Monitoring for Microconstituents in an Advanced Wastewater Treatment Facility and Modeling Discharge of Reclaimed Water to Surface Canals for Indirect Potable Use

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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Andrew Salveson, Jess Brown, Zhi Zhou
Carollo Engineers, P.C.

Jose L. Lopez
South Florida Water Management District

Cosponsors

Bureau of Reclamation
South Florida Water Management District
City of Plantation

WateReuse Research Foundation
Alexandria, VA

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For more information, contact:
WateReuse Research Foundation
1199 North Fairfax Street, Suite 410
Alexandria, VA 22314
703-548-0880
703-548-5085 (fax)
www.WateReuse.org/Foundation

WateReuse Research Foundation Project Number: WRF-06-019
WateReuse Research Foundation Product Number: 06-019-1

ISBN: 978-1-934183-29-8
Library of Congress Control Number: 2010921672

Printed in the United States of America

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ACRONYMS

AD	Advection-dispersion
ANOVA	Analysis of variance
APECs	Alkylphenol ethoxycarboxylates
APEOs	Alkylphenol polyethoxylates
AWT	Advanced wastewater treatment
BLM	Baseline model
BOD	Biochemical oxygen demand
BPA	Bisphenol A
CAPECs	Carboxyalkylphenol ethoxycarboxylates
CAS	Chemical Abstracts Service
CDPH	California Department of Public Health
CPC	Compounds of potential concern
CT	Conservative tracer
DBP	Di-*n*-butyl phthalate
DCMD	Direct contact membrane distillation
DDE	*p,p'*-Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DEET	*N,N*-Diethyl-*meta*-toluamide
DNF	Denitrifying filter
DO	Dissolved oxygen
DOM	Dissolved organic matter
ECCs	Emerging chemicals of concern
ECs	Emerging contaminants
EDCs	Endocrine disrupting chemicals
EDSP	Endocrine disruptor screening program
ELISA	Enzyme-linked immunosorbent assay
EP	Emerging pollutants
EPA	Environmental Protection Agency
E-Screen	Estrogen screen
FO	Forward osmosis
GAC	Granular activated carbon
H	Henry's constant
HRT	Hydraulic retention time
IMANS®	Integrated membrane-anaerobic stabilization
Kd	Dissociation constant
Koc	Soil and sediment sorption coefficients
LCS	Laboratory control standard
Log D	Octanol-water partition coefficient at difference pH
Log K_{ow}	Octanol-water partition coefficient
LOQ	Limit of quantification
MBLK	Method blank
MBR	Membrane bioreactor

MCF-7	Human mammary gland adenocarcinoma cell line
MF	Microfiltration
MHR	Moderately hard reconstituted
MS	Matrix spike
MSD	Matrix spike duplicate
ND	Not detected
NDMA	*N*-Nitrosodimethylamine
NF	Nanofiltration
OPWCD	Old Plantation Water Control District
PAHs	Polycyclic aromatic hydrocarbons
PC	Pollutants of concern
PCB	Polychlorinated biphenyls
PH	Phenol
PhACs	Pharmaceutically active compounds
pK_a	Acid dissociation constant
PPCPs	Pharmaceuticals and personal care products
PSD	Particle size distribution
QSPR	Quantitative structure-property relationship
RO	Reverse osmosis
SARs	Structure-activity relationships
SAT	Soil aquifer treatment
SFWMD	South Florida Water Management District
SM	Sulfamethoxazole
SRT	Sludge retention time
TCEP	Tris(2-carboxyethyl) phosphine
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate
TDS	Total dissolved solids
TOrCs	Trace organic compounds
TS	Triclosan
TSS	Total suspended solid
UF	Ultrafiltration
USGS	U.S. Geological Survey
UV	Ultraviolet
UV-C	Ultraviolet C
Vtg	Vitellogenin
WCD	Water Control District
WEF	Water Environment Federation
WRF	WateReuse Research Foundation
WWTPs	Wastewater treatment plants
YCT	Yeast, cereal, and trout chow
YES	Yeast estrogen screen

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.

A Research 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; and
- Economics and marketing of water reuse.

The Research 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 funding relationships.

This report discusses the results of an advanced wastewater treatment (AWT) pilot study designed to create a better understanding of the removal of microconstituents through AWT facilities and the potential impact of microconstituents to aquatic organisms. A secondary objective of this project was to examine the fate and transport of select microconstituents from a hypothetical canal discharge location to a drinking water aquifer.

David L. Moore
Chair
WateReuse Research Foundation

G. Wade Miller
Executive Director
WateReuse Research Foundation

ACKNOWLEDGMENTS

This project was funded by the WateReuse Research Foundation in cooperation with the Bureau of Reclamation, South Florida Water Management District, and the City of Plantation. Carollo Engineers gratefully acknowledges the WateReuse Research Foundation's financial, technical, and administrative assistance in funding and managing the project through which this information was discovered. Specifically, the project team is indebted to the following individuals for their cooperation and participation in this project:

Principal Investigator
Jess Brown, Ph.D., P.E., *Carollo Engineers, P.C.*

Co-Principal Investigator
Jose L. Lopez, P.E., *South Florida Water Management District*

Assistant Project Manager
Andrew T. Salveson, P.E., *Carollo Engineers, P.C.*

Research Project Team
Dr. Zhi Zhou, Sean Poust, Dr. Keith Bourgeous, Olivia Virgadamo, Dr. Graham Juby, Susanna Li, Dr. Balakrishnan Narayanan, *Carollo Engineers, P.C.*
Don Sullivan, Hank Breitenkam, Zoraida Gonzalez, *City of Plantation*
Maria Loinaz, Josepth Hughes, Peter deGolian, Mikkel Anderson, Claus Jørgensen, Dorte Rasmussen, and Morten Birkved, *DHI Water and Environment*
Isabel Johnson, *Golder Associates*
Richard Cisterna; Enrique Vadiveloo, Tony Greiner, Robert Harris, Robert E. Fergen, Patrick Davis, *Hazen and Sawyer*
Peter Myers, *Hydrosphere Research*
Debbie Frank, Bradley Cahoon, *Montgomery-Watson Harza*
Kevin Alexander, *Separation Processes, Inc.*
Dr. David Barber, Dr. Nancy Denslow, Kevin Kroll, *University of Florida at Gainesville*
Dr. Jocelyn Hemming, *Wisconsin State Laboratory of Hygiene*

Technical Advisory Committee
Jennifer Jurado, *Broward County Environmental Protection Department*
Dr. Jörg Drewes, *Colorado School of Mines*
Dr. Erin Snyder, *formerly of Intertox*
Carlyn Kowalsky, *South Florida Water Management District*
Mark Elsner, *South Florida Water Management District*
Dr. Shane Snyder, *Southern Nevada Water Authority*

Project Advisory Committee
Lisa Prieto, *formerly of Camp, Dresser, & McKee, Inc.*
Dr. David York, *formerly of Florida Department of Environmental Protection*
Dr. Richard C. Pleus, *Intertox*
Anthony Andrade, *Southwest Florida Water Management District*
Ken Yokoyama, *Bureau of Reclamation*

EXECUTIVE SUMMARY

Advanced wastewater treatment (AWT), which includes filtration, carbon adsorption, phosphorus removal, and nitrogen removal, can effectively remove the majority of pollutants. However, the remaining microconstituents (including potential endocrine disrupting compounds, pharmaceuticals, and personal care products) in reclaimed water may raise public health and/or aquatic health concerns. Although certain microconstituents may persist following wastewater treatment (Gomez et al., 2007; Stackelberg et al., 2004), current research suggests that advanced treatment technologies can effectively remove them (Tang et al., 2006) to concentrations below human health risk levels (Snyder et al., 2006a). In addition, some research suggests that advanced treatment technologies following conventional wastewater treatment can significantly reduce the risk to aquatic organisms (Schwatter et al., 2007) and that some microconstituents found in municipal wastewater have only negligible effects on invertebrates and plants in the effluents and receiving environment (Brun et al., 2006). However, existing literature also indicates that some microconstituents at or above 0.1 ng/L will induce endocrine-mediated changes in aquatic life (Purdom et al., 1994). Other research suggests that microconstituents, in some cases, have been shown to accumulate in aquatic organisms and to alter their natural growth (Kramer et al., 1998; Snyder et al., 2001).

To better understand the removal of microconstituents through AWT facilities and the potential impact of microconstituents to aquatic organisms, an AWT pilot study at the City of Plantation, FL, was funded by the WateReuse Research Foundation (WRF-06-019), the Bureau of Reclamation, the South Florida Water Management District (SFWMD), and the City of Plantation, Florida. The AWT facility consisted of a denitrifying filter (DNF), a membrane bioreactor (MBR), ultrafiltration (UF), and reverse osmosis (RO). Benchtop testing was also performed utilizing a nonbiological membrane process (IMANS®) to examine the role of biological treatment in the removal of microconstituents. In an attempt to correlate microconstituents with biological responses, the toxicological and hormonal impacts to various organisms and cell cultures exposed to effluent from the various AWT processes were evaluated concurrent with chemical analysis.

A secondary objective of this project was to examine the fate and transport of select microconstituents from a hypothetical canal discharge location in South Florida to a drinking water aquifer. To provide perspective on the potential impact to receiving water quality, limited testing of canal water near Plantation, FL, was performed.

All three membrane systems (MBR/RO, DNF/UF/RO, and IMANS®) in this project effectively removed microconstituents and bulk organic matter and salts as measured by 5-day biochemical oxygen demand, total suspended solids, total dissolved solids, and turbidity. The results within this report suggest that the discharge of reclaimed RO water would not degrade the water quality of surface canals and that any of the three tested systems can be used to remove microconstituents and improve the quality of reclaimed water for canal discharge.

The chronic toxicity tests include a chronic survival and growth test for *Pimephales promelas* and a chronic survival and reproduction test for *Ceriodaphnia dubia*. The survival rate of *P. promelas* and *C. dubia* in RO effluent was low during the first toxicity test, which was likely

caused by residual chloramine in RO-treated effluents. Additional tests on RO effluent samples that were quenched with sodium thiosulfate significantly reduced toxicity and increased the survival of *P. promelas* and *C. dubia* in RO effluents. The final batch of toxicity experiments without using chloramine indicated that there was no significant difference between RO effluent and control (deionized) water for the survival and growth of *P. promelas* and survival and reproduction of *C. dubia*. Similarly, there were no significant differences between surface (canal) water and control (deionized) water for the survival and growth of *P. promelas* and survival and reproduction of *C. dubia*. These facts suggest that discharge of reclaimed water (RO effluent) has no adverse toxic effect on aquatic organisms if chloramines are not used or properly quenched. However, unquenched chloramines or trace level of ammonia in AWT facilities may contribute to the toxicity to *C. dubia* and should be removed by break point chlorination followed by dechlorination, advanced oxidation, or other quenching methods. The process deserves further investigation.

The endocrine disrupting potential of microconstituents in RO effluent was evaluated with E-Screen bioassays, YES assays, fathead minnow Vtg assays, and steroid immunoassays. Results of the E-Screen bioassays showed that estradiol equivalents in all RO effluents were below detection limits, even though estradiol equivalents were detected in secondary effluent, DNF effluent, MBR effluent, and UF effluent. Results of the E-Screen bioassays showed that RO effluent did not provoke a significant response in MCF-7 cells. Results of the YES bioassays were similar to those of the E-Screen bioassays, and estradiol equivalents in RO effluent were below detection limits, although estradiol equivalents were detected in secondary effluent and DNF effluent, suggesting that RO effluent did not possess endocrine disrupting potential. Results of the fathead minnow Vtg assays and steroid immunoassays did not show an increase of plasma Vtg in male fish, indicating that they were not exposed to estrogenic components at the concentrations required to produce this effect. Results of the steroid immunoassays indicated that testosterone concentrations in all treatments were similar to those in the negative control group and that there was no significant difference in plasma testosterone for any of the treatments compared to negative controls. All of these results suggest that RO effluent was not estrogenic. It is interesting that although the effluent of the nonbiological membrane process IMANS® contains a few microconstituents, their impact on the endocrine disrupting potential was not appreciable. Therefore, biological processes (as part of secondary treatment) may not be necessary for the removal of microconstituents and estrogenic activity, as long as there is a RO step in the process.

