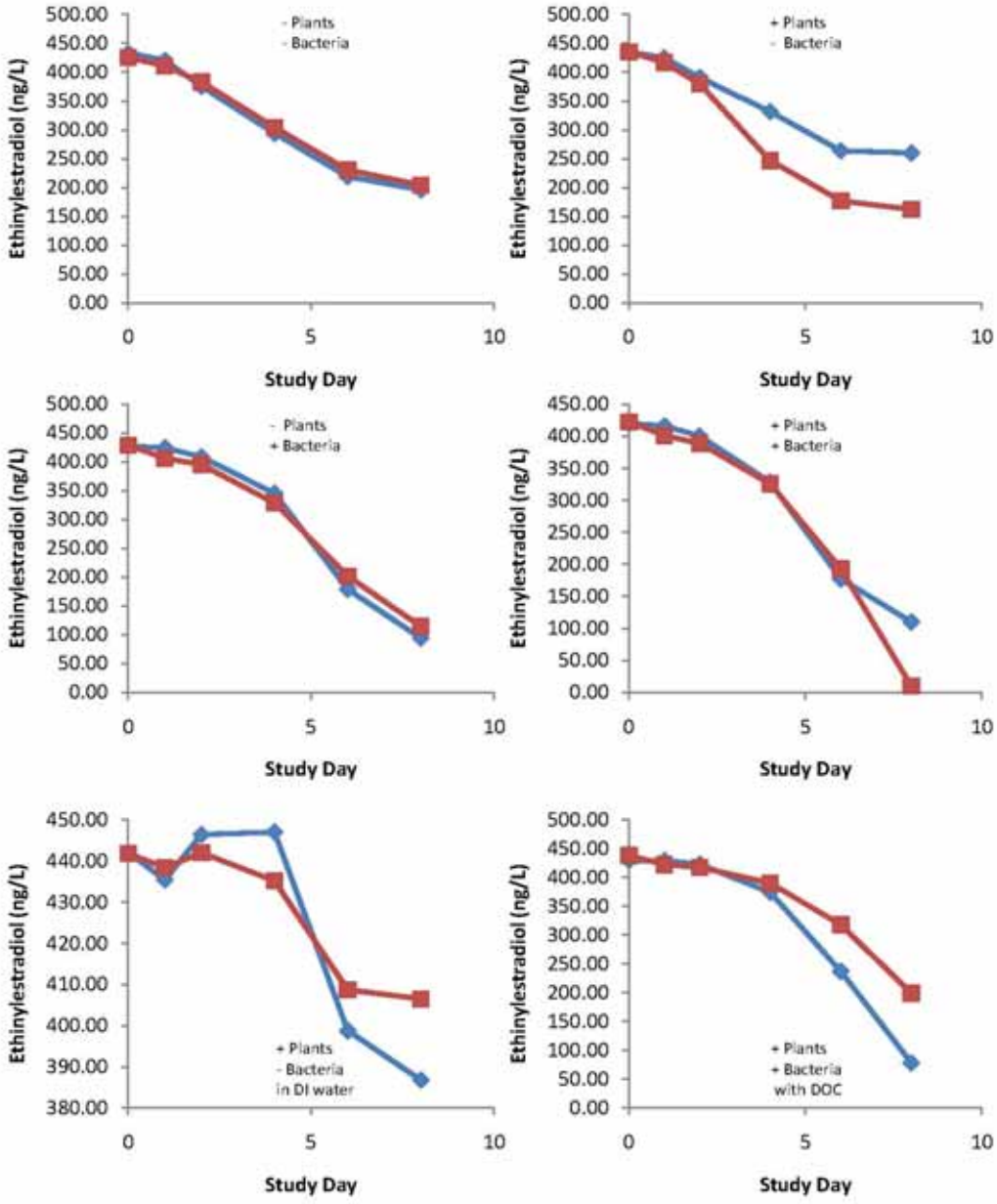
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent / present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure

Figure 7.4f. Atenolol concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



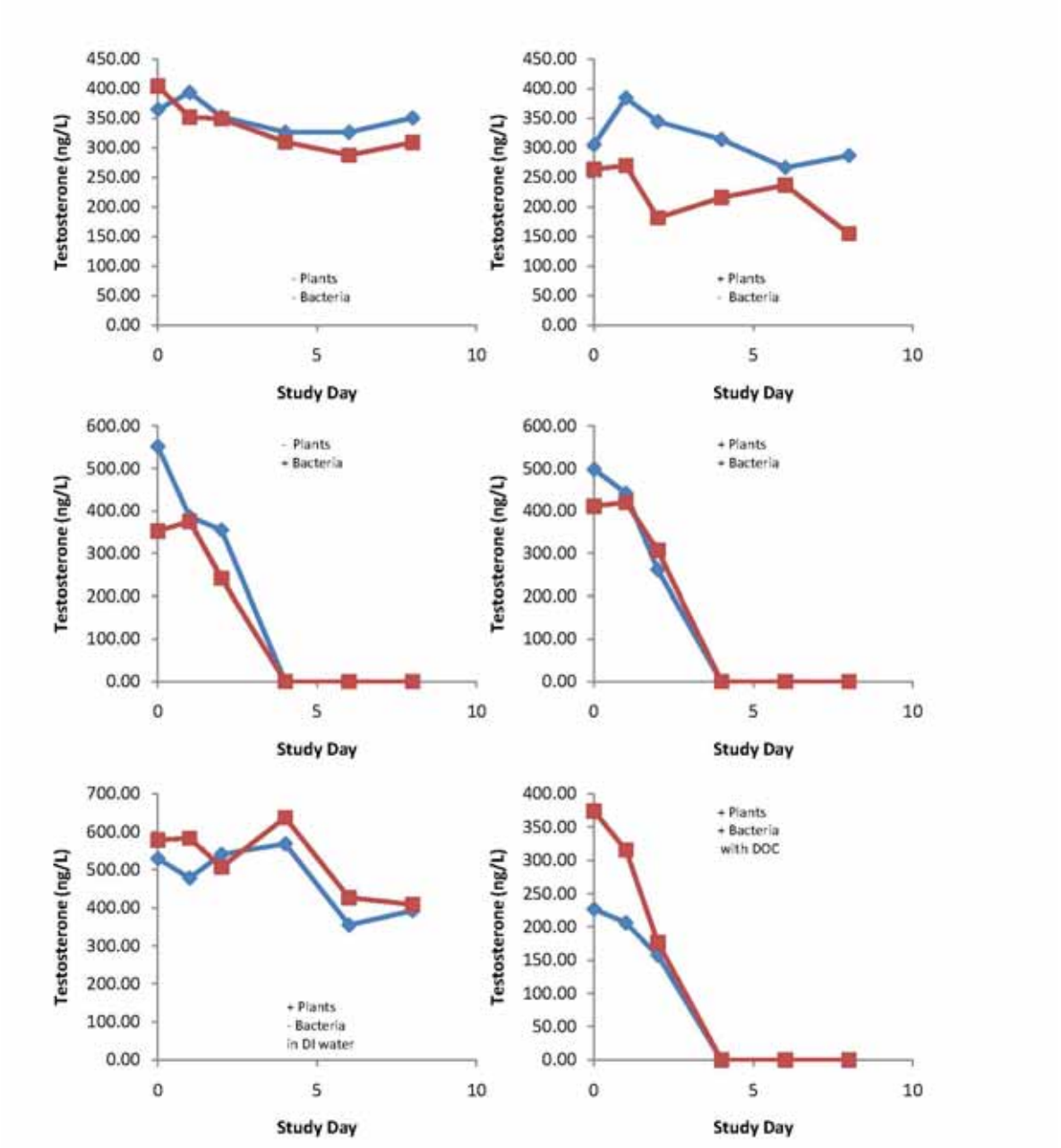
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent / present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure

Figure 7.5a. Estradiol concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



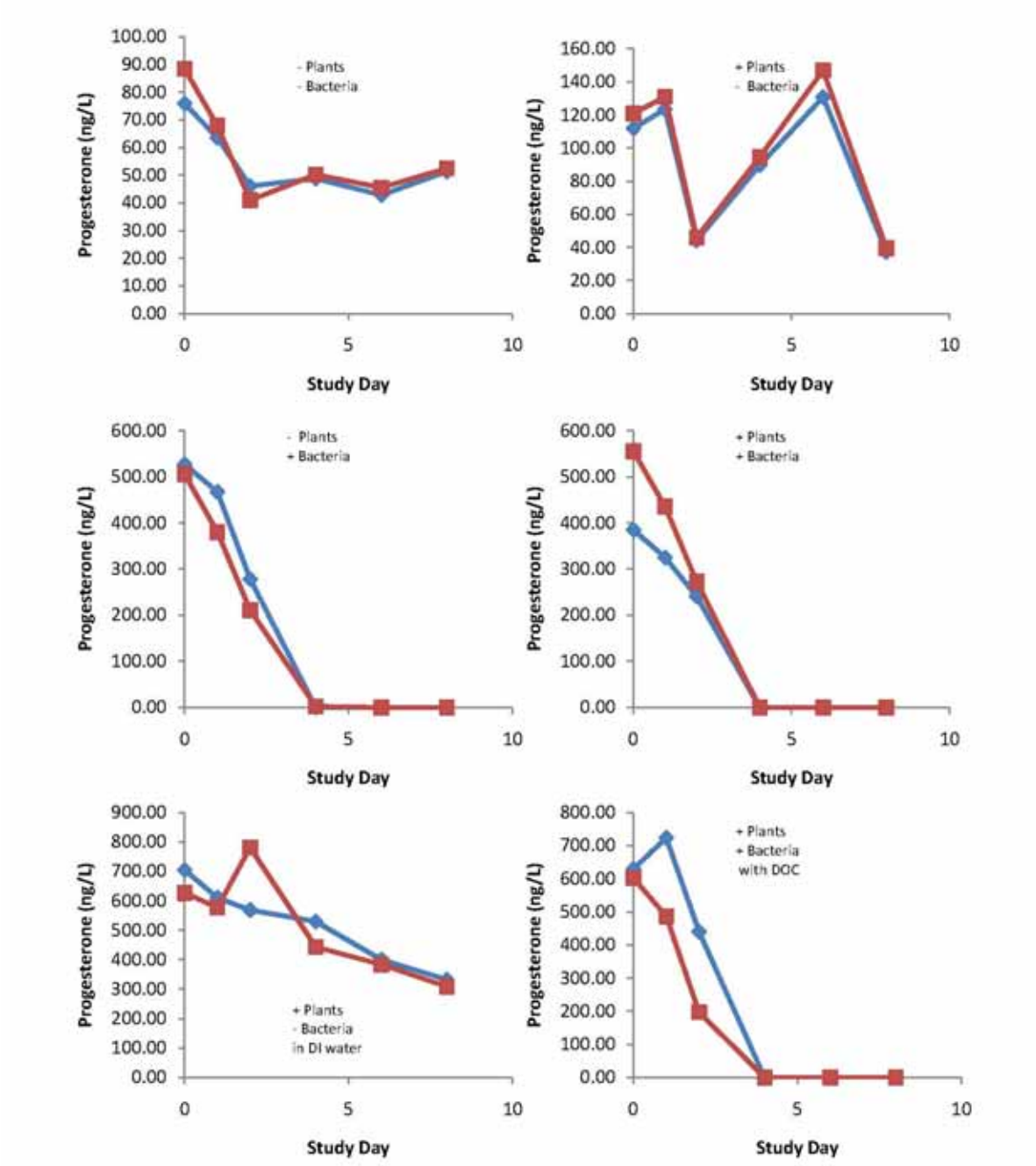
On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent/present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure

Figure 7.5b. Ethinyl estradiol concentrations (ng/L) in microcosms over an eight-day study period by treatment type.



On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent/present; –/+ Bacteria = sodium azide present / absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure

Figure 7.5c. Testosterone concentrations (ng/L) in microcosms over an eight-day study period by treatment type.