Three compounds (sulfamethoxazole, triclosan, and phenol) were selected as representative microconstituents for model development based on their physicochemical properties. Hydrodynamic and water quality models were developed to examine the fate and transport of these simulated microconstituents from the AWT through surface canals. The hydrodynamic model was run to simulate the historical conditions in 2001 and 2002, and the results indicated that the groundwater results follow the observed data closely. The hydraulic model includes the primary and secondary canals and main hydraulic structures (weirs, culverts, pumps, and gates) for these canals. It was shown that the surface water results are very sensitive to the structure operations. The water quality model predicted that adsorption plays a dominant role in the transport of the microconstituents in the canal network as well as in the aquifer system. While less significant, various pathways of decay do impact the fate and transport of microconstituents.

In this study, biotransformation was not considered (biodecay rate, zero). Therefore, the modeling prediction is conservative and dominated by adsorptive processes.

Transport of microconstituents in the canal network was found to be lower for compounds with higher adsorption coefficients. The higher adsorption coefficient decreases the fluctuations in the dissolved concentration in the canals, which is likely a consequence of the adsorbed mass in the sediment layer acting as a buffer. The water quality model was not calibrated; future efforts should focus on collecting the data necessary to perform this calibration. Additional work can be done to better estimate related parameters such as microconstituent biotransformation rate constants and the mass organic fraction and bulk density in groundwater and sediment layers.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Advanced wastewater treatment (AWT) (filtration, carbon adsorption, phosphorus removal, and nitrogen removal) can effectively remove the majority of pollutants. However, the remaining microconstituents (including potential endocrine disrupting compounds [EDCs] and pharmaceuticals and personal care products [PPCPs]) in reclaimed water may raise public health and/or aquatic health concerns. Although certain microconstituents may persist following wastewater treatment (Gomez et al., 2007; Stackelberg et al., 2004), current research suggests that they can be removed effectively by advanced treatment technologies (Tang et al., 2006) to concentrations below human health risk levels (Snyder et al., 2006a). In addition, some research suggests that advanced treatment technologies following conventional wastewater treatment can significantly reduce the risk to aquatic organisms (Schwatter et al., 2007) and that some microconstituents found in municipal wastewater have only negligible effects on invertebrates and plants in the effluent and receiving environment (Brun et al., 2006). However, existing literature also indicates that some microconstituents at or above 0.1 ng/L will induce endocrine-mediated changes in aquatic life (Purdom et al., 1994). Other research shows that, in some cases, microconstituents accumulate in aquatic organisms and alter their natural growth (Kramer et al., 1998; Snyder et al., 2001).

1.2 PROJECT OBJECTIVES

To better understand the removal of microconstituents through AWT facilities and the potential impact of microconstituents to aquatic organisms, an AWT pilot study in the City of Plantation, FL, was funded by the WateReuse Research Foundation (WRF-06-019), the Bureau of Reclamation, the South Florida Water Management District (SFWMD), and the City of Plantation, Florida. The AWT facility consisted of a denitrifying filter (DNF), a membrane bioreactor (MBR), ultrafiltration (UF), and reverse osmosis (RO). As part of a related project, the City of Plantation, the SFWMD, and Hazen and Sawyer evaluated the pilot treatment trains for the removal of conventional pollutants, including suspended solids, total dissolved solids (TDS), biochemical oxygen demand (BOD), and nutrients. For WRF-06-019, Carollo led the monitoring effort for the removal of microconstituents through the AWT processes, while Plantation and Hazen and Sawyer operated the AWT facilities. In an attempt to correlate microconstituents with biological responses, the toxicological and hormonal impacts to various organisms and cell cultures exposed to effluent from the various AWT processes were evaluated concurrent with chemical analysis. A secondary objective of this project was to examine the fate and transport of select microconstituents from a hypothetical canal discharge location to a drinking water aquifer. The potential discharge of highly treated reclaimed water may be part of an effort to expand wastewater reuse throughout the SFWMD's 16-county service area. The SFWMD has evaluated the feasibility of using highly treated reclaimed water for augmentation of freshwater flows to several canals and other natural areas in Southeast Florida to offset a portion of the demand for water from the Okeechobee-Everglades Regional Water Management System. To provide

perspective on the potential impact to receiving water quality, limited testing of canal water near Plantation, FL, was performed.

1.3 LITERATURE REVIEW

A brief literature review is provided below. The review was designed only to provide perspective on this project, not to serve as an exhaustive compilation of associated literature. Covered topics include the definition, sources, occurrence, health impacts, regulations, and removal of microconstituents.

1.3.1 Microconstituents

1.3.1.1 *Definition*

Microconstituents were defined by the Water Environment Federation (WEF) as "natural and manmade substances, including elements and inorganic and organic chemicals, detected within water and the environment." There are many terms for microconstituents. Alternative terms used to describe these chemicals include: "EDCs," "endocrine disruptors," "hormonally active agents," "endocrine active substances," "pharmaceuticals and personal care products (PPCPs)," "pharmaceutically active compounds (PhACs)," "compounds of potential concern (CPC)," "pollutants of concern (PC)," "emerging contaminants (ECs)," "emerging pollutants (EPs)," "emerging chemicals of concern (ECCs)," "compounds of potential concern," "unregulated contaminants," "persistent bioaccumulative toxins," "trace organic compounds (TOrCs)," "microcontaminants," and similar variations. One of the most commonly used terms, though not all-encompassing, is the EDC term referring to substances that interfere with functioning of the endocrine system in humans or other animals. There exists no consensus among experts regarding the definition of an EDC or the criteria that should be used to determine whether a chemical is an EDC. Some definitions require that an effect must be demonstrated in vivo (namely, in a live animal), while others stipulate only that the potential for an effect be demonstrated, for example, through in vitro receptor binding or structure-activity relationships (SARs). Other definitions seek to distinguish adverse effects from merely compensatory responses (a nonadverse but measurable effect) (Damstra et al., 2002; EPA-EDSTAC, 1998), but this practice also has been a source of controversy. The term "microconstituents" is a broad term that does not prejudge the impact of various trace level compounds in water.

Hundreds of chemicals have been implicated as potential EDCs based on a variety of criteria (IEH, 2005). While screening-level evidence such as SARs, in vitro receptor binding activity, and certain short-term in vivo tests might suggest the potential for endocrine disruption, such effects often are not demonstrated in the more definitive in vivo tests (for example, tests conducted on multiple generations of exposed animals). Standardized test methods are generally unavailable. At this time, only certain in vivo bioassays conducted with intact animals and by using appropriate protocols (for example, encompassing susceptible life stages) provide data that are useful for risk assessment, and few chemicals have been subjected to this type of testing because of the cost and time required to conduct it. Most chemicals have not been tested by any means for endocrine activity.

The U.S. Environmental Protection Agency (U.S. EPA) established the Endocrine Disruptor Screening Program (EDSP) to develop a battery of standardized toxicity tests that can be used to determine whether a particular chemical is an EDC by the U.S. EPA's definition (EPA-

EDSP, 2008). The program focuses exclusively on chemicals that act by interfering with estrogen, androgen, or thyroid action (EPA-EDSP, 2008); these are the best characterized modes of action. However, EDCs may also interfere with the functions of other hormones (Damstra et al., 2002). The process will use a two-tiered testing strategy, with Tier 1 consisting of screening-level tests and Tier 2 consisting of in vivo bioassays that will generate data suitable for use in risk assessments (EPA-EDSP, 2008). This process is not yet complete, but Tier 1 screening of an initial set of chemicals is expected in 2008 (Draft List, 2007).

1.3.1.2 *Sources and Occurrence in the Water Cycle*

Known or potential EDCs encompass a wide variety of chemicals and a diversity of structures. They include both natural and synthetic chemicals (Table 1.1). Among them, EDCs arising from natural sources include hormones excreted by humans and other animals, substances found in plants (phytoestrogens and phytosterols) or fungi (mycoestrogens), metals, inorganic ions, and by-products of natural combustion processes (for example, volcanic activity and forest fires) (IEH, 2005; Damstra et al., 2002). Some of these EDCs occur normally in the environment or in dietary items, but their concentrations may be elevated by human activities. For example, metals may be mobilized in the environment during mining (Wilkin, 2007), and endocrine-active phytosterols may be released to water in effluents from processing of forest products (MacLatchy et al., 1997; Mellanen et al., 1996). Synthetic EDCs include certain biocides (pesticides, herbicides, and fungicides) and their degradates, PPCPs (including veterinary and human drugs), industrial chemicals and intermediates or by-products in their production as well as their environmental degradates, and combustion by-products that are not produced intentionally but result from human activities such as burning of fossil fuels and incineration of industrial and municipal waste (IEH, 2005; Damstra et al., 2002).

Table 1.1. Examples of Known or Potential EDCs[a]

Derivation	Chemical Class	Representative Chemicals
Naturally occurring	Hormones	Estradiol, estrone
	Phytoestrogens and plant sterols	Genistein, ß-sitosterol
	Mycoestrogens	Zearalenone
	Metals	Arsenic, cadmium, lead, mercury
	Inorganic ions	Perchlorate, thiocyanate
	Combustion by-products	Dioxins, certain PAHs
Synthetic	Biocides or their degradates	Atrazine, DDT, DDE, tributyltin
	PPCPs	Ethinylestradiol, trenbolone
	Industrial chemicals, intermediates, by-products or degradates	PCBs, bisphenol A, octylphenol
	Combustion by-products	Dioxins, certain PAHs

[a]PAH, polycyclic aromatic hydrocarbons; DDT, dichlorodiphenyltrichloroethane; DDE, dichlorodiphenyldichloroethylene; PCBs, polychlorinated biphenyls.

Effluents from municipal wastewater treatment plants (WWTPs) have been identified as a major source to surface waters (Anderson, 2005). WWTPs receive microconstituents from

sources including plant material, plastics, items treated with fire retardants, cleaning products, pesticides, other household chemicals and consumer products, hormones excreted by humans, and PPCPs excreted or washed from the body or flushed to the sanitary sewer. WWTPs might also treat industrial or hospital effluents and stormwater runoff that contain microconstituents from the same and additional sources. Although wastewater treatment processes remove some microconstituents to various degrees, recalcitrant chemicals may remain at detectable levels in WWTP effluents. If discharged to surface water or groundwater, microconstituents may be diluted, sequestered (for example, in sediment), or degraded by physical or biological processes, but some persist in the environment or are detected because of relatively constant loading.

WWTP effluents and reclaimed water are not the only sources of microconstituents to the environment or even to water. Examples of other potential sources include private septic systems (Swartz et al., 2006), untreated stormwater flows and urban runoff (Boyd et al., 2004), industrial effluents (Boyd et al., 2004), landfill leachate (Coors et al., 2003), discharges from fish hatcheries and dairy facilities (Kolodziej et al., 2004), fish spawning in natural waters (Kolodziej et al., 2004), runoff from agricultural fields and livestock enclosures (Orlando et al., 2004), and land amended with biosolids or animal manure (Hanselman et al., 2003; Khanal et al., 2006).