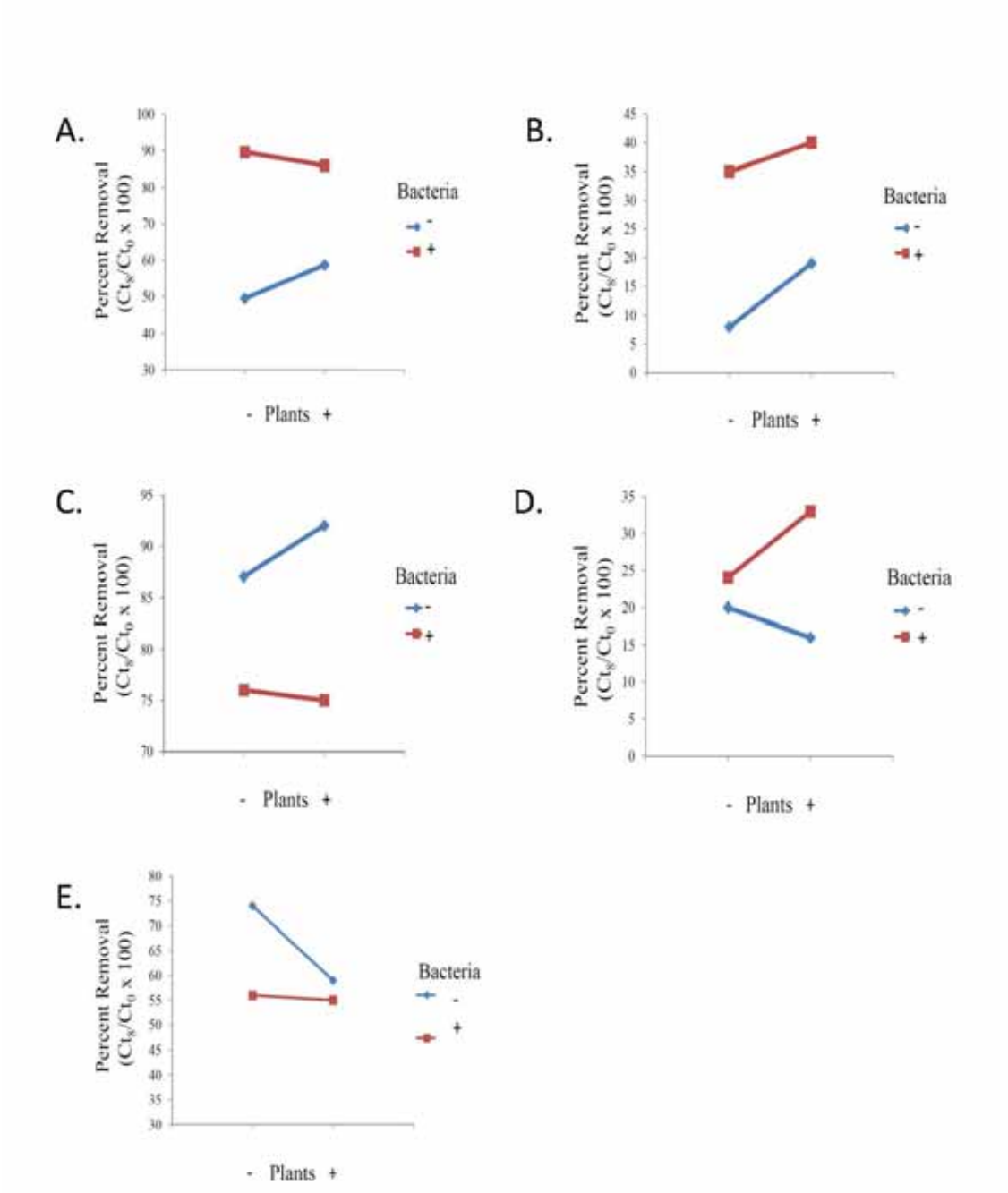


On each figure square and diamond lines represent replicate microcosms. –/+ Plants = plants absent/present; –/+ Bacteria = sodium azide present/absent; DOC = dissolved organic carbon cattail extract (~5 mg/L). DI = Nanopure

Figure 7.5d. Progesterone concentrations (ng/L) in microcosms over an eight-day study period by treatment type.

In addition to significant reduction of select target analytes by bacterial transformation, photolysis appeared to be an important mechanism for reduction of acetaminophen, codeine, and diltiazem, but not as important for diazepam and atenolol. In experimental units not containing plant material and receiving sodium azide treatment to limit biotransformation, photolysis would probably be the most important transformation process. Approximately 50%, 50%, 87%, and 74% mean reductions from Day 0 levels were observed in the no-plant, no-bacteria treatment for acetaminophen, progesterone, codeine, and diltiazem, respectively (Figure 7.6). Such potential reductions by photolysis are in contrast to observations for atenolol (7%), ethinyl estradiol (15%), estradiol (20%), and diazepam (20%) in the same treatments (Figure 7.6). Although the presence of bacteria treatments (no sodium azide) did increase reduction of both atenolol and diazepam, both molecules appeared relatively recalcitrant compared to acetaminophen, codeine, and diltiazem (Figure 7.6). Among all compounds tested, diazepam was the most stable across the experimental treatment structure (Figure 7.5d). In the case of acetaminophen, photolysis and bacterial transformation appeared to be particularly important degradation pathways. For example, maximum mean reduction of acetaminophen was observed in experimental units containing bacteria (and subjected to ambient light), resulting in almost 90% reduction in these treatments after an eight-day study (Figure 7.6).

Although significant effects of plant adsorption were not observed in this study, this area deserves more study. Two hundred grams of cattail were included to 70L microcosms; it is possible that increasing this mass to volume ratio could have increased potential adsorption of target analytes. However, it is also critical to examine how ambient pH influences log D values of each of these molecules, which range in pKa values from 3.3 for diazepam to 9.86 for acetaminophen (ACD Labs). Log D is conceptually similar to log Kow; however, this partition coefficient accounts for influences of ambient pH on ionization state, based on the pKa of a chemical (Kah and Brown 2008). Thus, under the conditions tested, several of the compounds would be present mainly as ionized and thus relatively polar molecules.



Note. -/+ Plants = plants absent/present; -/+ Bacteria = sodium azide present/absent.

Figure 7.6. Mean (*n*=2) percent removal of (A) acetaminophen, (B) atenolol, (C) codeine, (D) diazepam, and (E) diltiazem concentrations (ng/L) in microcosms after an eight-day study period by treatment combination.

7.2.2 Pilot-Scale Constructed Wetland Study

The pilot-scale constructed wetland study involved testing both a cold season event and a warm season event. Each of these events provided information valuable to this research effort; however, operational issues associated with the cold season event limited the amount of data developed.

Because of problems with regulation of the inlet flow, the hydraulic retention time of the wetland was much shorter than expected during the cold season spiking study. As a result of the unexpectedly short HRT, the initiation of sample collection started after the peak concentrations of lithium had already passed through the pilot-scale wetland system. The rapid passage of the spike through the wetland was not detected with the bromide-selective electrode, possibly because the locations where samples were collected (i.e., along the edges of the wetland) were outside of the main flow path of the water. The first sample collected for analysis of lithium (and steroid hormones, pharmaceuticals), which was collected approximately 40 hours after spiking, contained approximately 35 μg/L of lithium. Lithium concentrations decreased to concentrations near background (i.e., <10 μg/L) approximately 65 hours after spiking. The only steroid hormone detected in the samples was ethinyl estradiol, which decreased from a concentration of approximately 20 ng/L 40 hours after spiking to less than 1 ng/L at 60 hours. On the basis of the lithium recovery (i.e., comparing the concentration of lithium detected at 40 hours with the maximum concentration detected in the subsequent study), it was concluded that the HRT was less than 24 hours in this study. The steroid hormone data are consistent with removal of 17β-estradiol, testosterone, and progesterone. With these limited data it is difficult to determine if ethinyl estradiol, which is the most recalcitrant of the steroid hormones, was removed during passage through the pilot-scale wetland.

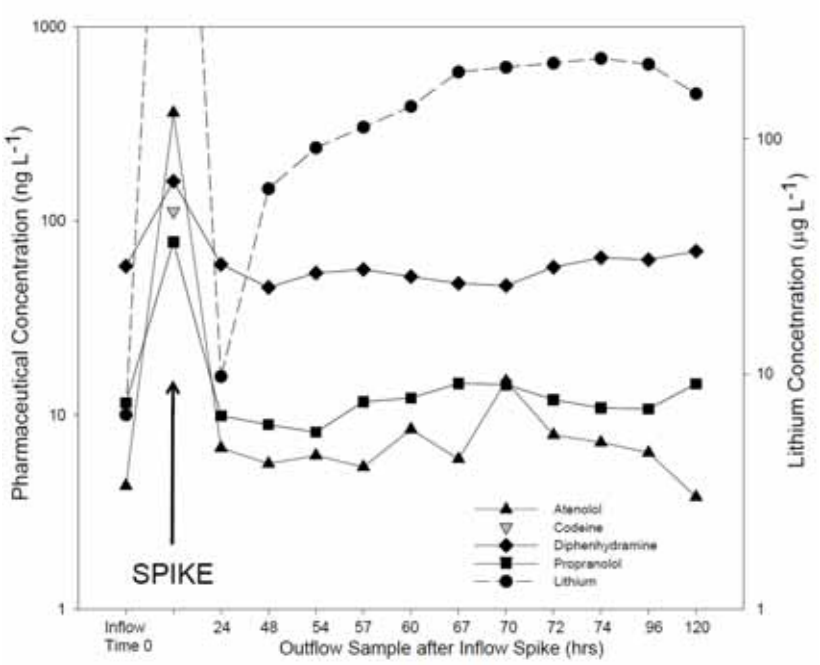
The warm season spiking study yielded results that provided insight into the removal of WDOCs in the wetland because the hydraulic retention time was longer and samples were collected before, during, and after the pulse reached the outlet. Data on the concentration of the lithium tracer indicated that breakthrough of the spike started between 24 and 48 hours after spiking (Figures 7.7 and 7.8). The peak concentration of lithium was detected 74 hours after spiking. Lithium concentrations decreased by approximately 25% between the peak and the end of sample collection (i.e., 120 hours after spiking).

Figure 7.7 depicts pharmaceutical and lithium concentrations at the City of Denton wetland inflow immediately prior to and immediately after the warm season spiking event, and pharmaceutical and lithium levels at the wetland outfall through time after initial spiking. Maximum Li concentrations were observed 74 hours after the spiking event. It is interesting to note that all pharmaceutical concentrations in the outflow of the City of Denton wetland were reduced by the end of the study (at 120 hours), suggesting removal of these target analytes by this pilot-scale constructed wetland facility. Specifically, at the 120 hr sampling event, acetaminophen, atenolol, codeine, diazepam, diphenhydramine, diltiazem, gemfibrozil, and propranolol levels at the wetland outflow were 95.3%, 99%, 81.1%, 92.2%, 56.4%, 89.4%, 95.2%, and 81.4%, respectively, less than introduced concentrations in the wetland inflow at sample time 0. Similar results were observed by the Sedlak group at UC Berkeley for spiked steroid levels (Figure 7.8).

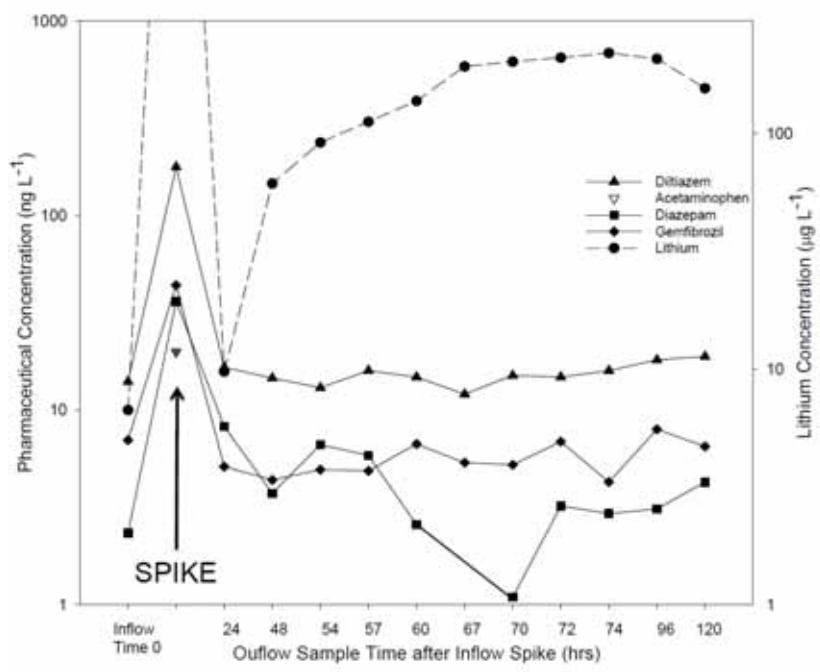
Among the steroid hormones, ethinyl estradiol and 17β-estradiol were detected at concentrations up to approximately 6 ng/L after the spike as shown in Figure 7.8. For comparison, municipal wastewater typically contains between 0.2 and 2 ng/L of 17β-estradiol

and between 0.05 and 1 ng/L of ethinyl estradiol. The highest concentrations of both steroid hormones were detected 60

A.



B.



A. Atenolol, diphenhydramine, and propranolol were reduced to background effluent levels, and codeine was removed below limit of detection. B. Diazepam, diltiazem, and gemfibrozil were reduced to background effluent levels, and acetominophen was removed below limit of detection.

Figure 7.7. Target pharmaceutical and lithium tracer levels at City of Denton constructed wetland outfall through time following inflow spike (SPIKE) at Time 0.

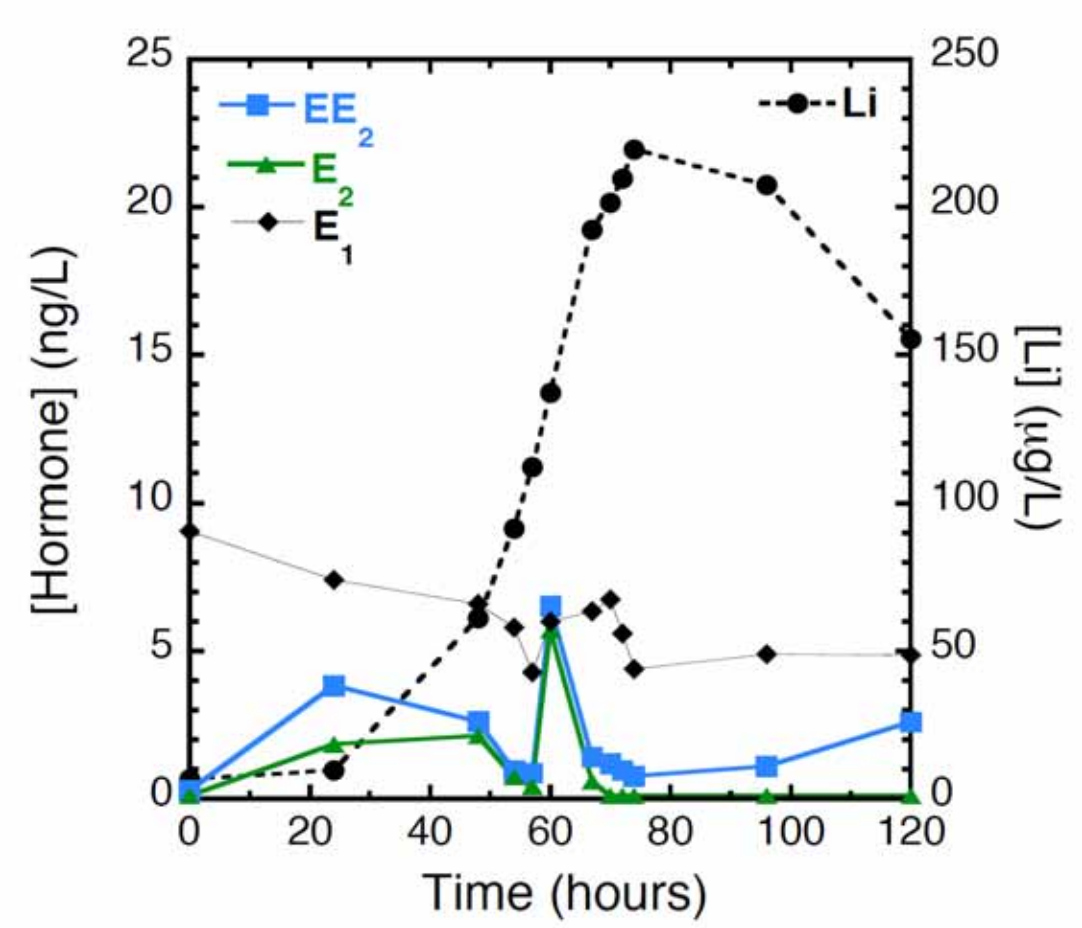


Figure 7.8. Target hormone and lithium tracer levels at City of Denton constructed pilot wetland outfall through time following inflow spike at Time 0.

hours after spiking, which coincides with the highest concentrations of lithium measured in the wetland effluent. Furthermore, the concentration of ethinyl estradiol was always greater than that of 17β-estradiol, which is consistent with the resistance of ethinyl estradiol to biotransformation. Using the ratio of the mass of lithium to steroid hormones added in the spike, the expected maximum steroid hormone concentrations would have been approximately 500 ng/L if there was no attenuation, which is approximately two orders of magnitude higher than what was measured in the samples.

Among the remaining steroid hormones, testosterone and progesterone were never detected and estrone (which was not spiked into the wetland) was consistently detected at concentrations between 5 and 10 ng/L, which is consistent with concentrations typically detected in municipal wastewater effluent. These data suggest that the wetland removed testosterone and progesterone but not estrone.

7.2.3. Large-Scale Constructed Wetland Study

The assessment of the large-scale constructed wetland confirmed that its performance is similar to the results reported for other wetlands. Based on information included in Chapters 3, 4, and 5 and the results of assessing the GWSWWRF field-scale wetland (as presented in Appendix D), it is critical that the constructed wetland be properly designed and operated in order to maximize the treatment effectiveness. Of utmost importance to the design will be establishing a system that provides effective flow distribution through the wetland in a manner that minimizes short-circuiting. In addition, it is critical to provide a design that enables maintaining the operating water depth of marsh area within a range of 6 inches to 18 inches (shallower is better). When selecting the appropriate aquatic plants for the wetlands, the site-specific climate and the depth of water in which they will be located must be considered. Also, the operation and maintenance program needs to be performed in a manner that will manage undesirable wildlife (i.e., nutria, wild hogs, etc.) that could be detrimental to the wetlands performance. Improved performance for removal of nitrogen and phosphorus indicated the need for increased cover of emergent vegetation, reduction in average water depths, improvements in flow distribution, and correlation of hydraulic and mass loading rates with wetland treatment area. Because of limitations regarding removal rates of WDOCs, wetland design will need to be based on treatment coefficients applied to nitrogen and phosphorus removal and/or the results of pilot-scale wetland testing until a sufficient database is available to develop treatment coefficients specifically for WDOCs.

7.2.4. Summary of Study Results

Removal mechanisms identified for WDOCs are summarized in Table 7.2. Table 7.3 lists the mean percent removals observed in this study for the targeted analytes and water quality parameters.

Table 7.2. Removal Mechanisms for WDOCs

Parameters	Physical	Chemical	Biological	Comments
Acetaminophen	Not applicable	***Photolysis***	***Biotransformation***	Insufficient data to determine sorption effects
Atenolol	Not applicable	Photolysis	***Biotransformation***	Insufficient data to determine sorption effects
Codeine	Not applicable	***Photolysis; sorption***	Biotransformation	
Diazepam	Not applicable	Photolysis	Biotransformation	Insufficient data to determine sorption effects
Diltiazem	Not applicable	***Photolysis***	Biotransformation	Insufficient data to determine sorption effects
Diphenhydramine	Not applicable	Photolysis; ***adsorption***	***Biotransformation***	
Gemfibrozil	Not applicable			Not available for microcosm study
Propranolol	Not applicable			Not available for microcosm study
Estradiol (E2)	Not applicable	Photolysis	***Biotransformation***	Insufficient data to determine sorption effects
Ethinyl Estradiol (EE2)	Not applicable	Photolysis	***Biotransformation***	Insufficient data to determine sorption effects
Testosterone	Not applicable		***Biotransformation***	Insufficient data to determine sorption effects
Progesterone	Not applicable	***Photolysis***	***Biotransformation***	Insufficient data to determine sorption effects

Note. Significant removal mechanisms are italicized and bolded**.**

Table 7.3. Performance Matrix

Study Component	TSS	TN	TP	Acetaminophen	Atenolol	Codeine	Diazepam	Diltiazem	Diphenhydramine	Gemfibrozil	Propranolol	Estradiol (E2)	Ethinyl Estradiol (EE2)	Testosterone	Progesterone
Microcosm Study[1]															
No-Plants No-Bacteria	NA	NA	NA	49.8	8.6	71.6	24.4	80	38.1	NA	83.8	62.6	53.4	14.2	36.8
No-Plants Bacteria Present	NA	NA	NA	89.4	32.9	71.6	21.6	63.3	40	NA	62.3	95.4	75.6	99.9	99.9
Plants No-Bacteria	NA	NA	NA	39.5	13.2	77.8	10.5	56.7	34	NA	66.8	61.2	51.5	22.4	66.9
Plants Bacteria Present	NA	NA	NA	85.9	16.2	45.1	30.8	31.7	22.9	NA	46.5	97.2	85.7	99.9	99.9
Plants No-Bacteria DI Water	NA	NA	NA	2.5	42.4	77.8	66.9	55.9	76.3	NA	91.2	22.5	10.2	27.6	51.9
Plants Bacteria with DOC	NA	NA	NA	85.7	27.5	46.5	16.9	52.6	39.7	NA	52.9	96.6	67.9	99.9	99.9
Pilot-Scale Wetland Warm Season Study[2]															
	NA	NA	NA	95.3	99	81.1	92.2	89.4	56.4	95.2	81.4	99.9	99.9	99.9	99.9
Large-Scale Wetland Study[3]															
	96	67	44	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

[1]Microcosm studies conducted for 8 days using 75 L glass units with treated effluent from the City of Denton's Pecan Creek Water Reclamation Plant (except for units using deionized (DI) nanopure water). Transformation was experimentally manipulated at two levels: "no-bacteria" and "bacteria." The treatment water was spiked with a mixture of the target analytes.

[2]Pilot-scale spiking event study was conducted at the pilot-scale wetland located at the City of Denton's Pecan Creek Water Reclamation Plant and received treated effluent from the plant. HRT during the warm-season spiking event was 65–70 hours. Samples were collected over 120 hours.

[3]Large-scale wetland study refers to evaluation of data from the Tarrant Regional Water District's 243-acre field-scale wetland of the George W. Shannon Wetlands Water Recycling Facility. Average HRT over the 3.5 years operational period was 8.18 days (196.32 hours).

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

Research and analyses undertaken by this project supports continuing consideration of constructed wetlands as an option for providing polishing treatment to protect aquatic ecosystems and potable water supplies. The findings of the project indicate that constructed wetlands can be used to consistently and cost effectively reduce concentrations of conventional pollutants remaining in reclaimed wastewaters and can also further reduce levels of certain WDOCs. However, additional experience and research is needed to confirm the effectiveness of these systems. There are a number of conclusions based on the research performed for this project.

1. Constructed treatment wetlands are a proven technology for removal of conventional pollutants in a variety of wastewaters and stormwaters. Thousands of wetland treatment systems have been constructed worldwide to effectively reduce concentrations of BOD, TSS, nitrogen, phosphorus, pathogens, and trace metals.

2. In the United States, constructed treatment wetlands are most commonly utilized as one of the final steps in an overall treatment train that generally includes primary and secondary pretreatment using more energy intensive processes and constructed wetlands for final polishing and compliance with advanced wastewater treatment (AWT) standards.

3. Many of these large-scale constructed treatment wetlands also incorporate public use facilities and include design features to optimize the ancillary benefits of wildlife habitat and support and passive human recreation and nature study. In addition, treated effluent may be used as water supply for ecological enhancement including created aquatic habitats.

4. Extensive efforts have been undertaken to gather and assess data and information about the performance of constructed wetlands to treat conventional parameters, particularly phosphorus and nitrogen.

5. Pollutant removal rates are generally predictable and reproducible between differing treatment wetland designs and geographical locations. Based on assessment of treatment removal mechanisms and actual performance data, design criteria and design models have been fairly well established for conventional parameters.

6. Only recently have constructed wetlands been considered as a possible reliable technology for removal of trace organic contaminants and WDOCs. Research is needed to determine if the design criteria for conventional parameters also are effective for WDOCs.

7. Limited data are currently available for assessing the efficacy and reliability of constructed wetlands for removal for more than a handful of specific WDOCs at trace

concentrations typical of reclaimed wastewater. Almost no data for WDOCs removal in full-scale SF constructed wetland projects currently exists.

8. Existing data indicate that wetlands may be as effective as and possibly more effective than more energy intensive conventional wastewater treatment technologies at reducing the concentrations of degradable and adsorbable trace contaminants. Wetlands often have the advantage of much longer hydraulic and solids residence times than conventional tank-based treatment processes and have more diverse environmental conditions.

9. Research conducted for this project demonstrated some of this potential but also illustrated the highly individualistic properties that are of importance in these removal processes. Additional research is needed to better describe the effectiveness of constructed wetlands for polishing of individual trace contaminants and for extrapolation to other unstudied compounds. Conclusions of this research are summarized in the following (numbers 10–14).

10. Concentrations of all spiked pharmaceuticals (including acetaminophen, atenolol, codeine, diazepam, diphenhydramine, diltiazem, gemfibrozil, and propranolol) were significantly reduced at the end of the 120 hours (5 days) study conducted at the City of Denton wetland.

11. The steroid hormones included in the spiking study at the City of Denton wetland showed similar removals as the pharmaceuticals, with testosterone and progesterone never detected at the outfall and peak concentrations detected for ethinyl estradiol and 17β-estradiol approximately two orders of magnitude less than calculated concentrations expected with no attenuation representing approximately 99.9% removals.

12. Estrone (which was not spiked into the wetland) was consistently detected at concentrations between 5 and 10 ng/L, consistent with concentrations typically detected in municipal wastewater effluent, suggesting that the wetland did not provide effective removal for this compound.

13. Biotransformation within a wetland environment was determined to be a major removal mechanisms for acetaminophen, atenolol, diphenhydramine, estradiol, ethinyl estradiol, testosterone, and progesterone.

14. Based on the microcosm study results, photolysis was also determined to be an important mechanism for reduction of acetaminophen, codeine, diltiazem, and progesterone, but not as important for diazepam and atenolol.

15. Constructed treatment wetlands are being utilized for polishing treatment in projects that involve indirect utilization of reuse water to augment potable water supplies. The constructed treatment wetlands, in general, were originally selected to remove conventional constituents; however, they are now being recognized as an additional barrier along with other barriers to protect the quality of the potable water supplies.