Various microconstituents have been reported to occur in WWTP effluents, surface water, groundwater, reuse water, and drinking water, usually at concentrations in the nanograms-per-liter (0.000000001 g/L) range. In general, microconstituents are reported to occur with greatest frequency and at highest levels in WWTP effluents. Because of dilution and environmental degradation, concentrations and frequency of detection are typically lower for surface water after transportation in the environment (Barel-Cohen et al., 2006; Baronti et al., 2000; Ternes et al., 1999). Based on limited information, microconstituents generally occur only at exceedingly low levels and very infrequently in finished municipal drinking water because they are diluted and undergo degradation in the environment and then must survive advanced drinking water treatment processes to remain in potable water at the tap (Falconer, 2006; Kim et al., 2007; Rodriguez-Mozaz et al., 2004; Westerhoff et al., 2005).

1.3.1.3 *Microconstituent Properties*

The name, uses, and properties of examined microconstituents for this project are listed in Table 1.2. Their chemical structures are shown in Appendix A.

1.3.1.4 *Implications for Aquatic Organisms*

Typical biological impact of microconstituents on wildlife may include:

- feminization of male fish or masculinization of female fish;
- delayed sexual development in fish;
- intersex of frogs;
- delayed metamorphosis in frogs;
- embryo mortality;
- abnormal hormone levels;
- impaired reproductive systems and immune systems; and
- structual and neurological damage.

Table 1.2. Chemical Names, Uses, and Properties of Examined Microconstituents

Name	Use	Mol. Wt (g/mol)[a]	Solubility (mg/L)[a]	Log K_{ow}[a]	Log D[b] pH = 1	pH = 4	pH = 7	pH = 8	pH = 10
2,6-di-*tert*-Butylphenol	UV stabilizer and antioxidant	206.33	2.5	4.92	4.86	4.86	4.86	4.86	4.85
4-Methylphenol	dissolvent, disinfectants	108.14	21,500	1.94	1.94	1.94	1.94	1.94	1.74
4-Nonylphenol	surfactant metabolite	220.36	7	5.76	6.19	6.19	6.19	6.19	5.96
Acetaminophen	fever relief drug	151.17	14,000	0.46	-0.45	0.34	0.34	0.33	-0.04
Alpha chlordane	pesticide	409.78	0.056	6.16	5.57	5.57	5.57	5.57	5.57
Amoxicillin	antibiotic	365.41	3430	0.87	-2.44	-1.89	-2.21	-2.79	-3.5
Bisphenol A	anti-inflammatory drug	228.29	120	3.32	3.43	3.43	3.43	3.43	3.03
Caffeine	stimulant drug	194.19	21,600	-0.07	-0.32	-0.13	-0.13	-0.13	-0.13
Carbamazepine	anticonvulsant drug	236.28	17.7	2.45	2.66	2.67	2.67	2.67	2.67
Carbaryl	insecticide	201.23	110	2.36	2.4	2.4	2.4	2.4	2.39
Chlorpyrifos	insecticide	350.59	1.12	4.96	4.77	4.77	4.77	4.77	4.77
N,N-Diethyl-*m*-methylbenzamide	insect repellent chemical	191.28	912	2.18	1.96	1.96	1.96	1.96	1.96
Diazinon	insecticide	304.35	40	3.81	3.81	3.81	3.81	3.81	3.81
Dieldrin	insecticide	380.91	0.195	5.40	4.88	4.88	4.88	4.88	4.88
Estradiol	sex hormone	272.39	3.6	4.01	4.13	4.13	4.13	4.13	3.94
Estrone	estrogenic hormone	270.37	30	3.13	3.69	3.69	3.69	3.69	3.49
17α-Ethinylestradiol	oral contraceptive pill	296.41	11.3	3.67	2.2	1	-1.41	-1.53	-1.72
Fluoxetine	antidepressant drug	309.33	60.3	4.05	0.99	0.99	1.31	2.06	3.76
Gemfibrozil	Lipid-lowering drug	250.34	10.9	4.77	4.39	4.32	2.15	1.26	0.65
Ibuprofen	anti-inflammatory drug	206.29	21	3.97	3.72	3.58	1.16	0.36	-0.02
Iopromide	radiopaque contrast agent	791.12	23.8	-2.05	-2.95	-2.95	-2.95	-2.95	-3.05
Methyl parathion	pesticide	263.21	37.7	2.86	2.78	2.78	2.78	2.78	2.78
Phenol	resins, nylons, disinfectant	94.11	82,800	1.46	1.48	1.48	1.48	1.48	1.11
Progesterone	steroid hormone	314.47	8.81	3.87	4.04	4.04	4.04	4.04	4.04
Sulfamethoxazole	antibiotic	253.28	610	0.89	0.35	0.88	-0.27	-0.9	-1.11
Tris(1,3-dichloro-2-propyl) phosphate	flame retardant	430.91	7	3.65	1.79	1.79	1.79	1.79	1.79
Testosterone	steroid hormone	288.43	23.4	3.32	3.47	3.47	3.47	3.47	3.47
Triclosan	antibiotic	289.55	10	4.76	5.17	5.17	5.17	5.17	3.02
Trimethoprim	antibiotic	290.32	400	0.91	-1.71	-1.63	0.38	0.73	0.79
Triphenyl phosphate	flame retardant and plasticizer	326.29	1.9	4.59	4.1	4.1	4.1	4.1	4.1
Tris(2-butoxyethyl) phosphate	floor polishes and plasticizer	398.48	1100	3.75	4.3	4.3	4.3	4.3	4.3
Tris(2-chloroethyl) phosphate	flame retardant	285.49	7000	1.44	0.48	0.48	0.48	0.48	0.48

[a] Interactive PhysProp Database Demo, 2010.
[b] Provided by Dr. Jörg Drewes at Colorado School of Mines.

There is a substantial and growing body of evidence indicating that microconstituents at levels found in WWTP effluent can cause endocrine disruption in fish and other aquatic life, with the literature suggesting that some microconstituents at or above 0.1 ng/L will induce endocrine-mediated changes in aquatic life (Purdom et al., 1994; Vanderford et al., 2003). This issue first gained public attention when male fish collected downstream of WWTPs in the United Kingdom were found to have elevated levels of vitellogenin (Vtg), a female-specific egg yolk protein, in their blood. Vtg induction in male fish is a symptom of exposure

to estrogens from external sources. Vtg induction generally is not considered to be an adverse effect. Later studies suggest a link between exposure to WWTP effluents and adverse or potentially harmful effects on the reproductive organs and fertility of fish (Jobling et al., 2002; Jobling and Tyler, 2003). The findings in the U.K. studies spurred research in other European countries (Diniz et al., 2005; Petrovic et al., 2002), North America (Bevans et al., 1996; Folmar et al., 2001; Folmar et al., 1996; Giesy et al., 2003; Hemming et al., 2004; Nicholas et al., 1999; Patino et al., 2003; Schoenfuss et al., 2002; Snyder et al., 2004; Woodling et al., 2006), and in other locations where WWTP effluents have been implicated in endocrine-related effects on fish.

WWTP effluent contains a mixture of microconstituents, and in most cases researchers have been unable to pinpoint the specific chemicals responsible for effects indicating endocrine disruption in exposed fish. Estradiol, estrone, ethinylestradiol, nonylphenol, octylphenol, alkylphenol ethoxylates, and bisphenol A have been identified as potential causes (Purdom et al., 1994; Damstra et al., 2002) based on their concentrations in effluents and their potency in laboratory studies. Natural hormones produced in the bodies of humans and other animals (for example, estradiol and estrone) and synthetic hormones intended to mimic the actions of endogenous hormones (for example, the oral contraceptive ingredient ethinylestradiol) are particular concerns because they are potent at very low concentrations and are commonly detected in WWTP effluents.

While hormonal disruption of aquatic life by wastewater-derived EDCs has clearly been demonstrated, limited information exists on the possibility of long-term aquatic life population effects. This topic is an area for further research.

1.3.1.4 *Impact on Human Health*

Although there are well-substantiated links between environmental exposure to microconstituents in water supplies (Blazer et al., 2007) and effects in fish, there is little evidence to suggest that typical low-level environmental exposures to microconstituents (in WWTP effluent, reclaimed water, and drinking water) have had any adverse effect on human health (Damstra et al., 2002). The Global Water Research Coalition (GWRC) concluded that uptake of microconstituents by humans from treated drinking water is relatively low in comparison to uptake from other sources such as foods (GWRC, 2003). There are important differences in exposure to wastewater contaminants between fish and humans. Fish may be immersed in effluents at their point of entry into surface water where concentrations are greatest and can take up contaminants directly across body surfaces, particularly the gills. Fish can also be exposed to microconstituents and other effluent contaminants that accumulate in their food or associate with particulate material and sediments. In contrast, people tend to receive little direct exposure to microconstituents in WWTP effluent, so concerns related to potential human health effects generally center around drinking water contamination. Microconstituents discharged in WWTP effluents or in reclaimed water to surface water or groundwater undergo dilution, environmental degradation, and water treatment processes that can substantially reduce their concentrations before they reach the tap. However, the science of endocrine disruption is relatively new, and research into exposure to microconstituents and the potential human health consequences of these exposures continues.

1.3.1.4 *Regulations*

Although some chemicals that might be considered to be microconstituents are regulated in WWTP effluent for the protection of aquatic organisms, regulations, with one noted exception, are not based on endocrine modes of action except to the extent that they are captured in effects on more traditional ecotoxicologic endpoints (for example, mortality and reproduction) (EPA, 2005). Likewise, chemicals that might be classified as microconstituents are federally regulated in drinking water but not on the basis of their potential to cause endocrine disruption. In Massachusetts, the level of perchlorate in drinking water is regulated on the basis of its potential to act as an EDC (namely, by interfering with thyroid function) (Massachusetts DEP, 2006), but to date no other state has regulated any drinking water contaminant as a putative EDC. The California Department of Public Health (CDPH) has mandated monitoring and reporting for a list of potential microconstituents for indirect potable reuse projects in California (CDPH, 2008).

1.3.2 Removal of Microconstituents

This project focused on evaluating membrane systems for removing microconstituents from wastewater. However, as the results of this study will show, select microconstituents may pass through RO membranes at very low levels. Thus, it is prudent to consider further reduction of microconstituents through biological (as part of secondary treatment) or chemical oxidation processes. This literature review includes information related to these two processes and also includes a brief review of other useful processes, specifically activated carbon adsorption, membrane filtration, and enzymatic treatment.

Several comprehensive studies were conducted to compare the removal efficiency of various processes. One study of full- and pilot-scale drinking water and wastewater treatment processes demonstrated that most conventional drinking water treatment methods were relatively inefficient for contaminant removal, while granular activated carbon (GAC) can effectively remove microconstituents (approximately equal to 99%) in drinking water treatment (Kim et al., 2008). Membrane filtration processes using RO and nanofiltration (NF) showed excellent removal (>95%) for all targeted microconstituents in wastewater treatment (Kim et al., 2007). For the UV process, the use of UV radiation and H_2O_2 or O_3 that can generate OH radicals was capable of degrading the microconstituents faster than UV radiation alone in a batch reactor (Kim et al., 2008). Snyder et al. (2007) evaluated the efficacy of various membranes and activated carbons for the removal of microconstituents and found that GAC, NF, and RO were more effective at removing a suite of structurally diverse microconstituents than microfiltration (MF) and UF were. However, the results also showed that the activated carbon filters need regular regeneration and nonregenerated activated carbon filters displayed no removal of microconstituents (Snyder et al., 2007). Drewes et al. found that lower-pressure, high-intensity UV radiation did not remove microconstituents and that medium-range UV radiation and chlorination only partially removed phenolic compounds, while activated carbon, high-pressure membranes, and soil aquifer treatment (SAT) can effectively remove microconstituents and reduce biological activity to below detection limits in reclaimed water (Drewes et al., 2006a).

A summary of the range of percent removal of microconstituents with various treatment technologies is presented in Table 1.3. Details are discussed in the following sections.