16. Utilization of constructed treatment wetlands may result in changes to the quality characteristics of the wetlands treated water (i.e., changes in levels of TOC and DOC, etc.), which could be important relative to the drinking water treatment plant

processes. Therefore, a better understanding of this consideration is needed with respect to determining the role of constructed treatment wetlands in indirect reuse projects to augment potable water supplies.

8.2 RECOMMENDATIONS

Treated effluents have been used for ecological enhancement and creation of habitat areas. In addition, application of constructed wetlands to reuse projects is an emerging application of an existing technology. New questions need to be asked and answered as reclaimed water is used to recharge potable aquifers and supplement public water supplies.

1. Constructed wetlands should continue to be considered as a viable option for reduction of WDOCs. However, additional research should be performed to confirm the treatment effectiveness for various WDOCs. Also the effects of WDOCs on plants and wildlife within surface flow constructed treatment wetlands should be an important area of research.

2. A review of all constructed wetlands projects in the United States that are currently used for the direct or indirect recharge of potable water supplies should be conducted and summarized. Existing wetland design criteria, input/output data, and special studies related to pollutants that may be chronically or acutely toxic to humans and wildlife need to be summarized. This review will form the basis for implementing additional focused sampling of parameters of greatest interest concerning beneficial reuse.

3. Representative large-scale constructed treatment wetlands being utilized for recycling reclaimed water to potable water supplies should be studied for the occurrence and fate of a variety of trace contaminants, including a variety of pharmaceuticals, trace organics, and trace metals. Comparative ecological and human health risk assessment should be performed for waters entering and leaving the constructed wetland environment to examine efficacy of wetlands as a risk mitigation approach.

4. Pilot-scale testing of constructed wetlands should be performed for a period of three to four years to confirm treatment effectiveness for selected WDOCs and to develop design criteria considerations prior to constructing a large-scale wetland for the specific purpose of removing WDOCs. The requirement for pilot-scale testing will most likely diminish as information is developed based on data obtained from full-scale wetland operations and testing.

5. Further research should be performed to address specific issues and uncertainties, particularly with regards to WDOCs removal, relative to the application of constructed wetlands for indirect water reuse projects to augment potable water supplies. Hybrid technologies, including the incorporation of SF and SSF constructed wetlands and pond and wetland cells in treatment trains should also be evaluated for WDOCs removal.

6. Consideration should be given to constructed wetlands serving as a “natural” (i.e., providing benefits associated with nature) aspect of a water reuse system. Including a natural aspect was identified as a major consideration for the public to accept using reuse water to augment potable water supplies at the Research Needs Assessment Workshop: Human Reactions to Water Reuse (Haddad, 2004).

CHAPTER 9

FUTURE RESEARCH NEEDS

Available data indicate that constructed treatment wetlands have the potential to help remove WDOCs prior to discharge to surface waters. However, most previous research has consisted of empirical studies of compound removal without detailed assessment of removal mechanisms or rigorous quantification of system performance under a variety of conditions. To improve our understanding of the potential uses of constructed treatment wetlands, additional research is needed. Several important areas are summarized here:

- More data are needed on the ability of existing full-scale constructed treatment wetlands to remove WDOCs. The collection of data from large-scale treatment wetlands is important because non-ideal flow paths and variability in microbial communities that develop in large systems cannot be fully simulated in pilot- or laboratory-scale systems. Collection of data from large-scale systems is particularly challenging because variations in inlet concentrations for trace contaminants leads to considerable variability, whereas quantification of the low concentrations of WDOCs has considerable uncertainty. As a result, studies of large-scale treatment systems will require the collection of numerous samples accompanied by state-of-the-art analytical methods.

- A better understanding is needed of the potential importance of sorption and uptake of contaminants by aquatic plants and sediments in wetlands. Most previous studies of these processes have focused on hydrophobic compounds, whereas many of the WDOCs are hydrophilic. For example, many pharmaceuticals are ionizable at surface water pH, which may influence partitioning and transport in wetland systems. Such studies may also help to differentiate between the role of biofilms on the surfaces of plants and the plants themselves.

- More research is needed on the role of the microbial community in the wetland on the biotransformation of WDOCs. In particular, research is needed to define the role of substrates (i.e., labile organic carbon and ammonia) and electron acceptors (i.e., oxygen and nitrate) on the microbial community and the rate of compound transformation.

- Photolysis has the potential to help remove compounds that are not amenable to removal by biotransformation. However, it has not been exploited in most constructed treatment wetlands. Data are needed on the potential for designing a hybrid treatment wetland system that could help exploit the tendency of many trace organics to undergo photolysis.

- WDOC studies in constructed wetlands need to be focused on both fates and effects. The ecological risk of WDOCs in constructed wetlands should be carefully examined to see if these substances are below acute or chronic toxicity levels in constructed wetlands.

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APPENDIX A

A.1 MICROCOSM METHODOLOGY

The microcosm study site was directly adjacent to the City of Denton wetland. An area was cleared and plywood sheets were used to create flat working space for the microcosm experimental units. Twelve 75L clean glass experimental units were arranged on the plywood study site such that there were no gaps between them (Figure A.1a). Sides of all microcosms were wrapped in white plastic to provide equivalent light transmission into all tanks. On Day 0, microcosms were filled to 70L with final treated effluent from the PCWRP on Day 0. Treatment E in Table 1 was an exception because it was filled with Nanopure water transported from Baylor University (BU) laboratory to the study site. Inflow effluent water was run through the transfer hose for 15 minutes prior to filling microcosms.

Experimental units were assigned numbers and treatments according to randomized experimental design (Figure A.1b) and each microcosm was assigned a treatment according to the experimental design summarized in Tables A.1 and A.2. Bacterial transformation was experimentally manipulated at two levels, “no bacteria” and “bacteria,” by applying sodium azide to experimental units that specified “no bacteria” (Table A.1). Adsorption to plant material was also experimentally manipulated at two levels, “no plants” and “plants,” by using mature cattails. Cattails were harvested from the City of Denton wetland and cut into 15 cm sections. Only the portion of the cattail that extended from the sediment to the surface of the water was used. Experimental units with “plants” received ~200 g of harvested cattails, which was less than 1% of the total mass in the treatment. Cattails were submerged in the middle of the microcosms using pre-cleaned stainless steel wire and weights to prevent movement or floatation. Bacterial transformation and adsorption to plant material experimental factors were cross-classified resulting in a replicated 2^2 factorial design (or eight experimental units) In the case of Treatment C, which contained “bacteria” with “no plants,” periphyton was scraped off of 200 g of sectioned cattails and added directly to each of the replicate microcosms. The cattail sections used for treatment C were discarded. The appropriate spiking solutions of target analytes for each treatment, including the sodium azide, were added to the first 40L of treatment water. The treatment water (effluent or Nanopure) and the target analyte spike solution (acetaminophen, codeine, diphenhydramine, diltiazem, diazepam, 17β-estradiol, 17α-ethinyl estradiol, and testosterone in Nanopure water to reduce solvent use as a microbial substrate) were mixed in the tank to ensure the solution was homogenous. After which, the remaining 30L of treatment water was added.

a)

b)

4	6
10	9
1	12
7	8
3	2
5	11

Figure A.1. (a) Arrangement of glass microcosms adjacent to the City of Denton wetland; (b) experimental numbers assigned to microcosms using a random number generator.

Table A.1. Treatment Letters and Corresponding Treatment Types

Treatment Letter	Treatment Type Description
A	2 microcosms with no plants, no bacteria (due to sodium azide treatment)
B	2 microcosms with plants, no bacteria (due to sodium azide treatment)
C	2 microcosms with no plants, bacteria (due to NO sodium azide treatment)
D	2 microcosms with plants, bacteria (due to NO sodium azide treatment)
E	2 microcosms with plants in DI water
F	2 microcosms with plants, bacteria (due to NO sodium azide treatment) and DOC extract

Table A.2. Treatment Letters Designations and Corresponding Experimental Units

Treatment Letter	Experimental Unit Number
D	1
D	2
E	3
A	4
A	5
B	6
C	7
F	8
B	9
E	10
F	11
C	12

Replicate microcosms, Treatment E (Table A.1), were used to measure DOC released from plants. These microcosms contained Nanopure water as described earlier. Two additional

replicate microcosms received plants and cattail extract prepared by UC Berkeley to determine the influence of DOC (~5 mg/L) on target compound fate (Lim, 2008). Thus, a total of 12 microcosms were included in the study.

Each microcosm was sampled on study days 0, 1, 2, 4, 6, and 8 for steroid and pharmaceutical analysis. The order in which microcosms were randomly sampled on each study date was also determined using a random number generator (Table A.3). Sample blanks were included for each study day. All samples were collected in 4L amber bottles and then distributed to smaller sample bottles for various analyses. On each study day at least 15% of the experimental units were randomly sampled in duplicate for quality assurance/quality control (QAQC) purposes. For these samples, two separate 4L sample bottles were filled simultaneously, after which they were considered as separate samples and treated accordingly. Samples were shipped on ice to laboratories at BU and UC Berkeley where they were processed for the various analytes. Extraction and analysis of pharmaceuticals and steroids are summarized in Chapter 7.2.1 and Lim (2008), respectively.

Table A.3. Sampling Schedule for Day 0 Through Day 8 With Corresponding QAQC Designates

	Sampling Schedule					
	Day 0	**Day 1**	**Day 2**	**Day 4**	**Day 6**	**Day 8**
	11.6.07	**11.7.07**	**11.08.07**	**11.10.04**	**11.12.07**	**11.14.07**
	11	5	6	8	6	11
	2	2	5	6	3	12
	6	9	12	4	4	7
	1	8	7	3	#	2
	7	11	2	11	2	8
	3	12	10	12	#	10
	9	1	8	10	7	6
	8	6	11	5	#	10
	5	3	9	2	8	3
	4	10	1	1	5	1
	12	4	4	7	1	5
	10	7	3	9	9	9
QAQC	2	12	1	11	#	4
QAQC	11	2	7	3	2	8

APPENDIX B

B.1 PILOT-SCALE WETLAND METHODOLOGY

The initial phase of the pilot-scale wetland study was to install an AgriDrain unit at the outlet of the City of Denton wetland by municipal personnel. This apparatus allowed for more accurate control of wetland water volume and consistency in sampling outflowing water. The hydraulic retention time of the wetland was then determined using depth measurement for volume calculations (Figure B.1) and several bromide tracer studies through the wetland. For each tracer study, a bromide ion selective electrode was calibrated daily using a 5-point calibration curve (e.g., always r^2>0.97). Cold season tracer studies showed a hydraulic retention time (HRT) of 36–42 hours. During the warm season spiking study, the HRT was reduced because of increased vegetative mass. The measured HRT was adjusted from 18–26 hours to 65–70 hours by reducing the inflow into the wetland from 1.7 L/sec to 0.5 L/s (a 70% reduction of inflow). After base flow conditions had been running at optimal HRT for two weeks, the full pharmaceutical/steroid spiking studies were initiated.

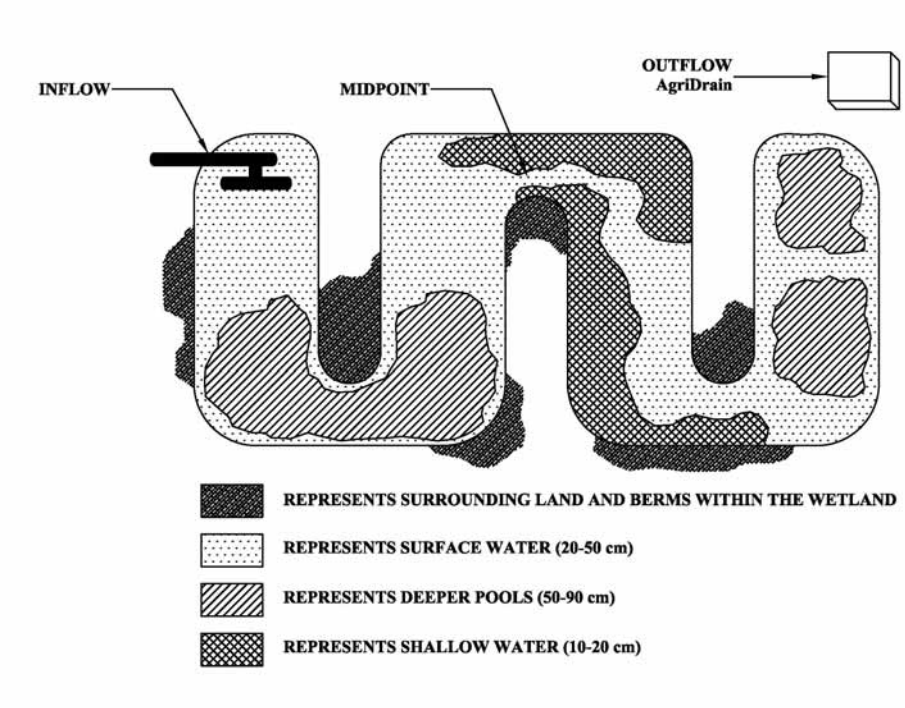


Figure B.1. Diagram of the City of Denton constructed wetland flow path and approximate depths.

Solutions were prepared for each spiking event separately (cold season; warm season). Each spike contained two different sets of analytes: pharmaceuticals and steroids. The steroid analyte solutions were received from the Sedlak lab at UC Berkeley. Steroid solutions were made up in California and shipped overnight 24 hours before use. The pharmaceutical solutions were prepared by the Brooks lab at Baylor University. Pharmaceutical analytes were added to DI water for the purpose of the spiking event. For both wetland spiking events, lithium (Li) and bromide (Br) tracers were utilized. Bromide was used for onsite real-time tracking, whereas lithium

analyses performed at UC Berkeley were used for laboratory confirmation. For the wetland spiking event, 1 kg of LiBr and 2.6 kg of NaBr were dissolved in 9L of DI water. This provided high enough Br^- and Li concentrations (based on our preliminary spiking studies) to measure continuously as they moved through the wetland. Density calculations were preformed a priori to ensure that LiBr additions would not cause appreciable stratification and affect transport of spiked compounds at the inflow. Pharmaceutical and tracer solutions were prepared 24 hours prior to spiking the wetland inflow. Figure B.2 provides a diagram of a spiking apparatus, which was designed and installed by the project team. All solutions were kept on ice and in the dark until just before spiking to prevent degradation.

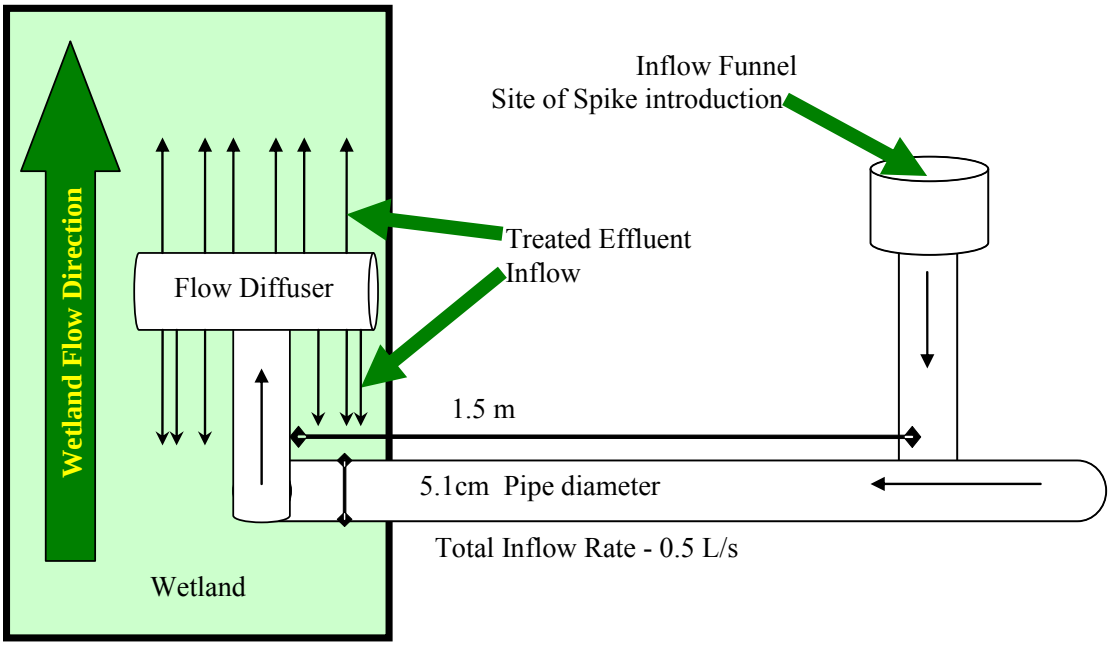


Figure B.2. Diagram of the City of Denton wetland treated effluent inflow and spiking apparatus.

Two spiking studies were completed, January 2008 (cold season) and October 2008 (warm season).

The January 2008 spiking event was conducted after the region had experienced several periods of below freezing temperatures so that the wetland vegetation was dormant as shown by the photographs included as Figures B.3 and B.4. Weather conditions during the January 2008 spiking event were characterized by daily high temperatures ranging from 5.0 to 11.1 ºC (41 to 52 ºF) and nightly low temperatures ranging from -10 to 3.3 ºC (14 to 38 ºF). Overall average temperature during the study was 0.9 ºC (33.6ºF). Water temperature ranged from 7 to 10 ºC (44.6 to 50 ºF) during this spiking event. A trace of rain (0.076 cm (0.03 inch) occurred on January 21, 2008 during the time period of the spiking study.

The October 2008 spiking event was conducted toward the end of the growing season while the vegetation was still robust as shown in the photographs included as Figures B.5 and B.6. Weather conditions during the October 2008 spiking event were characterized by daily high

Figure B.3. Inlet to Denton wetland with spiking apparatus for January 2008 spiking event.

Figure B.4. Dormant vegetation in Denton wetland during January 2008 spiking event.

Figure B.5. Inlet to Denton wetland with spiking apparatus during October 2008 spiking event.

Figure B.6. Dense emergent vegetation in Denton wetland during October 2008 spiking event.

temperatures ranging from 22.8 to 29.4 ºC (73 to 85ºF) and nightly low temperatures ranging from 8.3 to 22.2 ºC (47 to 72 ºF). Overall average temperature for the 12-day spiking event was 21 ºC (69.8 ºF). Water temperature during this study ranged from 25 to 29 ºC (77 to 84.2 ºF). A very light shower (0.05 cm [0.02 inch]) occurred on October 15, 2008, during the middle of the study and another (0.03 cm [0.01 inch]) the morning the study concluded on October 22. The rainfall events experienced during the two spiking events did not produce any detectable influence on the tracers used during the study.

For both spiking events, the same procedures were followed. To initiate the spike all three solutions (steroids, pharmaceuticals, tracers) were poured into the wetland inflow funnel simultaneously and continually over a designated period (Figure B.2) (3 min cold season, 6 min warm season—adjusted for reduced inflow). One hour prior to introduction of the chemical spike, a sample was taken at both the inflow and outflow (at the AgriDrain) (Figure B.1) of the City of Denton wetland. Once the spiking event was initiated, a sample was taken immediately from the area of the inflow. The progress of the spike through the wetland was monitored via bromide tracer. All other samples for analytical analysis were taken from the outflow AgriDrain. Analytical samples were initiated when bromide tracer information indicated the spike was potentially starting to approach the outflow. All samples were collected in 4L amber bottles and then distributed to smaller sample bottles for various analyses. At each sampling point, two 1000ml samples were collected for steroid analysis, one 100ml sample for lithium analysis, and a 2000ml sample for pharmaceutical analysis were taken. At designated times duplicate samples were taken for QAQC purposes. For these samples two separate 4L sample bottles were filled simultaneously, after which point they were considered as separate samples and treated accordingly.

Steroid and lithium samples were placed in bottles provided by the UC-Berkley group and were kept in the dark, on ice until shipped. Samples were shipped within 48 hours (and when possible 24 hours). Samples for pharmaceutical analysis were brought back to the lab at Baylor University.

Table B.1. Sample Collection Times over the Course of the Warm Season Wetland Spiking Experiment

Sample ID	Date	Hours Post Spike	Volume (L)	Location	Notes
SUM-IN-pre	10/17/2008	-1	4	Inflow	prespike
SUM-OUT-pre	10/17/2008	-1	4	Outflow	prespike
SUM-FB	10/17/2008	0	4	DI blank	
SUM-000	10/17/2008	0	4	Inflow	Immediately post spike
SUM-024	10/18/2008	24	4	Outflow	
SUM-048	10/19/2008	48	4	Outflow	
SUM-054	10/19/2008	54	4	Outflow	
SUM-057	10/19/2008	57	8	Outflow	Duplicate samples taken
SUM-060	10/20/2008	60	4	Outflow	
SUM-067	10/20/2008	67	4	Outflow	
SUM-070	10/20/2008	70	4	Outflow	
SUM-072	10/20/2008	72	8	Outflow	Duplicate samples taken
SUM-074	10/20/2008	74	4	Outflow	
SUM-096	10/21/2008	96	4	Outflow	
SUM-120	10/22/2008	120	4	Outflow	

Note. Each 4L sample was split into two 1L samples for steroid analysis, 100ml for lithium analysis, and 2L for pharmaceutical analysis. For those samples with duplicates, two separate 4L samples were collected and subsequently partitioned for various analyses.

APPENDIX C

ANALYTICAL METHODS

C.1 Sample Collection and Preservation

Water samples were collected in 4L amber glass bottles from each experimental unit located at the Denton Water Treatment Plant. Sample bottles were kept on ice and brought to the laboratory within 10 hours of collection where they were store at 4^{o} C. Samples were extracted within 24 hours of collection.

C.2 Solid-Phase Extraction (SPE)

After collection, 1L of each sample was prefiltered with 0.8µm and 0.45µm pore size cellulose filters. Sample pH was adjusted until it was 4 using diluted nitric acid. Samples were spiked with a solution of isotopic labeled standards that contained a stable isotope of each target analyte. The extraction was achieved by using 20 cc (1g) hydrophilic–lipophilic balance HLB cartridges. All extractions were performed on an Auto Trace automated SPE system. The SPE cartridges were sequentially preconditioned with 10mL acetone, 10mL methanol, and 10mL nano pure water at pH 4. The sample was then loaded onto the cartridges at 15mL/min. The SPE cartridges were stored in the freeze until analyses were performed.

Before analysis, the SPE cartridges were eluted with 10mL of methanol in 10mL test tubes. The resulting extract was concentrated with a gentle stream of nitrogen to dryness. Samples were reconstituted in 1 mL of mobile phase. Prior to analysis, samples were sonicated for 1 min and filtered using hydrophobic Teflon Support membrane syringe filters (13-mm diameter; 0.2-µm pore size).

Initial isotope spike amounts were determined based on the amount of analyte present in the sample. Generally 1L of sample was spiked with 50μL of approximately 2000μg/L of isotope solution to result in a final concentration of approximately 100ng/L in 1L sample. This resulted in a concentration factor of 1000 and a final extract concentration for the isotopes of 100μg/L.

C.3 LC-MS/MS Analysis

A Varian ProStar model 210 binary pumps equipped with a model 410 autosampler was used in this study. Analytes were separated on a 15 cm _ 2.1 mm (5μm, 80 Å) Extend-C18 column. A binary gradient consisting of 0.1% (v/v) formic acid in water and 100% methanol was employed to achieve chromatographic separation. This gradient is shown in Table C.1. Additional chromatographic parameters were as follows: injection volume, 10μL; flow rate, 350 µL/min. Eluted analytes and isotopes were monitored by MS/MS using a Varian model 1200L triple-quadrupole mass analyzer equipped with an electrospray interface (ESI). Figure C.1 provides a chromatogram for target analytes, labeled compounds for pharmaceuticals examined in this study.

Table C.1. Time-Scheduled Gradient Elution Program for LC-MSMS Analysis

	Mobile Phase Composition (%)	
Time (min)	**0.1% Formic Acid**	**Methanol**
0	97	3
2	97	3
3	95	5
4	95	5
6	95	5
8	85	15
10	60	40
12	55	45
14	55	45
16	54	46
18	53	47
20	52	48
[22]	51	49
24	30	70
26	2	98
28	2	98
30	97	3
35	97	3

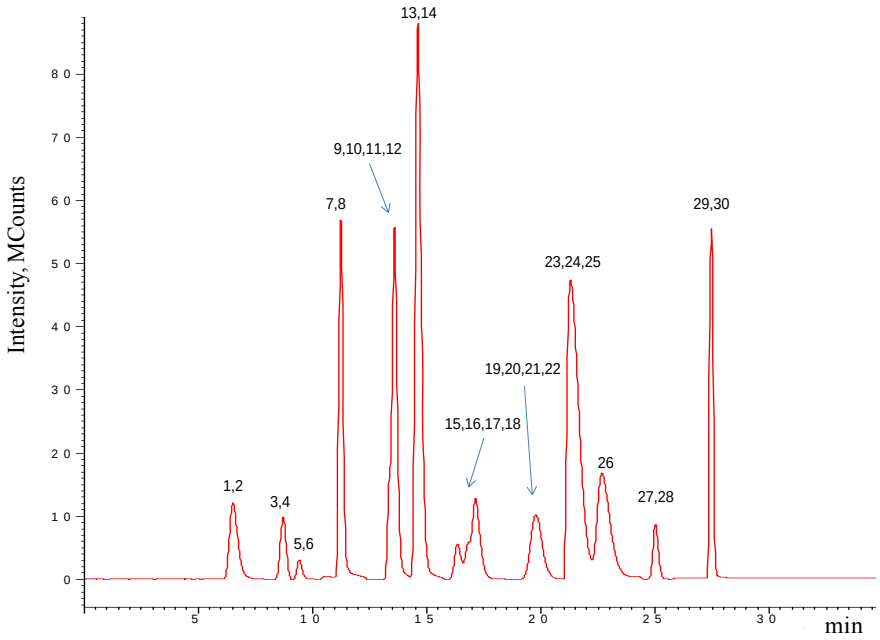


Figure C.1. LC-MS/MS total ion chromatogram resulting from analysis of a mixture of pharmaceutical standards and isotopically labeled standards.