Table 1.3. Range of Percent Removal of Microconstituents with Various Treatment Technologies

Technology	Range of % Removal of Microconstituent
Conventional activated sludge	Generally ineffective, 51–99% removal for limited microconstituents
Coagulation	Generally ineffective, 10–70% removal for limited microconstituents
Activated carbon adsorption	Effective, 10–51% removal for many microconstituents
MBR	Effective, 68–90% removal for most examined microconstituents
O_3/H_2O_2/UV oxidation	Effective, 50–99% removal for most examined microconstituents
Chlorination	Generally ineffective, 75–99% removal for limited microconstituents
Membrane filtration	Effective, 70–99% removal for most examined microconstituents
Enzymatic treatment	Effective, 92–100% removal for most examined microconstituents
Ferrate(VI) oxidation	Effective, 50–99% removal for most examined microconstituents

1.3.2.1 *Conventional Activated Sludge*

Most microconstituents could not be effectively removed by conventional activated sludge. A study at a municipal wastewater treatment showed that only 4 out of 35 microconstituents were degraded by more than 90%, while 17 compounds are removed by less than 50% (Joss et al., 2006). In another study in Japan, 66 microconstituents could not be efficiently removed by using physicochemical wastewater treatment after conventional activated sludge treatment (Okuda et al., 2008). The removal efficiencies of carbamazepine and crotamiton were less than 30%. Conversely, an ozonation process followed by a biological activated carbon process could efficiently reduce all the residual microconstituents below their quantification limits (Okuda et al., 2008).

Similarly, the average removal efficiency of tested microconstituents in 12 sewage treatment plants in Finland was less than 65%, and the removal efficiency varied greatly between the treatment plants. Fluoroquinolones were eliminated by more than 80% in the treatment plants, while carbamazepine was removed poorly and even increased in the treated sewages, possibly because of enzymatic cleavage of the glucuronic conjugates of carbamazepine (Vieno et al., 2007a).

In another study, the removal efficiency of acidic microconstituents (ibuprofen, naproxen, mefenamic acid, ketoprofen, and diclofenac), caffeine, and triclosan during secondary treatment ranged from 51 to 99% (Thomas and Foster, 2005).

1.3.2.2 *Coagulation*

The removal of selected microconstituents (diclofenac, ibuprofen, bezafibrate, carbamazepine and sulfamethoxazole) by chemical coagulation was studied in jar tests (Vieno et al., 2006). In Milli Q water coagulation, the microconstituents were poorly removed (< 10%) with the exception of diclofenac (66% with ferric sulfate). In lake water coagulation, only diclofenac was removed (30%) with ferric sulfate. In the presence of dissolved humic matter, diclofenac as well as ibuprofen and bezafibrate could be removed by ferric sulfate coagulation. Although conditions such as high humic material content and low coagulation pH and a small amount of ferric coagulant can increase the removal of certain ionic microconstituents, it was determined that coagulation cannot effectively remove microconstituents from water (Vieno et al., 2006). The removal of 18 microconstituents (and metabolites) and of seven *s*-triazine

herbicides was evaluated, and the flocculation-coagulation and dual media filtration steps without ozone treatment resulted in no decrease in analyte concentrations, while ozonation removed 66 to 100% (< 0.05 to 1 ng/L) of the microconstituents and was highly effective in depleting carbamazepine, caffeine, cotinine, and atrazine in drinking water treatment processes (Hua et al., 2006). Similarly, the removal efficiency of 13 studied microconstituents was only 13% following coagulation, sedimentation, and rapid sand filtration, but the following ozonation at 1 mg/L removed all microconstituents below detection limits except ciprofloxacin in a pilot-scale drinking water treatment plant (Vieno et al., 2007b). The removal of some selected microconstituents in sewage (galaxolide, tonalide, diazepam, carbamazepine, ibuprofen, naproxen, and diclofenac) by coagulation-flocculation was around 50 to 70%, except that carbamazepine and ibuprofen were not removed at all. Conversely, flotation removed galaxolide and tonalide by 35 to 60%, followed by diazepam (40 to 50%), diclofenac (20 to 45%), carbamazepine (20 to 35%), ibuprofen (10 to 25%), and naproxen (10 to 30%) (Carballa et al., 2005). It is apparent that coagulation is more effective in waters with high organic content, possibly related with the coagulation removal of particles with sorbed microconstituents.

1.3.2.3 *Activated Carbon Adsorption*

Activated carbon has been found to be effective in removing microconstituents. In the same study by Vieno et al., GAC adsorption effectively removed 10 microconstituents except for three hydrophilic microconstituents (atenolol, sotalol, and ciprofloxacin) in a pilot-scale drinking water treatment plant (Vieno et al., 2007b).

Activated carbon adsorption can also effectively remove estrone and 17β-estradiol in pure water; however, the absorbability of estrone and 17β-estradiol in river water and secondary effluent fell significantly, possibly because of site competition and pore blockage and the presence of surfactant and humic acid (Fukuhara et al., 2006; Zhang and Zhou, 2005). In another study at a conventional drinking water treatment plant, GAC adsorption accounted for 53% of the removal of 113 organic compounds including microconstituents, while chlorination and clarification accounted for 32% and 15% of the removal of 113 organic compounds (Stackelberg et al., 2007).

The removal of microconstituents in secondary effluent by coagulant-assisted GAC was investigated, and the results showed that coagulant-assisted GAC adsorption removed most microconstituents except carbamazepine, clofibric acid, gemfibrozil, ibuprofen, *p*-toluenesulfonamide, caffeine, butylated hydroxyanisole, butylated hydroxytoluene, and *N*-butyl benzenesulfonamide (Soliman et al., 2007).

1.3.2.4 *MBR*

An MBR was found to perform better than a conventional activated sludge system in removing microconstituents and in the removal of estrogenicity. Radjenovic et al. found the performance of MBRs to be better (removal rates of >80%) than that of a conventional activated sludge system for most of the investigated microconstituents. Carbamazepine was the most persistent pharmaceutical and passed through both the MBR and activated sludge systems untransformed (Radjenovic et al., 2007). Estrogen and 17β-estradiol can be effectively removed (Chang et al., 2006). However, substantial amounts of estrone, estrone-3-sulfate, estrone-3-glucuronide, and 17β-estradiol-glucuronides passed through treatment systems (Hu et al., 2007a). Bisphenol A was removed well with a removal efficiency of 68.9 to 90.1%, but 4-nonylphenol concentration was amplified after MBR treatment, a result that

could have been caused by the transformation of its parent compounds, nonylphenol polyethoxylates (Hu et al., 2007a). The removal of 19 microconstituents by an MBR was evaluated, and more than 90% of bisphenol A, ibuprofen, or bezafibrate was removed, while no carbamazepine was removed (Clara et al., 2005).

The removal efficiency by MBRs is related to sludge retention time (SRT) as activated sludge treatment but can reach a higher SRT with a compact MBR than with a conventional activated sludge treatment system (Clara et al., 2005). The effect of SRT on microconstituent removal was confirmed in another study (Kimura et al., 2007). The removal of six acidic microconstituents (clofibric acid, diclofenac, ibuprofen, ketoprofen, mefenamic acid, and naproxen) in a WWTP by using an activated sludge system and MBRs was evaluated, and the SRTs of the WWTP and the two MBRs were 7, 15, and 65 days, respectively. The MBRs exhibited higher removal rates for the examined six acidic microconstituents than did the WWTP, possibly because of the longer SRTs. The MBR that was operated with a longer SRT of 65 days also showed better performance than did the MBR with a shorter SRT of 15 days. Batch elimination tests revealed that the main mechanism of elimination of the microconstituents was due to biotransformation (Kimura et al., 2007).

1.3.2.5 *O_3/H_2O_2/UV Oxidation*

Advanced oxidation of wastewater using ozone (O_3), O_3/UV, or H_2O_2/UV successfully led to the reduction of carbamazepine, diazepam, diclofenac, and clofibric acid to below detection limits, although these microconstituents were poorly removed by biological treatment in conventional activated sludge and in MBRs (Gebhardt and Schroder, 2007).

Ozone and ozone/H_2O_2 oxidation are effective techniques to reduce microconstituents. In a wastewater study (filtered secondary effluent), the majority of target microconstituents were reduced by greater than 90% by O_3, while atrazine, iopromide, meprobamate, and *tris*-chloroethylphosphate were removed less than 50%. The addition of H_2O_2 for advanced oxidation was of little benefit for contaminant removal as compared to O_3 alone. O_3/H_2O_2 provided a marginal increase in the removal of dilantin, diazepam, DEET, iopromide, and meprobamate, while decreasing the removal efficacy of pentoxifylline, caffeine, testosterone, progesterone, and androstenedione (Snyder et al., 2006b).

The removal efficiency of six microconstituents (4-nonylphenol, bisphenol A, 17α-ethinylestradiol, 17β-estradiol, estrone, and estriol) by ozonation was over 95% with ozone exposures of 2×10^{-3} mg × min/L in water treatment processes (Deborde et al., 2005), confirming that ozonation can effectively remove 17α-ethinylestradiol, estrone, and estradiol (Huber et al., 2004). The estrogenicity was reduced by a factor of more than 200 after ozonation using yeast estrogen screen (YES) assays (Huber et al., 2004). Similarly, macrolide and sulfonamide antibiotics, estrogens, and the acidic microconstituents diclofenac, naproxen, and indomethacin were oxidized by more than 90 to 99% for O_3 doses over 2 mg/L in a pilot-scale column study of municipal wastewater (Huber et al., 2005a). The suspended solids have only a minor influence on the oxidation efficiency of nonsorbing microconstituents (Huber et al., 2005a). During ozonation of a natural estrogen (17β-estradiol) in water, several by-products were formed at pH 7 and 11, while only testosterone could be observed at pH 3. Higher estrogenic activity was detected at pH 11 with use of the YES assay, possibly because the oxidation via OH radical forms more by-products with estrogenic activity. Complete removal of estrogenic activity was obtained only at pH 3 (Bila et al., 2007). The removal of 17β-estradiol and bisphenol A by O_3 alone and that by O_3/UV advanced oxidation were compared. The results showed that coupling of UV decreased the O_3 consumption by 22.5% in converting the same amount of 17β-estradiol, while there was no significant difference in

O_3 consumption for complete conversion of bisphenol A by O_3 and O_3/UV systems (Irmak et al., 2005).

The removal efficiency of bisphenol A with an initial concentration of 1.0 mg/L was measured up to 70%, 82%, and 90% within 30 min when the dosage of ozone was 1 mg/L, 1.5 mg/L, and 2 mg/L respectively, and the results showed that major degradation of bisphenol A was contributed by ozone dosage instead of contact time (Xu et al., 2006). Another study indicated complete removal of bisphenol A in water by ozonation, and the direct reaction rate constants were 1.3×10^4 M^{-1} s^{-1} for bisphenol A at pH 2 and 1.6×10^9 M^{-1} s^{-1} for dissociated bisphenol A at pH 12. Use of hydrogen peroxide did not alter the main degradation route, and the molecular ozone remained a principal oxidant, as a substantial portion of the OH radical was scavenged by hydrogen peroxide (Lee et al., 2003). Another study on the degradation and mineralization of bisphenol A in water by the UV/H_2O_2/microaeration process showed that the mineralization rate of bisphenol A increased linearly with the enhancement of intensity of UV radiation. When the dosages of H_2O_2 changed from 5 to 20 mg/L, the mineralization rate of bisphenol A grew eightfold (Hu et al., 2007b).

Ozonation also could remove more than 80% of the phenolic antiseptics, crotamiton, sulfonamide and macrolide antibiotics, and 17β-estradiol among 24 microconstituents during sand filtration and ozonation, while sand filtration was generally inefficient in removing microconstituents, probably because of their low hydrophobicities. The combination of ozonation and sand filtration with activated sludge treatment gave efficient removal (>80%) of all the target compounds except carbamazepine and diethyltoluamide (Nakada et al., 2007).