Peak identifications are as follows: (1) acetaminophen-d4, (2) acetaminophen, (3) atenolol-d7, (4) atenolol, (5) codeine-d3, (6) codeine, (7) caffeine-d9, (8) caffeine, (9) propranolol-d7, (10) propranolol, (11) diphenhydramine-d3, (12) diphenhydramine, (13) diltiazem-d3, (14) diltiazem, (15) paroxetine-d6, (16) paroxetine, (17) carbamazepine-d10, (18) carbamazepine, (19) fluoxetine-d6, (20) fluoxetine, (21) norfluoxetine-d6, (22) norfluoxetine, (23) sertraline-d3, (24) desmethylsertraline, (25) sertraline, (26) desmethylsertraline-d4, (27) diazepam-d5, (28) diazepam, (29) gemfibrozil-d6, (30) gemfibrozil (-ESI).

To determine the best ionization mode (ESI + or -) and optimal MS/MS transitions for target analytes and labeled analytes, each compound was infused individually into the mass spectrometer at a concentration of 1μg/mL in aqueous 0.1% (v/v) formic acid at a flow rate of 10 µL/min. All analytes were initially tested using both positive and negative ionization modes although the first quadrupole was scanned from *m/z* 50 to [M + 100]. This enabled identification of the optimal source polarity and most intense precursor ion for each compound. Once these parameters were defined, the energy at the collision cell was varied, whereas the third quadrupole was scanned to identify and optimize the intensity of product ions for each compound. Additional instrumental parameters held constant for all analytes were as follows: nebulizing gas, N2 at 60 psi; drying gas, N2 at 19 psi; temperature, 300°C; needle voltage, 5000 V ESI+, 4500 V ESI-; declustering potential, 40 V; collision gas, argon at 2.0 mTorr. Tables C.2 and C.3 provides mass spectrometry parameters for labeled and target compounds, respectively.

Table C.2. Compound-Dependent Mass Spectrometry Parameters for Labeled Compounds

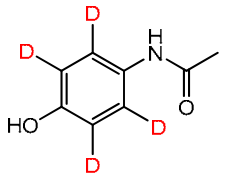
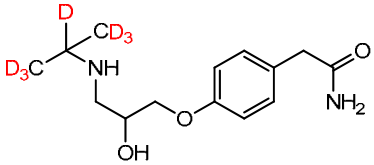
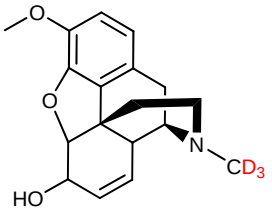
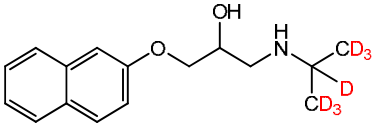
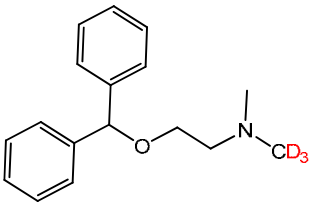
Labeled Compound	Structure	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (eV)
			ESI positive	
Acetaminophen-D4		156 [M+H]+	114	-14
Atenolol-D7		274 [M+H]+	145	-22.5
Codeine-D3		303 [M+H]+	215	-21.5
Propranolol-D7		267 [M+H]+	123	-15.5
Diphenhydramine-D3		259 [M+H]+	167	-12.5

Table C.2. Compound Dependent Mass Spectrometry Parameters for Labeled Compounds (continued)

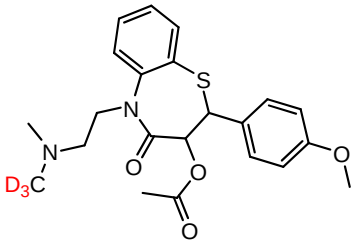
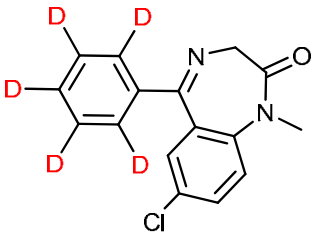
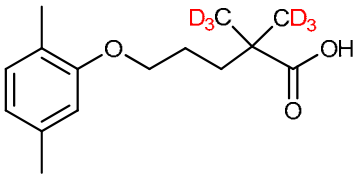
Labeled Compound	Structure	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (eV)
Diltiazem-D3		418 [M+H]+	178	-19.5
Diazepam-D5		290 [M+H]+	154	-23.5
			ESI negative	
Gemfibrozil-D6		255 [M-H]-	121	13

Table C.3. Compound-Dependent Mass Spectrometry Parameters for Target Compounds

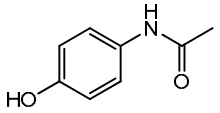
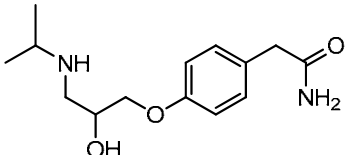
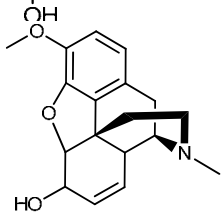
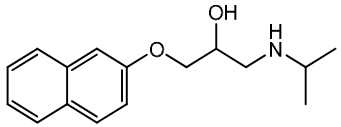
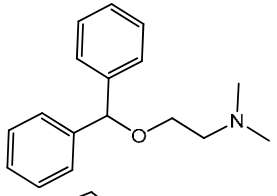
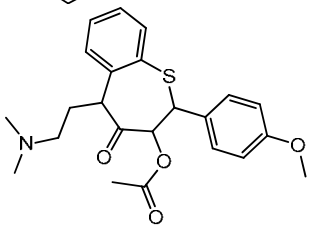
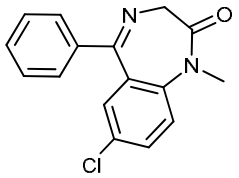
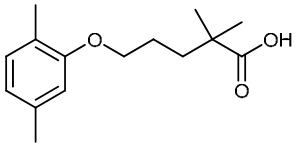
Compound	Use	Structure	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (eV)
				ESI positive	
Acetaminophen	Analgesic		152 $[M+H]^+$	110	-14
Atenolol	anti-hypertension		267 $[M+H]^+$	145	-22
Codeine	analgesic		300 $[M+H]^+$	215	-21,5
Propranolol	anti-hypertension		260 $[M+H]^+$	116	-15

Table C.3. Compound-Dependant Mass Spectrometry Parameters for Target Compounds (Cont.)

Analyte	Use	Structure	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (eV)
Diphenhydramine	antihistamine		256 $[M+H]^+$	167	-8,5
Diltiazem	anti-hypertension		415 $[M+H]^+$	178	-19
Diazepam	antidepressant		285 $[M+H]^+$	153	-22
				ESI negative	
Gemfibrozil	antilipemic		248 $[M-H]^-$	120	14,5

An isotopic labeled version of each analyte, corresponding to the isotopes added to each sample prior to extraction, was added to each calibration point at a concentration of 100μg/L to generate a relative response ratio. Recoveries of the isotopes were compared with the relative response ratio and a concentration for the unlabeled analyte was calculated. Linear or quadratic regression $r^2 \geq 0.998$ was used for all analytes. Instrument calibration was monitored through the use of continuing calibration verification (CCV) samples with an acceptability criterion of ±20%. In a given run, one CCV sample was interspersed between every 12 samples for quality assurance purposes.

Analytical methods for steroid analyses by GC-MS are provided in Lim (2008).

C.4 Statistical Analyses

Differences in target analyte reduction data from microcosm experimental treatments were determined using a general linear model approach for the factorial design (GLM, SPSS).

APPENDIX D

LARGE-SCALE CONSTRUCTED WETLAND SYSTEM

Tarrant Regional Water District (TRWD) has completed more than three years of operation of its 243-acre field-scale constructed wetland to perform further research regarding the treatment expectations of the wetland system and verification of the performance capabilities documented during the eight-year pilot-scale study. The George W. Shannon Wetlands Water Recycling Facility (GWSWWRF) concept was developed by the TRWD to meet future water supply requirements. The staged development of the wetland system was formulated by TRWD to research financial aspects, operation and maintenance issues, as well as treatment performance and further refinement of design criteria for the large-scale wetland system. The initial operation of the field-scale wetland, designated as Phase 1, includes the period from June 3, 2003, through January 9, 2007.

The GWSWWRF at Richland-Chambers Reservoir started with the design, construction, and eight years of operation of a 2.5-acre pilot-scale wetland demonstration system, which enabled development of information regarding the operational aspects and treatment effectiveness of a constructed wetland system within the proposed context of the Trinity River floodplain. Multiple objectives of the pilot-scale system included development of data to determine effectiveness and operating requirements for treating water diverted from the Trinity River to be introduced into TRWD's water supply reservoirs without degradation of the water quality. Potential for application of wetland systems for treatment of tributary inflows to reservoirs as a Best Management Practice for watershed management and reservoir protection was also evaluated.

The pilot-scale system, designed for a flow of 0.1 million gallons per day (MGD), had two settling basins followed by three parallel wetland trains, each with three wetland cells in series. The design enabled concurrent evaluation of multiple operational scenarios and routing of flows so that individual cells or trains could be taken off-line for maintenance. Based on the eight years of intensive study at the pilot-scale wetland system, it was determined that the system could achieve target levels for nutrient and sediment that would protect water quality within the reservoir. Treatment performance as well as other conclusions related to operations and design of a large-scale system were documented in a summary report finalized in 2002 (Alan Plummer Associates, 2002). Based on the conclusions from the pilot-scale study, the TRWD elected to proceed with the construction of the larger field-scale wetland system.

The purpose of the field-scale constructed wetland system is to demonstrate wetland treatment effectiveness while allowing for development of data sufficient to verify the treatment design coefficients and operating requirements of a constructed wetland system to treat water diverted from the Trinity River before supplementing TRWD's water supply reservoirs and to provide information for the TRWD's Board of Directors to support water supply decisions.

Specific research objectives for the field-scale wetland system included:

- Confirm pollutant removals/performance observed at the pilot-scale wetland system.
- Evaluate management issues at the field-scale level including:
  - Effects of bioturbation from fish, waterfowl, and feral hogs.
  - Techniques for minimizing impacts of wildlife on water quality.
- Evaluate methods of vegetation establishment.
- Assess challenges of water level management over larger wetland cells.
- Evaluate water balance issues.
- Confirm sedimentation rates at the sedimentation basins.
- Confirm the projected frequency and management of accumulated sediments.
- Evaluate flow distribution through larger wetland cells.

The field-scale wetland system consists of one sedimentation basin followed by a series of four wetland cells totaling about 243 acres. The system is designed to handle a maximum output of 15.15 MGD with normal operation at 12.6 MGD. Nominal detention time through the system based on the design flow rate of 12.6 MGD is about seven days. The design of Cells 1 and 2 of the field-scale wetland incorporate internal deep water zones to facilitate flow distribution across the cells whereas Cell 3 was designed with two finger dikes to direct flow through the cell. Inlet deep water zones were included in the design of all four cells to promote even distribution of flow. An aerial photograph of the TRWD field-scale wetland is included as Figure D.1.

Monitoring of water quality at the Trinity River pump station, sedimentation basin outflow and each wetland cell outflow is conducted on a weekly basis. Monitoring on a weekly basis is also conducted downstream of the wetland at the future relift station location in Alligator Creek. Other studies regarding operations and maintenance issues include water depth management, establishment of vegetative cover and diversity, flow distribution through the wetland cells, impacts of bioturbation, and rate of sediment accumulation.

Initial operations identified design, operation, and management issues including severe short-circuiting of flows through the wetland cells, erosion issues from high velocities where flows were channeled, and excessive water depths in the marsh areas. Design modifications were conducted during summer 2004 to address the short-circuiting issues and generally improve utilization of the wetland treatment area. Tilting weir gates at the outflow of Cells 1, 2, and 3 were lowered completely with the gates at Cell 4 remaining slightly tilted during the second half of Phase 1 operations. Despite the various efforts to reduce water depths in the marsh areas, water depths within a substantial portion of the marsh zones remained in the 17- to 24-inch range.

Tracer studies were conducted within the TRWD field-scale wetland cells during summer 2008. At an inflow rate of 10.59 MGD, the detention time through the four cells was determined to be about 9.5 days. The recovery of the Rhodamine WT dye used in the tracer studies indicated less than ideal flow conditions through the wetland cells with some short-circuiting still present and some pulsing of flows through cell 2 that were due to previously installed modifications. Figures D.2 through D.5 show the results of the dye studies through the sedimentation basin and each of the wetland cells.