N-Nitrosodimethylamine (NDMA), a carcinogenic microconstituent, can effectively be removed by O_3/H_2O_2 oxidation, even though it can't be effectively removed by membrane filtration. The results indicated that the reaction with hydroxyl radical dominates the NDMA oxidation during ozonation. Conventional ozonation with up to 160 mM ozone led to less than 25% NDMA oxidation in natural waters, and the O_3/H_2O_2 oxidation with 160 to 320 mM ozone can achieve 50 to 75% NDMA oxidation. However, multiple injections of ozone can improve the oxidant utilization efficiency. Bromate formation may be the limiting factor for NDMA oxidation during ozonation and O_3/H_2O_2 oxidation in bromide-containing waters (Lee et al., 2007).

The removal efficiency of microconstituents in drinking water by ozonation can be affected by the water compositions, with the highest removal efficiency found in ultrapurified water, while other factors such as filtered water and river water reduced the removal efficiency by 26.5 to 50.3% and 57.3 to 72.0%, respectively (Liu et al., 2007). A three-dimensional quantitative structure-property relationship model was developed to evaluate removal mechanisms during chlorination and ozonation in typical water treatment processes (Lei and Snyder, 2007).

UV radiation was shown to be effective in removing select microconstituents. It was found that more than 90% of di-*n*-butyl phthalate (DBP) can be degraded within 1 h of UV irradiation at 254 nm, especially in neutral to basic conditions. The major decomposition mechanism of DBP is believed to involve the hydrolytic photolysis of the carbon in the α and/or β position of the ester chain with the production of aromatic carboxylic derivatives (Lau et al., 2005).

Bisphenol A, ethinylestradiol, and estradiol were more effectively degraded during UV/H_2O_2 advanced oxidation than when direct UV photolysis treatment was utilized (Rosenfeldt and Linden, 2004). The UV/H_2O_2 processes using either low- or medium-pressure lamps can degrade microconstituents in lab water by 80 and 99.3% at a 15-ppm H_2O_2 concentration and a UV dose of 1000 mJ/cm^2. The results indicated that a dose of less than 200 mJ/cm^2 completely removed estrogenic activity in lab water (Linden et al., 2007).

The kinetics of UV C (UV-C)-induced direct phototransformation of four microconstituents (17α-ethinylestradiol, diclofenac, sulfamethoxazole, and iopromide) was investigated in dilute solutions of pure water buffered at various pH values using a low-pressure and a medium-pressure mercury arc lamp. At the UV-C (254-nm) drinking water disinfection dose of 400 J/m^2, the degree of depletion of the select microconstituents at pH 7.0 in pure water was 0.4% for 17α-ethinylestradiol, 27% for diclofenac, 15% for sulfamethoxazole, and 15% for iopromide, indicating that phototransformation should be seriously taken into account during evaluation of the possibility of formation of UV transformation products (Canonica et al., 2008).

1.3.2.6 *Chlorination*

ClO_2 was effective at oxidizing only certain microconstituents such as the investigated sulfonamide, macrolide antibiotics, and estrogens in lake water and groundwater (Huber et al., 2005b). Similar to ozonation, chlorination removed 75% to 99% of the test microconstituents (bisphenol A, 17β-estradiol, and 17α-ethinylestradiol) in distilled water; however, chlorination reached a stabilized estrogenic level in more than 120 min after transformation of test microconstituents, while ozone oxidation reached a stabilized estrogenic level in 10 min (Alum et al., 2004).

1.3.2.7 *Membrane Filtration*

Membrane filtrations, such as MF, NF, and RO, have proven effective in removing microconstituents.

Soliman et al. found that lime/RO treatment in secondary effluent at a wastewater treatment plant and two water reclamation facilities reduced clofibric acid, ibuprofen, caffeine, butylated hydroxyanisole, and *N*-butyl benzenesulfonamide from influent levels up to 71 ng/L to below 10 ng/L and that the MF/RO treatment reduced concentrations to levels below their detection limits except for butylated hydroxytoluene at one facility (Soliman et al., 2007). The removal of pentachlorophenol by low-pressure RO membrane was higher than 80%. The rejection increased with the increase of pH (Razak et al., 2007).

The mechanisms of removing microconstituents by NF and RO membranes were shown to be size exclusion and adsorption. Furthermore, deprotonation of estrone led to a significant decrease in retention by an NF membrane but not for a tight RO membrane, suggesting that the extent of hormone retention may be very susceptible to maintenance of membrane adsorptive capacity and solution chemistry (Schafer et al., 2003). Another study indicated that adsorption (or partitioning) of hormones to the membrane polymer is the dominant removal mechanism at the early stages of NF of hormones but that size or charge exclusion of the membrane dominated at the later filtration stage (Nghiem et al., 2004).

The rejection of microconstituents by a variety of commercial RO, NF, and ultralow-pressure RO membranes was investigated. The results indicated that the presence of effluent organic matter improved the rejection of ionic organics by tight NF and RO membranes. Rejection of

ionic pharmaceutical residues and pesticides ranged from 89% to over 95% by NF membranes. Rejection of hydrophobic nonionic compounds was initially high but decreased significantly after 10 h of operation because of solute partitioning through the membranes (Xu et al., 2005). Drewes et al. also evaluated the rejection of microconstituents by high-pressure membranes and identified the following solute parameters affecting microconstituent rejection: molecular weight, molecular size, acid disassociation constant, hydrophobicity/hydrophilicity, and the diffusion coefficient. Membrane properties, such as molecular weight cutoff, pore size, surface charge, hydrophobicity/hydrophilicity, and surface morphology, also affect microconstituent rejection. Feed water composition, such as pH, ionic strength, hardness, and the presence of organic matter, plays a role in microconstituent rejection as well (Drewes et al., 2006b). In addition, Drewes et al. developed a rejection diagram based on the physicochemical characteristics (dissociation potential, hydrophobicity, and molecular size) to predict the rejection of microconstituents. Rejection of the sodium dibasic arsenate, the arsenate anion, and pesticides by the NF membranes is high. The charge exclusion, size exclusion, and the specific physicochemical phenomena were found to be important for rejection by the NF membranes (Košutić et al., 2005).

The removal of estrone and 17β-estradiol by direct contact membrane distillation (DCMD) and by forward osmosis (FO) was investigated for wastewater treatment in advanced life support systems (for example, space missions), and DCMD provided >99.5% hormone rejection, constant flux, >99.9% urea and ammonia rejection, and high water recovery. Similarly, FO provided from 77 to 99% hormone rejection (Cartinella et al., 2006).

1.3.2.8 *Enzymatic Treatment*

Enzymatic treatment was found to be efficient in removing microconstituents. A horseradish peroxidase enzyme-catalyzed process was capable of achieving 92 to 100% removal of estrone, 17β-estradiol, estriol, and 17α-ethinylestradiol within 1 h of treatment of water with a horseradish peroxidase activity of 0.017 μ/mL (Auriol et al., 2006). The effects of temperature, pH, and wastewater constituents significantly impact the horseradish peroxidase-catalyzed estrogen removal (Auriol et al., 2006). In another study, estrone, 17β-estradiol, estriol, and 17α-ethinylestradiol can be completely oxidized in the synthetic water and municipal wastewater after a 1-h treatment with either horseradish peroxidase (8 to 10 μ/mL) or laccase (20 μ/mL), and both enzymatic treatments were found to be efficient in removing the estrogenic activity of the studied steroid estrogens (Auriol et al., 2008). Estrone can be removed by 98% after 5 days of treatment and the activities of ligninolytic enzymes, possibly produced extracellularly by white rot fungus, *Phanerochaete sordida* YK-624. Further experiments showed that estrone was completely removed after 1 h of treatment with either manganese peroxidase or laccase and that both enzymatic treatments completely removed the estrogenic activity of estrone after 2 h, suggesting ligninolytic enzymes are effective in removing the estrogenic activity of estrone (Tamagawa et al., 2006).

1.3.2.9 *Ferrate(VI) Oxidation*

Ferrate (Fe[VI]) can effectively reduce microconstituents to very low levels (10 to 100 ng/L), and ferrate was shown to be more effective than electrochemical oxidation to reduce COD concentration in wastewater (Jiang et al., 2005). The ferrate oxidation of the four steroid estrogens (17α-ethinylestradiol, estrone, β-estradiol, and estriol) had higher reaction rates than bisphenol A did. It is concluded that ferrate oxidation could be an effective treatment method for the purification of waters containing these particular microconstituents (Li et al., 2008). Approximately 90% of the bisphenol A was degraded by ferrate after 60 s (Li et al., 2005). The photocatalytic oxidation efficiency in the presence of Fe(VI) was much greater

than that without Fe(VI) (Li and Li, 2007), and the effectiveness of Fe(VI) for the oxidative removal of phenolic microconstituents also was confirmed in both natural water and wastewater (Lee et al., 2005). Potassium ferrate(VI) (K_2FeO_4) can be used to remove sulfamethoxazole (Sharma et al., 2006). The extent of degradation of three chlorinated microconstituents (4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol) by Fe(VI) was found to be highly pH dependent (Graham et al., 2004).

In another recent study by Lee et al., the potential of Fe(VI) was assessed to oxidize various microconstituents and to remove phosphate by a subsequent ferric phosphate precipitation during treatment of municipal wastewaters. The results showed that Fe(VI) doses of less than 8 mg/L are capable of oxidizing many kinds of microconstituents and of removing phosphate below 0.8 mg/L. Fe(VI) and O_3 exhibited similar removal efficiencies. Fe(VI) was stabler (minutes) than ozone (seconds) in the tested wastewater because of a slower consumption of ferrate by matrix components. Ozone achieved better removal than Fe(VI) for some microconstituents without reactive moieties (for example, ibuprofen) because of the formation of OH radicals (Lee et al., 2008).

1.3.3 Representative Microconstituents for Recharge Modeling

1.3.3.1 *Introduction*

The recharge modeling of reclaimed water to surface canals was conducted by DHI Water and Environment (DHI). To select the representative microconstituents for recharge modeling, DHI completed a limited literature review on the fate and transport of six microconstituents in surface water and in groundwater. This review focused on six of the 31 monitored microconstituents. The six researched microconstituents were chosen based on degradation processes resulting from photolysis, biotransformation, and sorption to organic matter. The selected microconstituents represent a range of different physical/chemical properties, fate processes, and anticipated uses of end products:

- sulfamethoxazole (antibiotic)
- triclosan (antibacterial agent that is widely used in personal care products)
- ibuprofen (nonsteroidal anti-inflammatory drug)
- 4-nonylphenol (pesticide products)
- methyl parathion (insecticide)
- phenol (mainly production of plastic)

The literature review reported decay rates for these microconstituents for each process (photolysis, biotransformation, and hydrolysis). Also, Henry constants (necessary to determine evaporation losses) and adsorption coefficients were reported. As discussed below, three of these six compounds were then selected for modeling of fate and transport as part of this project and were compared to a conservative “tracer” compound.

The relevant transport and fate processes for each of these microconstituents were investigated in both surface water and groundwater. The fate processes were sorption and degradation. Three different degradation processes can be relevant, namely, hydrolysis, photolysis and biotransformation. Typical transport mechanisms are advection, volatilization of dissolved fraction from the water column to the atmosphere, molecular diffusion into the

sediment, and turbulent dispersion and sedimentation of sorbed pesticides from the water column to sediment.

The physicochemical properties of the microconstituents are important in determining the fate of microconstituents. Among these properties are the octanol-water partition coefficient (K_{ow}), the soil and sediment sorption coefficients (K_{oc}), water solubility, vapor pressure, Henry's constant, and the acid-base ionization constant.

The focus of the literature review is to identify the most important removal processes, estimate a simple first-order half-life coefficient to be utilized in the modeling process, and find typical concentrations in surface water and groundwater after a hypothetical injection of highly treated reclaimed water to a surface water canal. Please note that microconstituents can also follow a zero kinetic but that only first-order coefficients are evaluated in this study based on reviewed literature.

Estimates of removal half-life for each of the six selected microconstituents and typical removal were obtained by applying the estimation software EPIwin v3.12 from the U.S. EPA. The software also contains a large database of literature values, although the training set of EPIwin does not include most microconstituents examined in this study. If database records were found, they were compiled instead of the estimates being used.

1.3.3.2 *Fate and Transport Parameters*

Sulfamethoxazole

Sulfamethoxazole is an antibacterial sulfonamide. It prevents the formation of dihydrofolic acid, a compound that bacteria must be able to make in order to survive. Although it was once a very useful antibiotic, it is almost obsolete as a single agent today because of the development of bacterial resistance to its effects. Sulfamethoxazole is now used primarily in combination with trimethoprim, a combination product known as Bactrim or Septra. It is commonly used to treat urinary tract infections.

Many microconstituents are not removed efficiently by coagulation and flocculation processes in wastewater treatment facilities because of relatively low log K_{ow} values. Sulfamethoxazole has a log K_{ow} of 0.89, the lowest among the selected microconstituents.

Sulfamethoxazole is reported as biodegradable under aerobic conditions in an adapted activated sludge culture. The lag period before initiation of degradation was 4 days (Drillia et al., 2005). In laboratory studies, no significant biotransformation was found in pond water over a period of 30 days (Lam et al., 2004). Kjølholt et al. report that sulfamethoxazole is not biodegradable (Kjølholt et al., 2003).

Ternes et al. reported that 4 of 54 studied PPCPs were found below a treated sewage infiltration site (45 years of operation) (Ternes et al., 2007). Three meters below the groundwater table (unsaturated zone, 1.5 to 2 m), sulfamethoxazole concentrations were between 0 and 20% of input concentrations.

Sulfamethoxazole adsorbs UV light and is susceptible to photodegradation. Half-lives in synthetic field water and synthetic sunlight were found to be between 2.7 and 6.6 h, depending on the dissolved organic matter (DOM) content (Lam and Mabury, 2005). Mean

half-life in 12 microcosms with fish, aquatic plants, zooplankton, phytoplankton, macrophytes, and bacteria was 19 days (Lam et al., 2004).

The reported surface water concentrations of sulfamethoxazole are summarized in Table 1.4.

Table 1.4. Reported Surface Water Concentrations of Sulfamethoxazole

Type	Location (state, waterway, or town)	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	MN	0.0039	0.5		Lee et al., 2004
Surface water	Huron River	0.0037	0.018	0.010	Skadsen et al., 2004
Raw Wastewater	Ann Arbor	0.23	1.2	0.69	Skadsen et al., 2004
WWTP effluent	Ann Arbor	0.35	0.86	0.56	Skadsen et al., 2004
Surface water	Boulder Creek	0.052	0.220		Barber et al., 2004

Triclosan

Triclosan is used as a preservative and an antibacterial agent that is widely found in personal care products such as shampoos, soaps, cosmetics, lotions, and toothpaste as well as in cleaning materials, paint, textiles, and plastic products.

Studies regarding the fate and effects of triclosan have been reviewed by Samsøe-Petersen et al. to describe the fate of triclosan in WWTPs and to make environmental risk assessments of triclosan (Samsøe-Petersen et al., 2003). The reviewed studies showed that triclosan degrades under aerobic conditions in WWTPs and is extensively degraded and removed in activated-sludge systems. Furthermore, triclosan does not adversely impact the treatment processes at levels up to 2 mg/L in the influent. However, monitoring studies indicate that little to no removal of triclosan occurs during anaerobic sludge digestion. Monitoring of triclosan concentrations at WWTPs in the United States, Sweden, Switzerland, and Denmark showed the following ranges of triclosan concentrations:

- Influent: 0.1 to 16.6 µg/L
- Effluent: 0.10 to 2.70 µg/L
- Sludge: 0.028 to 15.6 µg/g (dry weight)

Studies regarding photolysis of triclosan in surface water have demonstrated that it may be a significant pathway in the upper layers of lakes (for example, at pH 8, 4.6% of the parent compound was transformed to the dioxin 2,8-DCDD). Such a transformation can, however, be expected only in the upper layers of lakes because of sorption of light in the water column (Samsøe-Petersen et al., 2003).

A direct photolysis rate of 0.07/day was measured by using a water sample from Greifensee, Switzerland, tested under laboratory conditions. The rate corresponded to a photolysis half-life in water of 10 days; the elimination rate sum of different transport and transformation processes in this lake is 0.03/day, corresponding to a half-life of 21 days (HSDB, 2008).

The triclosan dissipation downstream was estimated by using standard first-order kinetics. A first-order rate constant, k, of 0.054 per h was used. Morrall et al. estimated the constant based on a river die-away study and corrected for dilution (Morrall et al., 2004). This study is, however, still unpublished and has not been available for the present evaluation. The physicochemical properties were collected by Reiss et al. and summarized in Table 1.5 (Reiss et al., 2002).

Table 1.5. Physicochemical Properties of Triclosan

Property	Value
Dissociation constant (pK_a)	8.14 at 20 °C
Vapor pressure	7×10^{-4} Pa at 25 °C
Partition coefficient (log K_{ow})	4.8
Aerobic biotransformation in soil	17.4- to 5.2-day half-life
Aqueous photolysis	41-min half-life at pH 7 and 25 °C
Adsorption to suspended solids (K_{oc})	47,454 mL/g

The following aspects were not considered significant for the estimation of the exposure concentrations, or data were not available (Reiss et al., 2002):

- Aquatic biotransformation or anaerobic degradation—no available studies
- Sorption to biota—no available data
- Biotransformation in benthic sediments—considered negligible
- Aquatic photolysis—considered negligible in the water bodies (inconsistent with Table 1.4, which gives a 41-min half-life for aqueous photolysis)

A study designed to determine the die-away rate of triclosan released into a river as part of the sewage treatment plant effluent matrix determined a first-order loss rate from measured data of 0.06 h^{-1}. Mathematical modeling indicated that sorption and settling accounted for approximately 19% of total triclosan loss over 8 km. When sorption and settling were removed, the remaining amount of triclosan had an estimated first-order loss rate of 0.25 h^{-1}, which was attributed to a combination of biotransformation and photolysis (Morrall et al., 2004).

Soil batch studies showed that triclosan could be biodegraded with half-lives of approximately 18 days under aerobic conditions, whereas no degradation was observed under anaerobic conditions (Ying et al., 2007).

According to HSDB (2008), a study showed a photolysis half-life in water of 10 days. The reported surface water concentrations of triclosan are summarized in Table 1.6.

Table 1.6. Reported Surface Water Concentrations of Triclosan

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	Various	0.0039	0.5	0.30	Barnes et al., 2002
Surface water	Huron River	0.088	4.3		Lee et al., 2004
WWTP effluent	U.S.	0.24	2.7		Samsøe-Petersen et al., 2003
WWTP effluent	Worldwide	2.7			Samsøe-Petersen et al., 2003

Ibuprofen

Ibuprofen is a nonsteroidal anti-inflammatory drug. It is used for relief of symptoms of arthritis, primary dysmenorrhoea, and fever and as an analgesic, especially where there is an inflammatory component.

Ibuprofen is generally resistant to hydrolysis. Therefore, hydrolysis is not expected to be an important removal process of ibuprofen from water systems (HSDB, 2008). Ibuprofen is not expected to directly photolyze because of the lack of adsorption in the environmental UV spectrum (>290 nm) (HSDB, 2008).

The AOECD Guideline 301B "Ready Biodegradability" Modified Sturm test (CO_2 evolution) showed a CO_2 evolution between 10 and 60%. Hence, the compound is not considered readily degradable (ESIS, 2010). It is, however, degradable to some extent. A half-life of 20 days was determined from a study using water samples from Lake Greifensee, Switzerland, that were incubated at room temperature for 37 days with 200 ng of racemic ibuprofen/L (HSDB, 2008).

A field investigation showed that 4 of 54 studied PPCPs were found below a treated sewage infiltration site (45 years of operation). Three meters below the groundwater table (unsaturated zone, 1.5 to 2 m) ibuprofen was undetectable (Ternes et al., 2007).

The reported surface water concentrations of ibuprofen are summarized in Table 1.7.

Table 1.7. Reported Surface Water and Groundwater Concentrations of Ibuprofen

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	Huron River		0.0071	0.0025	Skadsen et al., 2004
Raw wastewater	Ann Arbor	6.6	23	11	Skadsen et al., 2004
Treated wastewater	Ann Arbor	0.011	0.051	0.030	Skadsen et al., 2004
Surface water	Various	0.12	0.71		Lee et al., 2004
Surface water	Boulder Creek			0.108	Barber et al., 2004
Groundwater	Various			Negligible	Ternes et al., 2007

4-Nonylphenol

Nonylphenol and the related nonylphenol ethoxylates are used in pesticide products as "inert" ingredients.

Biotransformation of *p*-nonylphenol will occur rapidly in aerobic soils but is inhibited under anaerobic soil conditions. Degradation of 4-nonylphenol has been investigated in the laboratory using sediment and groundwater from an aquifer in Bolivar, South Australia. 4-nonylphenol degraded quickly under aerobic conditions with a half-life of 7 days (Ying et al., 2003). Studies of degradation in groundwater have not been identified.

Nonylphenol is susceptible to indirect photolysis. Half-lives of 10 to 15 h in both tap water and creek water, under continuous clear skies, at noon, and under summer sunlight conditions, were found at the surface. At a depth of 20 to 25 cm, half-lives were 1.5 times longer (Ahel et al., 1994).

Nonylphenol and its ethoxylates are frequently found in water, though it is difficult to identify contamination resulting from just pesticide-related uses. In a sample of New Jersey drinking water, seven nonylphenol ethoxylates were found with a total concentration of 725 parts per trillion (ppt). In addition, over-225-ppt nonylphenol carboxylates and over-175-ppt octylphenol ethoxylates and 49-ppt carboxylates were found. In a U.S. nationwide sampling of rivers with industrial or sewer effluent, 30% contained nonylphenol, 33% contained nonylphenol monoethoxylate, 42% contained nonylphenol diethoxylate, and 24% contained ethoxylates with more ethylene oxide units. The highest concentrations measured were about 1 part per billion (ppb) for the first three compounds and 15 ppb for the fourth. In another study, the attenuation of alkylphenol polyethoxylate (APEO) metabolites in two parcels of water (oxic and anoxic) was studied at a SAT site located in Arizona. APEO metabolites were rapidly (<7 days) removed under both aerobic and anoxic conditions. Under aerobic conditions, octylphenol and nonylphenol concentrations decreased by ~80% (w/w) within 3 m of the ground surface. Under anoxic conditions however, alkylphenol concentrations increased by ~38% within 3 m. During infiltration, the concentrations of alkylphenol ethoxycarboxylates and carboxyalkylphenol ethoxycarboxylates decreased by more than 95% within 3 m. Alternate flooding and drying cycles appear to enhance overall APEO metabolite removal efficiencies (Montgomery-Brown et al., 2003).

Limited information on surface water concentrations of 4-nonylphenol is summarized in Table 1.8.

Table 1.8. Reported Surface Water Concentrations of 4-Nonylphenol

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	Boulder Creek	0.011	0.28		Barber et al., 2000
Surface water	Hungary	0.008	0.428		Nagy et al, 2005
Surface water	Germany		0.458		Bolz et al., 2001
Surface water	Germany	0.006	0.135		Kuch and Ballschmiter, 2001

Methyl parathion

Methyl parathion is an organophosphate insecticide used to control insect pests of agricultural crops, primarily on cotton. It kills insects by contact and by stomach and respiratory action. Methyl parathion is available in dust, emulsifiable concentrate, ULV liquid, and wettable powder formulations. Methyl parathion is a highly toxic insecticide in EPA toxicity class I.