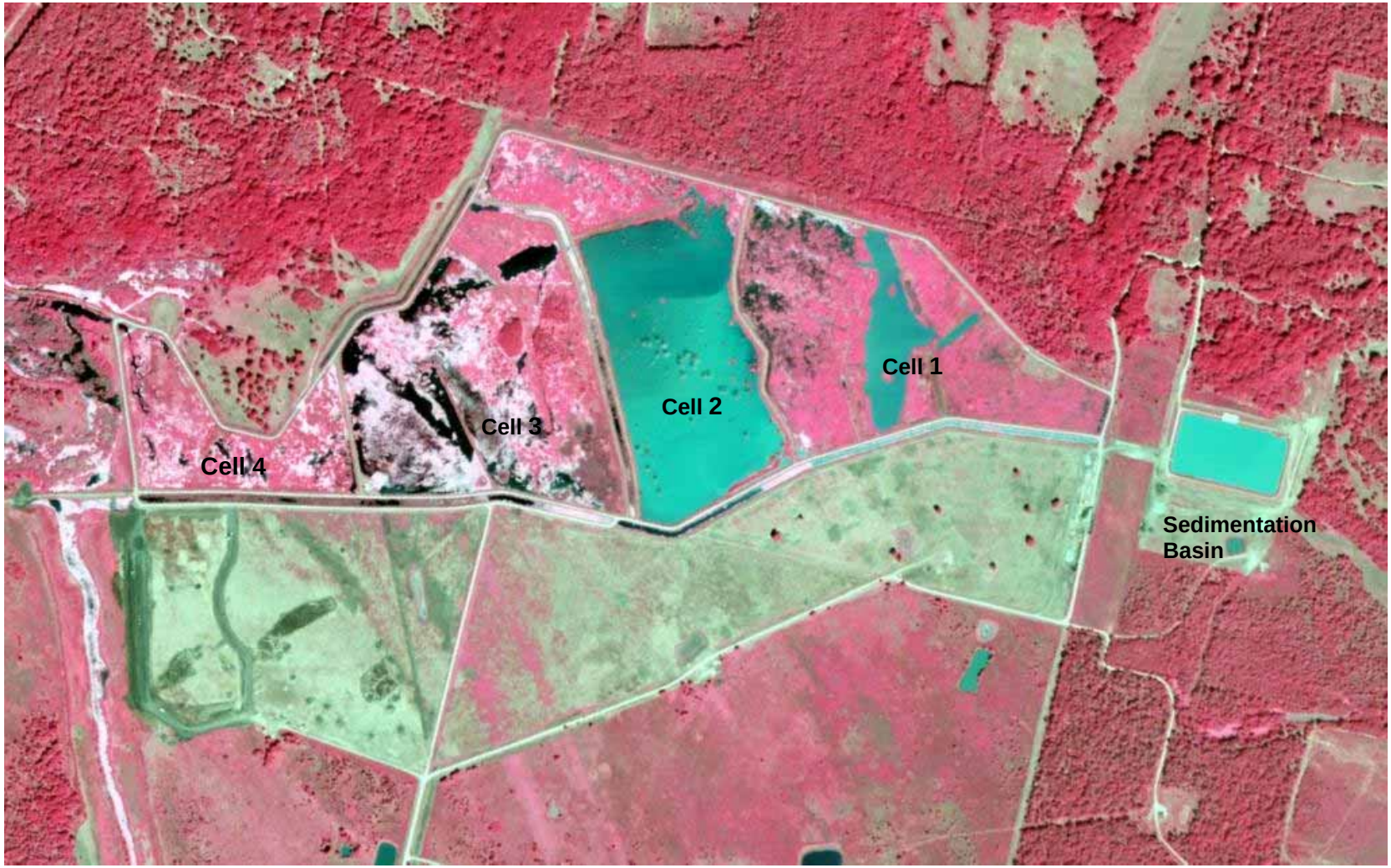


Figure D.1. Tarrant Regional Water District's field-scale wetland.

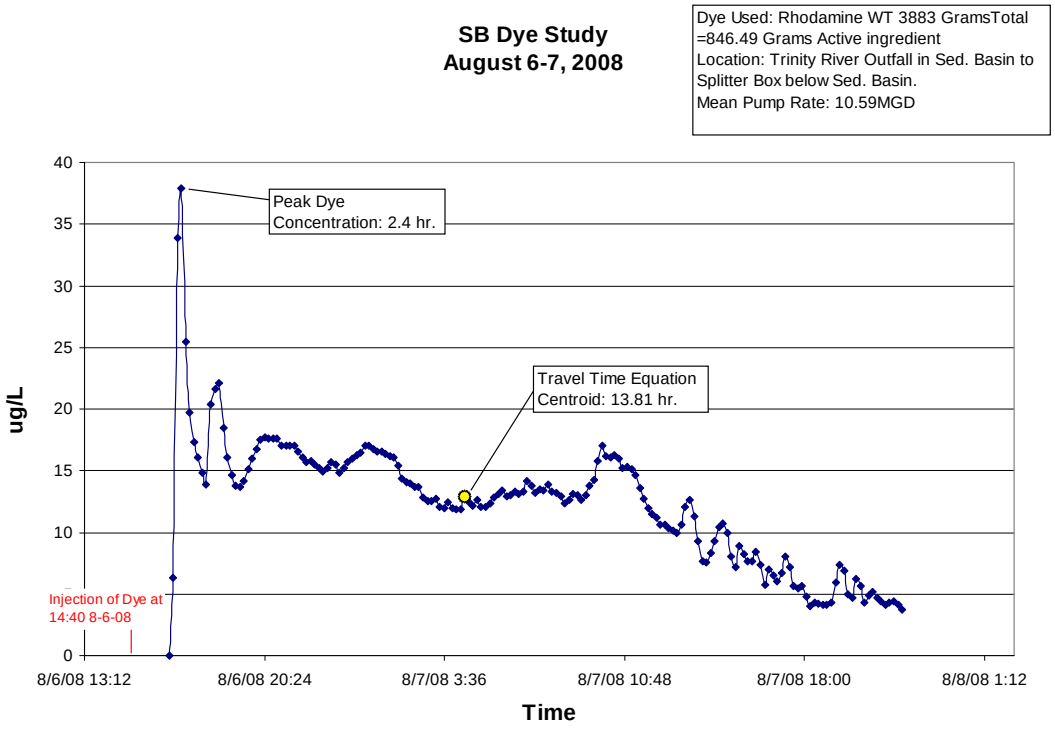


Figure D.2. Results of tracer study through TRWD field-scale wetland sedimentation basin.

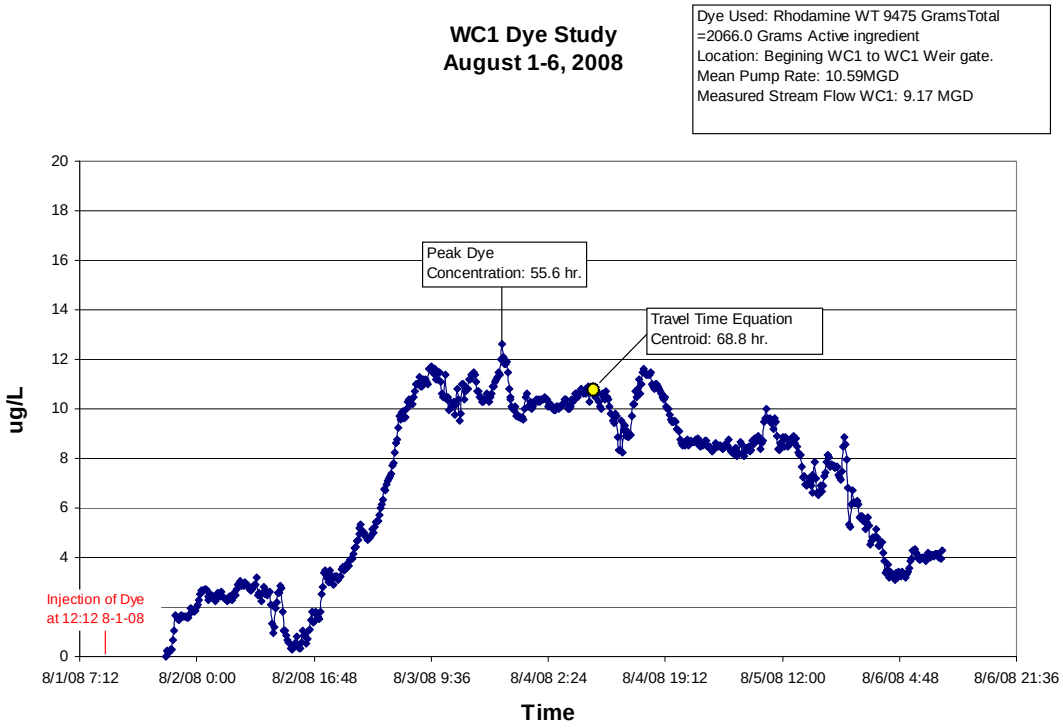


Figure D.3. Results of tracer study through TRWD field-scale wetland Cell 1.

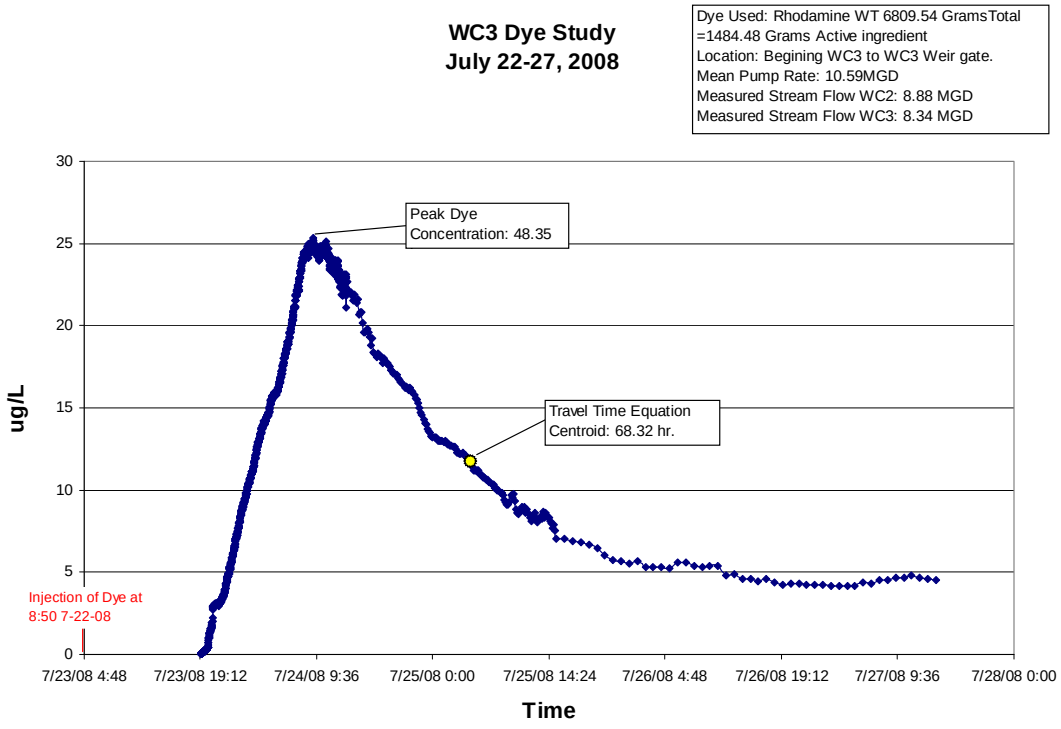


Figure D.4. Results of tracer study through TRWD field-scale wetland Cell 3.

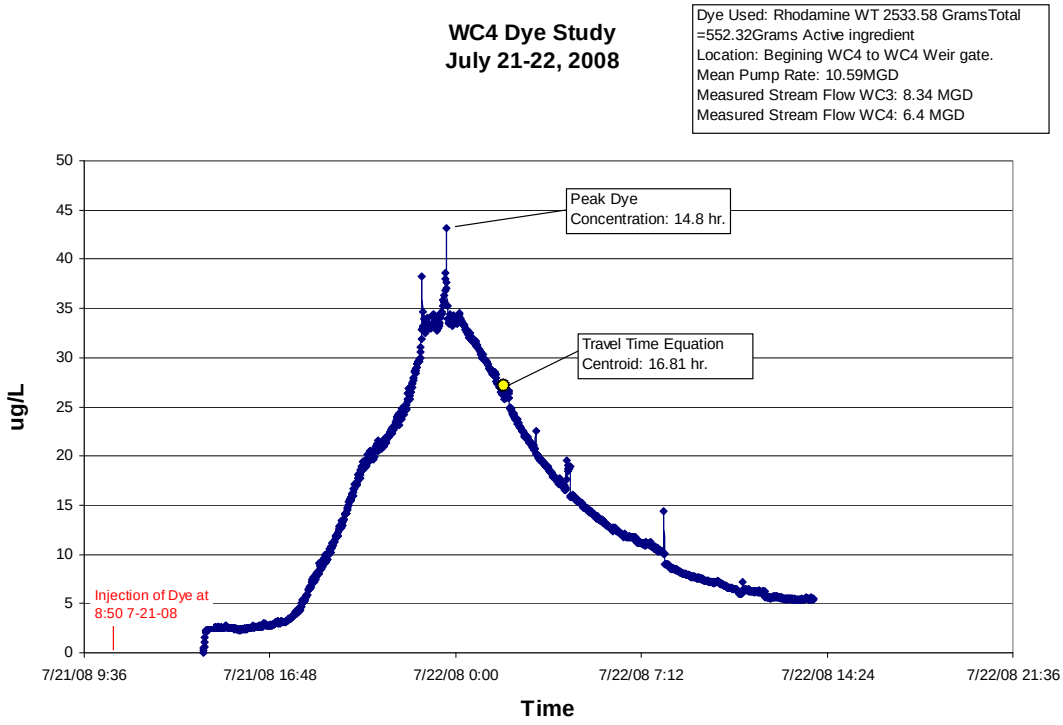


Figure D.5. Results of tracer study through TRWD field-scale wetland Cell 4.