In surface waters, methyl parathion degrades by biotransformation, hydrolysis, volatilization, and photolysis (ATSDR, 2008). Methyl parathion degrades rapidly in seawater and in lake and river waters, with 100% degradation occurring within 2 weeks to 1 month or more. Degradation is faster in the presence of sediments and is faster in freshwater than in saltwater. Complete breakdown occurs at a rate of 5 to 11% in 4 days in rivers and more slowly in marine waters. In water, methyl parathion is subject to photolysis, with a half-life of 8 days during the summer and 38 days in winter (ATSDR, 2008). Biotransformation is expected to be the predominant degradation process. Adsorption to sediment and suspended matter may significantly affect the degradation (ATSDR, 2008).

The degradation of methyl parathion by hydrolysis and biotransformation was studied in four types of water (ultrapure water, pH 6.1; river water, pH 7.3; filtered river water, pH 7.3; and seawater, pH 8.1) maintained at 6 and 22 °C in the dark. The half-lives of methyl parathion at 6 °C in the four water types were determined to be 237, 95, 173, and 233 days, respectively, and the half-lives at 22 °C were determined to be 46, 23, 18, and 30 days, respectively. The study shows that degradation rates increase with pH and temperature and are highest in river water (ATSDR, 2008).

Photolysis studies of methyl parathion have been reported. A study examining the photodegradation of methyl parathion in river water and in seawater at various temperatures showed the half-lives to be 11 and 34 days, respectively (ATSDR, 2008). During photolysis in natural water, 50% of the original methyl parathion concentration was degraded in 8 days in the summer and in 38 days in the winter. In a photolysis study of methyl parathion in freshwaters of Portugal, a half-life of 3 days in groundwater and a half-life of 4 days in river water were observed. The authors noted that the transformation products, which included methyl paraoxon, were stabler than the parent compounds studied (ATSDR, 2008).

Methyl parathion is of low persistence in the soil environment, with reported field half-lives of 1 to 30 days. A representative value is estimated to be 5 days. The rate of degradation increases with temperature and with exposure to sunlight. Because of its short residence time, soil binding affinity, and low solubility in water, it is not expected to be significantly mobile.

One of the most important factors affecting the mobility of methyl parathion in the environment is its strong adsorption to soils. One study showed that after a 49-day incubation, 54% of the initial applied methyl parathion remained in the soil (ATSDR, 2008). Factors affecting the adsorption of methyl parathion are the organic matter content of the soil and sediment and the cation-exchange capacity of the soil. Values for K_{oc} in five soil types were determined by the U.S. EPA and were found to average 496, equal to a log K_{oc} of 2.7 (ATSDR, 2008). Estimates of log K_{oc} calculated from the K_{ow}, solubility, and melting point data ranged from 2.93 to 3.47. McLean et al. estimated a lower K_{oc} of 39, equal to a log K_{oc} of 1.59 (McLean et al., 1988). More recently, a K_{oc} of 5100, equal to log K_{oc} 3.7, has been reported (HSDB, 2008). These K_{oc} values indicate that methyl parathion is moderately mobile to immobile in soil (ATSDR, 2008).

- Adsorption coefficient cm^3/g (K_{oc}): 476
- Hydrolysis half-life (average days): 45.0
- Aerobic metabolism soil (average days): 12
- Anaerobic metabolism soil (average days): 1

Several studies have been conducted to measure methyl parathion levels in streams, rivers, and lakes. A U.S. Geological Survey (USGS) study of Western streams detected methyl parathion in five river samples taken from four states during a 14-month period in 1970 and 1971. The amount of methyl parathion detected ranged from 0.04 to 0.23 µg/L. A later and more extensive USGS study analyzed water samples from major rivers of the United States four times yearly in the period of 1975 to 1985. Of the 2861 water samples, 0.1% had detectable levels of methyl parathion. In a study of Arkansas surface waters, samples of lake and river or stream water were collected and analyzed over a 3-year period. Of the 485 samples collected, methyl parathion was found in one river or stream sample at a maximum concentration of 3.5 µg/L (ATSDR, 2008).

Groundwater has also been surveyed for methyl parathion. In a study of well water in selected California communities, methyl parathion was not detected (detection limit of 5 ppb) in the 54 wells sampled, even though the insecticide had been used in the areas studied for over 15 years. An analysis of 358 wells in Wisconsin produced the same negative results. In a sampling of California well water for pesticide residues, no methyl parathion was detected in any of the well water samples (ATSDR, 2008).

The reported surface water concentrations of methyl parathion are summarized in Table 1.9.

Table 1.9. Reported Surface Water and Groundwater Concentrations of Methyl Parathion

Type	Location	Minimum (µg/L)	Maximum |(µg/L)	Mean (µg/L)	Source
Surface water	U.S.	0.04	0.23		Barnes et al., 2002
Groundwater	U.S.			Not detectable	Barnes et al., 2002

Phenol

Phenol is both a manufactured chemical and a natural substance. It is a colorless-to-white solid when pure. The commercial product is a liquid.

Small, single releases of phenol do not stay long in the air (usually half is removed in less than 1 day) and usually do not stay long in the soil (usually completely gone in 2 to 5 days), but can stay in water for longer than 9 days. Phenol has been found in materials released from landfills and hazardous waste sites, and it has been found in the groundwater near these sites. Phenol is usually found in the environment below 100 ppb, although much higher levels have been reported. One part per billion or less of phenol has been found in relatively unpolluted surface waters and groundwaters.

Although phenol does not absorb light at wavelengths of >290 nm, phenols react rapidly to sunlight in natural water via an indirect reaction with photochemically produced hydroxyl radicals and peroxyl radicals; reported half-lives for hydroxyl and peroxyl radical reactions are on the order of 100 and 19.2 h of sunlight respectively. The estimated half-life for the reaction of phenol with photochemically produced singlet oxygen in sunlit surface waters contaminated by humic substances is 83 days (ATSDR, 2008).

Available data indicate that phenol biodegrades in soil under both aerobic and anaerobic soil conditions. The half-life of phenol in soil is generally less than 5 days, but acidic soils and some surface soils may have half-lives of up to 23 days. Mineralization in an alkaline, parabrown soil under aerobic conditions was 45.5, 48, and 65% after 3, 7, and 70 days, respectively (ATSDR, 2008).

Limited information on surface water concentrations of phenol is summarized in Table 1.10.

Table 1.10. Reported Surface Water and Groundwater Concentrations of Phenol

Type	Location	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Source
Surface water	U.S.	0.08	0.4		Lee et al., 2004

1.3.3.3 *Summary of Fate and Transport of Six Microconstituents*

Estimates of removal half-life for each of the six selected microconstituents and typical removal were obtained from the various datum sources and also by applying the estimation software EPIwin v3.12 from the U.S. EPA. The software also contains a large database of literature values. If database records were found, these were compiled instead of the estimates being used. The results are show in Table 1.11. There is some variability, and some of the datum sources even give contradictory information.

It was difficult to obtain actual literature values for removal and degradation rates in groundwater. However, relative removal potential is estimated based on biotransformation, sorption, and general degradation potential. Half-life constants in groundwater for degradable compounds are estimated based on information from degradation in soil. As a conservative estimate, the half-life in groundwater is assumed to be 10 times the degradation in soil. The properties of selected microconstituents for recharge modeling are summarized in Appendix B.

Half-life estimates can be converted into a first-order degradation rate or vice versa by the following conversion:

Half-life: $t_{1/2} = \ln 2/k_{deg} \Rightarrow 0.6931/k_{deg}$

Degradation rate: $k_{deg\ g} = \ln 2/t_{1/2} \Rightarrow 0.6931/t_{1/2}$

Where:

$t_{1/2}$ = half-life [Time]

k_{deg} = rate constant [Time^{-1}]

From the six researched microconstituents, three were chosen for modeling alongside a conservative tracer (CT). The selected compounds were sulfamethoxazole, phenol, and triclosan based upon their photodegration, sorption, and biotransformation characteristics, as well as on their detection as a part of this project.

Table 1.11. Estimated Physicochemical Properties, Half-Lives, and Degradation Constants

Compound	Log K_{ow} Value[a]	Log K_{oc} Value[a]	WWT Removal (%)[a,b]	Ready Bioransformation	Half-life[a]			
					Photolysis	Volatilization (Surface Water)	Total (Surface Water)	Total (Groundwater)
Sulfamethoxazole	0.89	3.2	1.88	No,[a] Yes, aerobic activated sludge (Drillia et al., 2005), not biodegradable (Kjølholt et al., 2003)	2.7–6.6 h (Lam and Mabury, 2005)	9.75E+08 h	900 h	Insignificant[c]
Triclosan	4.76, 4.8 (Samsøe-Petersen et al., 2003)	4.3	83.1	No,[a] 432 h in soil (Ying et al., 2007)	10 days[d], 41 min (Reiss et al., 2002), Negligible (Reiss et al., 2002)	4.68E+04 h	1.44E+03 h, 504 h[d], 2.8 h Bio + photo (Morrall et al., 2004), 13 h (Samsøe-Petersen et al., 2003)	Moderate,[c] 180 days[e]
Ibuprofen	3.97	2.6	28.72	No,[a] Not readily, degradable to some extent[g]	No[d]	5534 h	360 h, 480 h[d]	Insignificant,[c] readily (Drewes et al., 2003)
4-Nonylphenol	5.76	4.8	99.88	No,[a] Yes, 168 h (Ying et al., 2003)	Indirect photolysis 10–15 h (Ahel et al., 1994)	27.08 h	360 h	Moderate,[c] 70 days[e]
Methyl parathion	2.86, 2.93-3.47 (McLean et al., 1988)	2.7, 1.59 (Lam et al., 2004), 3.7[d]	28.22	No,[a] Yes, 2280– 5688 h at 6 °C, 432–1104 h at 22 °C[f]	Yes,[e] 192 h summer 912 h winter 72 –96 h River[f]	9500 h	900 h, 100% removal 336–720 h[f]	Moderate,[c] 50 days[e]
Phenol	1.46	2.4, 1.21–1.96[f]	92.15	Yes,[a] Yes < 120 h[f]	1992 h[f]	1707 h	360 h, 216 + h,[f] 168 + h[f]	Readily,[c] 25 days[e]

[a]Unless specified, all values were estimated by using EPIwin software v3.12 from the U.S. EPA.

[b]WWT removal: wastewater removal percentage including removal by volatilization, biotransformation, and sorption.

[c]Relative degradation estimate based on physicochemical properties and biodegradation.

[d]HSDB, 2008.

[e]Half-life in groundwater is estimated based on information from degradation in soil. As a conservative estimate, the half-life is assumed to be 10 times the degradation in soil.

[f]ATSDR, 2008.

[g]ESIS, 2010.

CHAPTER 2

MATERIALS AND METHODS

2.1 PILOT TREATMENT UNITS

Three membrane treatment processes were used in this study. Two pilot treatment units (MBR/RO and DNF/UF/RO) at Plantation, FL, have been defined previously (Hazen and Sawyer, 2007) and are reviewed here. Another membrane system (IMANS®) tested on the benchtop at Orange County, CA, is described here as well. Five rounds of sampling were conducted. The operational schedule and sampling dates were listed in Table 2.1.