The field-scale system functioned as designed with the majority of the suspended solids removed within the sedimentation basin with some associated removal of nutrients as well. Overall, the field-scale system provided effective removal of suspended solids comparable to the performance documented at the pilot-scale system. The field-scale wetland system also provided effective removal of both TN and TP although the removals based on percent mass removed were not at the performance levels exhibited in the pilot-scale system. Table D.1 summarizes the efficiency results achieved for TSS and nutrient removal overall during the Phase 1 operational period.

Table D.1. Performance Summary for Field-Scale System

	Percent Mass Removed			Percent Concentration Reduction		
Station	**TSS**	**TN**	**TP**	**TSS**	**TN**	**TP**
PS-SB	65%	10%	12%	63%	5%	7%
SB-WC4	90%	63%	37%	89%	58%	34%
PS-WC4	96%	67%	44%	96%	61%	39%

Note. PS = Trinity River Pump Station; SB = Sedimentation Basin Outflow; WC4 = Wetland Cell 4 Outflow

Differences between the design and operation of the field-scale system and the pilot-scale system include substantially higher hydraulic loading rates resulting in higher mass loading rates (MLRs), reduced density of vegetation, and higher water depths. Field-scale system flows from the Trinity River were typically between 12 and 15 MGD but ranged higher than 15 MGD on several occasions. Based on the measured flows, the overall average flow from the Trinity River pump station for the Phase 1 operational period was 13.51 MGD (based on daily data), and from the sedimentation basin was 12.69 MGD (based on weekly data). Hydraulic loading rate (HLR) calculated for the entire field-scale system over the Phase 1 operational period was 5.90 cm/day, based on time-weighted averages of wetland system operational area in use. Because of drawdowns of wetland cells for maintenance requirements as well as for moist soil management, there were substantial periods where the system was operated with one or more wetland cells off line. As a result of various cells being off line, HLRs ranged from 4.98 cm/day to 11.57 cm/day for the system. Calculated treatment efficiency included periods representative of start-up and modification periods, which may not reflect actual seasonal variability expected to influence performance in a mature system. Phase 1 operational data combined periods of startup and restart-up as well as periods of relative extended operations when treatment equilibrium representative of long-term performance might be expected.

Higher pollutant concentrations in the river experienced during a significant drought period during 2005–2006 combined with the higher HLRs resulted in substantially higher mass loading rates to the wetland cells. Based on mass removal rates (MRRs), the field-scale system is performing as well or better than what was demonstrated during the pilot-scale study, as presented in Table D.2. Summaries of Phase 1 operational period calculated hydraulics and average flows through the field-scale system are provided in Tables D.3 and D.4, respectively.

Table D.2. Performance Comparison Between Field-Scale and Pilot-Scale Systems

Parameter	Mass Loading Rate (lbs/acre/day)		Mass Removal Rate (lbs/acre/day)		Percent Mass Removed (%)	
	Field-Scale	Pilot-Scale	Field-Scale	Pilot-Scale	Field-Scale	Pilot-Scale
Total Suspended Solids	117	56	113	55	96	95
Total Nitrogen	2.39	1.44	1.59	1.19	67	82
Total Phosphorus	0.58	0.26	0.26	0.17	44	66

Table D.3. Field-Scale Wetland Phase 1 Operational Period Calculated Hydraulics

Entire Period: Active Days = 877

Train	Hydraulic Detention Time (days)	Hydraulic Loading Rate (cm/day)
PS-SB	1.56	152.24
SB-WC4	6.62	5.66
PS-WC4	8.18	5.90

The loading rates and removal rates shown in Tables D.2 and D.3 were calculated on a time-weighted basis for actual wetland area in operation.

Table D.4. Average Flows by Season for Phase 1 Operational Period

Train	Average Flows (MGD)				
	Overall Average	Winter (Jan–Mar)	Spring (Apr–Jun)	Summer (Jul–Sept)	Fall (Oct–Dec)
Pump Station (PS)	13.51	13.72	14.47	13.63	12.68
Sedimentation Basin (SB)	12.69	12.66	13.71	12.64	11.95
Net Evap/Transpiration Calculated Based on Pan Evaporation Data (Sed Basin)	0.03	0.01	0.03	0.04	0.03
Net Evap/Transpiration Calculated Based on Pan Evaporation Data (Wetland Cells)	0.66	0.33	0.55	1.05	0.70
Wetland Cell #4 (WC4)	12.00	12.32	13.12	11.74	11.22

Phase 1 of field-scale wetland operations was a period of ongoing learning and changes including physical modifications and operational adjustments to address issues identified early during this stage. This phase included combined periods of startup and restart-up as well as periods of relatively extended operations when treatment equilibrium representative of long-term performance might be expected. As such, this phase has provided substantial information regarding cell design, construction, planting needs, and operational limitations that will be utilized to further the design criteria for full build-out of the GWSWWRF wetland system. The full-sized Trinity River diversion pump station enabled demonstration of hydraulic loading rates beyond what was possible at the pilot-scale wetland system. Coupled with the high nutrient concentrations in the river as a result of the drought conditions experienced during 2005–2006, substantially higher mass loading rates were also tested.

The treatment performances demonstrated by the eight-year pilot-scale study were a good indication of performance capabilities of the large-scale system. Performance of the field-scale wetland system in terms of mass removal rates matched or exceeded the performance exhibited by the pilot-scale wetland system despite less than optimal flow distribution, treatment area utilization, and vegetative cover. Improvement in TN and TP removal effectiveness with increased cover of emergent vegetation, reduction in average water depths, improvements in flow distribution, and correlation of diverted flows and mass loading rates with wetland treatment area in operation is indicated.

Further optimization of treatment performance is assumed possible for the field-scale wetland system, especially for TN and TP mass removal based on analysis of the Phase 1 operation data and observations during Phase 1 operations. Key factors to be enhanced to improve treatment performance include:

- Increasing and maintaining dense vegetative cover and resulting development of litter layer throughout the year.
- Maintenance of water depths at levels (average of 12 inches) to promote sustainable emergent vegetation.
- Improvement of flow distribution (may require regrading cells to eliminate preferential flow paths).
- Correlation of diverted flows and mass loading rates with treatment area in operation.

In addition to the monitoring conducted for evaluation of treatment performance for conventional parameters, annual sampling of water, sediment, and vegetation from the Richland-Chambers Wetland is conducted to assess potential accumulation of heavy metals and organic compounds. Analyses for organic compounds included organochlorine pesticides, organophosphorus pesticides, and semi-volatile and volatile organic compounds. The annual studies included analyses for 183 organic compounds in the water samples, 118 organic compounds in the sediment samples, and 216 samples in the vegetation samples. The data available from the 2003–2007 annual sampling studies of the TRWD field-scale wetland were reviewed. Approximately 98% of the analytical results were less than the method detection limits. Table D.5 lists the detected organic compounds and identifies the matrix in which they were detected. Although low levels of some organic compounds were occasionally detected within each of the media sampled, no trend of accumulation for any organic compound was observed. The reported data for organic compounds detected in water samples were compared to water quality criteria listed for protection of aquatic life, and maximum contaminant levels for organic chemicals in public drinking water supplies found in the Texas Commission on Environmental Quality (TCEQ) Guidance for Assessing Texas Surface and Finished Drinking Water Quality Data, 2004. The detected organic compounds were all about 3 orders of magnitude than the listed regulatory criteria for protection of public drinking water supplies. The detected levels were also less than criteria listed for protection of aquatic life except for one detection of an organochlorine pesticide (Endrin) with a detected level of 0.0023 µg/L versus 0.0002 µg/L freshwater chronic criteria. The reported detections in sediment samples were compared to screening levels for organic substances in sediment in the TCEQ Guidance (2004). There were two reported detections of organochlorine pesticides (Gamma-Chlordane and Endosulfan I) detected in sediment samples that were slightly more than the screening criteria for these compounds. Detected levels of organic compounds from vegetation samples were compared to screening levels for organic substances in tissue from the TCEQ Guidance (2004). However, there were no screening levels listed for any of the organic compounds detected in vegetation. The annual sampling program is not structured for evaluation of treatment performance for organic compounds.

Table D.5. Organic Compounds Detected in Annual Monitoring of Field-Scale Wetland

Year	Matrix	Category	Compound	Concentration
2003	Water	Volatile Organic Compounds	Toluene	1.25 µg/L
2005	Sediment	Semivolatile Organic Compounds	Aniline	451 µg/kg
2005	Sediment	Semivolatile Organic Compounds	Benzoic Acid	139 µg/kg
2006	Water	Semivolatile Organic Compounds	Phenol	1.2 µg/L
2006	Water	Semivolatile Organic Compounds	Naphthalene	0.32 µg/L
2007	Water	Organochlorine Pesticides	Gamma-BHC (Lindane)	0.00072 µg/L (0.0026 µg/L detected in method blank)
2007	Water	Organochlorine Pesticides	Endosulfan I	0.0013 µg/L
2007	Water	Organochlorine Pesticides	Endrin	0.0023 µg/L
2007	Water	Semivolatile Organic Compounds	Di-n-butyl Phthalate	0.26 µg/L
2007	Water	Volatile Organic Compounds	Acetone	7.3 µg/L
2007	Water	Volatile Organic Compounds	Methylene Chloride	0.34 µg/L (0.48 µg/L detected in method blank)
2006	Sediment	Semivolatile Organic Compounds	4-Methylphenol	15 µg/L
2006	Sediment	Semivolatile Organic Compounds	4-Methylphenol	70 µg/L
2006	Sediment	Semivolatile Organic Compounds	Fluoranthene	8.7 µg/kg
2006	Sediment	Semivolatile Organic Compounds	Pyrene	8.2 µg/kg

Table D.5. Organic Compounds Detected in Annual Monitoring of Field-Scale Wetland (continued)

Year	Matrix	Category	Compound	Concentration
2006	Sediment	Semivolatile Organic Compounds	Benzo(b)fluoranthene	7.8 µg/kg
2006	Sediment	Organophosphorus Pesticides	Methoxychlor	185 µg/kg
2006	Sediment	Organophosphorus Pesticides	Methoxychlor	121 µg/kg
2007	Sediment	Organochlorine Pesticides	Beta-BHC (Lindane)	3.0 µg/kg
2007	Sediment	Organochlorine Pesticides	Gamma-Chlordane	2.0 µg/kg
2007	Sediment	Organochlorine Pesticides	Endosulfan I	9.8 µg/kg
2007	Sediment	Organochlorine Pesticides	Endosulfan I	2.7 µg/kg
2007	Sediment	Organochlorine Pesticides	Methoxychlor	1.3 µg/kg
2007	Sediment	Organochlorine Pesticides	Methoxychlor	1.1 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Benzoic Acid	290 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Phenol	68 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Benzoic Acid	290 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Phenanthrene	8.9 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Phenanthrene	16 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Di-n-butyl Phthalate	21 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Di-n-butyl Phthalate	28 µg/kg

Table D.5. Organic Compounds Detected in Annual Monitoring of Field-Scale Wetland (continued)

Year	Matrix	Category	Compound	Concentration
2007	Sediment	Semivolatile Organic Compounds	Fluoroanthene	25 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Fluoroanthene	28 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Pyrene	23 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Pyrene	24 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Butyl Benzyl Phthalate	19 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Butyl Benzyl Phthalate	13 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Benz(a)anthracene	11 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Chrysene	18 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Chrysene	12 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Benzo(b)fluoranthene	36 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Benzo(k)fluoranthene	12 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Indeno (1,2,3-cd)pyrene	23 µg/kg
2007	Sediment	Semivolatile Organic Compounds	Benzo(g,h,l)perylene	22 µg/kg
2006	Vegetation	Semivolatile Organic Compounds	Bis (2-ethylhexyl) phthalate	0.64 µg/kg
2006	Vegetation	Semivolatile Organic Compounds	Bis (2-ethylhexyl) phthalate	0.74 µg/kg
2006	Vegetation	Semivolatile Organic Compounds	Bis (2-ethylhexyl) phthalate	0.55 µg/kg

Table D.5. Organic Compounds Detected in Annual Monitoring of Field-Scale Wetland (continued)

Year	Matrix	Category	Compound	Concentration
2006	Vegetation	Semivolatile Organic Compounds	Bis (2-ethylhexyl) phthalate	0.32 µg/kg
2007	Vegetation	Semivolatile Organic Compounds	Benzoic Acid	510 µg/kg
2007	Vegetation	Semivolatile Organic Compounds	Benzoic Acid	620 µg/kg
2007	Vegetation	Semivolatile Organic Compounds	Benzoic Acid	650 µg/kg
2007	Vegetation	Semivolatile Organic Compounds	Benzoic Acid	730 µg/kg

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