Table 2.1. Pilot System Operational Schedule and Sampling Dates

Pilot System Operational Schedule	Alum Dose	RO Loading Rate	No. of Operational Days	Start of Operation	Finish of Operation	Sampling Date
Process Startup			30			
MBR/RO System	none	low	10	10/18/07	10/27/07	
	none	high	10	10/28/07	11/06/07	10/29/07
	low	low	10	11/07/07	11/16/07	
	low	high	10	11/17/07	11/26/07	11/26/07
	high	low	10	11/27/07	12/06/07	
	high	high	10	12/07/07	12/16/07	
Decommissioning of MBR/RO System			4	12/17/07	12/20/07	
Installation and Startup of DNF/RO System			5	12/21/07	12/25/07	
DNF/UF/RO System	low	low	8	12/26/07	01/02/08	
	low	high	8	01/03/08	01/10/08	
	medium	low	8	01/11/08	01/18/08	01/14/08
	medium	high	8	01/19/08	01/26/08	
	high	low	8	01/27/08	02/03/08	01/31/08
	high	high	8	02/04/08	02/11/08	
	NA	low	8	02/12/08	02/19/08	
	NA	high	4	02/20/08	02/23/08	02/21/08

During the startup of the pilot system, the following operational difficulties were encountered: damage to the electronic control system by power outages and the equipment failure of an aeration blower coupling, a dissolved oxygen (DO) probe, a return activated sludge recirculation pipe, and tank mixers. These difficulties were remedied, and sampling was conducted as scheduled in Table 2.1.

The first two rounds of sampling were performed on the MBR/RO system on October 29, 2007; and November 26, 2007. The following three rounds of sampling were performed on the DNF/UF/RO system on January 14, 2007; January 31, 2008; and February 21, 2008. The

sampling for the IMANS® system also happened on February 21, 2008. Details about these three systems and their operational conditions are described below.

2.1.1 MBR/RO

The MBR/RO treatment process consists of primary clarification, MBR, and RO systems. The MBR system, Zenon ZeeWeed 500, is manufactured by GE Water & Process Technologies. It consists of an activated sludge basin and a UF membrane system. The nominal pore size of the UF membrane is 0.04 μm. The SRT is 12 days. The RO system, Osmonics E4H-16K-DLX, is manufactured by GE Water & Process Technologies. The spiral-wound polyamide thin film composite membrane (4820 ULP) used in the RO system is manufactured by Koch Membrane Systems.

During the first sampling event on October 29, 2007, the flow rate of the MBR system was 10 gpm with a 2-gpm bleeding system. The mixed liquor suspended solids (MLSS) in the MBR system was 5330 mg/L. Flux in the MBR system was 22.25 gal per sq. ft per day (gfd). The SRT of the MBR system was 13 days, and hydraulic retention time (HRT) was 6.24 h. The internal recycle ratio from aerobic to anoxic phases in the MBR system was 4. The flow rates of RO influent, RO effluent, and RO brine were 8, 4, and 4 gpm respectively. The DO in the aeration tank was 1.74 mg/L. The water temperature was 29.2 °C. The operational conditions for the second sampling event on November 26, 2007, were the same as for the first sampling event, except that MBR flow was 12.4 gpm, MLSS was 2670 mg/L, MBR flux was 22.13 gfd, DO was 1.97 mg/L, and the temperature was 28.3 °C.

For both sampling events, air scour rates of the MBR system were between 18 and 20 cu. ft per min (cfm). The RO system was backwashed for 30 s every 12 min of operation. The membrane-cleaning time was 20 min.

2.1.2 DNF/UF/RO

The DNF/UF/RO treatment process consisted of primary clarification, activated sludge secondary treatment, secondary clarification, tertiary clarification, use of a DNF, and UF and RO. The denitrification system was the elimi-NITE Denitrification System, manufactured by ITT Leopold. The UF (Zenon ZeeWeed 500) and RO (Osmonics E4H-16K-DLX) systems are the same as those used in the MBR/RO process.

During the third sampling event on January 14, 2008, the flow rate of the DNF system was 16 gpm. The nitrate concentration in DNF effluent was 2.70 mg/L. The water temperature was 25.8 °C. The methanol concentration in the DNF system was 35 mg/L. The flow rates of UF influent, UF effluent, and UF brine were 7.2, 3.4, and 3.8 gpm, respectively. The flow rates of RO influent, RO effluent, and RO brine were 7.8, 3.9, and 3.9 gpm, respectively. During the fourth sampling event on January 31, 2008, the flow rate of the DNF system was 12 gpm. The concentration of methanol in the DNF system was 48 mg/L. The concentrations of nitrate in DNF influent and DNF effluent were 12.9 and 1.9 mg/L, respectively. The water temperature was 25.0 °C. The flow rates of UF influent, UF effluent, and UF brine were 10, 7.4, and 2.6 gpm, respectively. The flow rates of RO influent, RO effluent, and RO brine were 9.6, 3.8, and 3.8 gpm, respectively. During the fifth sampling event on February 21, 2008, the flow rate of the DNF system was 12 gpm. The concentration of nitrate in DNF influent was 13.7 mg/L. The flow rates of UF influent, UF effluent, and UF brine were 12,

10, and 2 gpm, respectively. The flow rates of RO influent, RO effluent, and RO brine were 9.5, 3.9, and 4.0 gpm, respectively. The RO system was backwashed for 30 s for every 30 min of operation.

2.1.3 IMANS®

Carollo contributed time, materials, and cash to cover all aspects of benchtop testing of membrane processes to supplement this project. This additional effort was intended to provide a comparison of treatment by membranes with and without the biological secondary treatment component. The IMANS® approach involves conventional primary settling of the wastewater, followed by UF or MF. The UF step separates the soluble and residual insoluble organic material. Solid material removed by the UF membranes may be returned to anaerobic digesters with the solids from primary clarification. The UF product stream containing soluble organic material is treated in a RO or NF process (Juby et al., 2000). For this project, the RO process was utilized. The UF module (UF100XL S2, molecular weight cutoff: 100,000 Da) was manufactured by Polymem, and the RO system (ESPA1-2012 [sub] +) was manufactured by Big Brand Water Filter, Inc.

The RO permeate is a high-quality water ready for final disinfection and use, while the RO brine contains rejected salts and concentrated soluble organic material. The organic-rich RO concentrate stream, which is free of suspended material, can be stabilized in a high-rate anaerobic digestion process. The concept potentially eliminates the need for conventional secondary activated sludge treatment.

2.2 SAMPLING LOCATIONS AND SAMPLE HANDLING

There were five sampling events spaced over 3 months of pilot system operation. Figure 2.1 outlines the sampling locations in the AWT trains. The first two sampling events were conducted on the MBR/RO train, and the third, fourth, and fifth sampling events were conducted on the UF/RO train. The final sampling event also included the benchtop testing of the membrane-only (IMANS®) process and the sampling of canal water to provide some perspective on background water quality.

To reduce the potential for contamination, sample collectors were requested to be nonsmokers; wear gloves during sample collection; and refrain from using lotions, perfumes, sunscreen, and lip balm prior to sample collection (Rosen, 2007). Hazen and Sawyer staff collected all grab samples from the pilot systems with assistance and coordination by Carollo staff. All samples were hand delivered or were shipped on ice to the appropriate laboratories for analysis via overnight delivery. Part of the samples for microconstituent analysis (LC-MS-MS) were preserved in acidified amber glass bottles. No preservatives were added to other samples. The sampling and analysis protocols for each test are further detailed in the following sections.

2.3 WATER QUALITY MEASUREMENTS

Measured water quality parameters included pH, total suspended solids (TSS), biochemical oxygen demand (BOD), total dissolved solids (TDS), and particle size distribution (PSD).

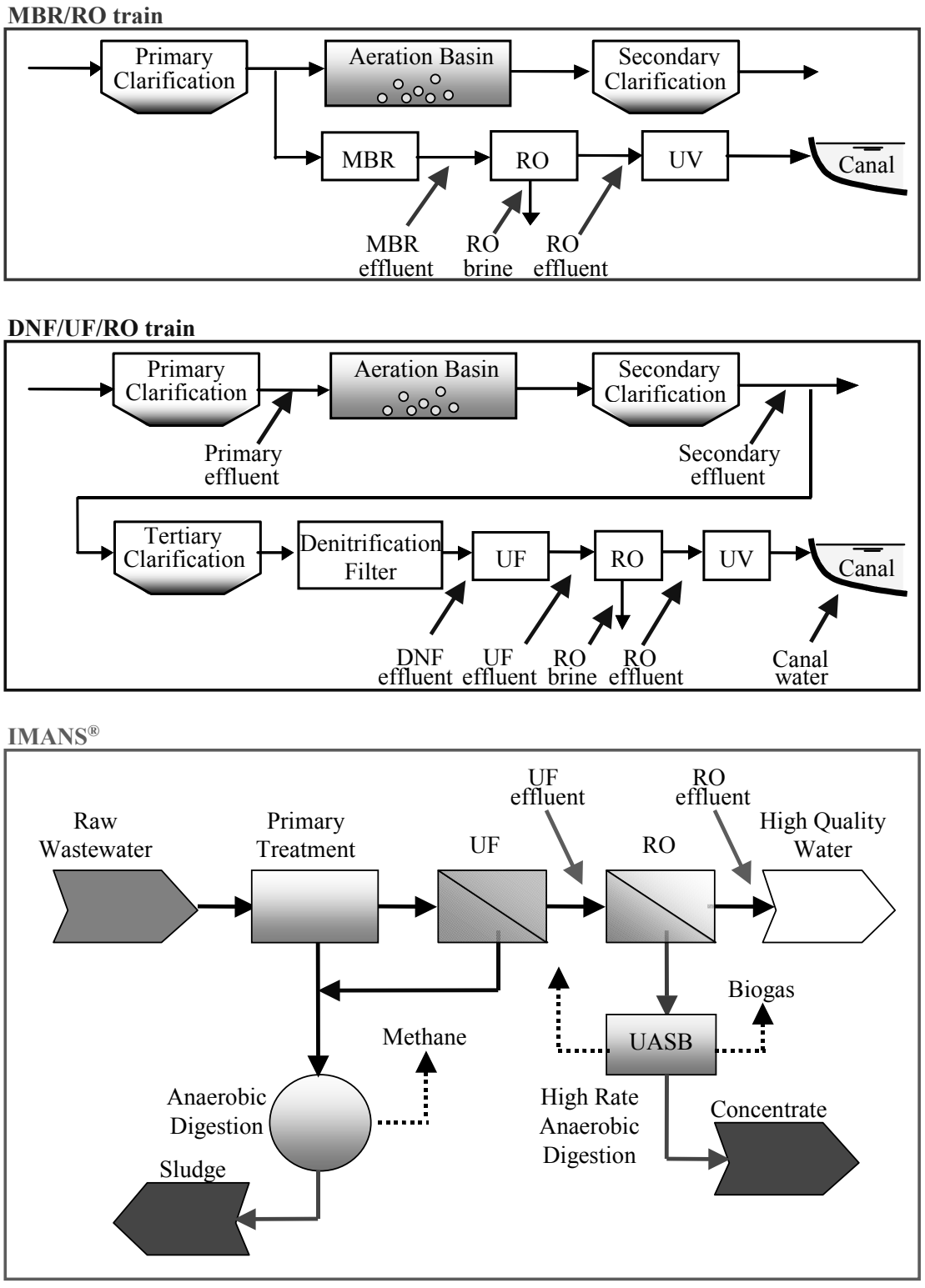

Figure 2.1. Process scheme and sampling locations.

Three 1-L samples were collected for each sampling location for TSS, BOD, and TDS analysis by the Plantation WWTP analytical laboratory staff. One 500-mL sample was collected at each location for PSD analysis by Carollo Engineers. These results were used to evaluate the efficiency of the advanced treatment process in improving water.

2.4 MICROCONSTITUENT TESTING

Microconstituent concentrations were measured in the RO effluent and RO brine for the MBR/RO train; primary effluent, secondary effluent (secondary clarifier effluent), DNF effluent, RO effluent, and RO brine for the UF/RO train; and UF effluent and RO effluent for the IMANS® system. Microconstituent analysis was performed by Montgomery Watson Harza (MWH) Laboratories, following test method USGS 4 MOD and LC-MS-MS. The isotope dilution method was used to prevent interference from the water matrix, as part of MWH Laboratories' analysis of microconstituent concentrations. The analysis methods and detection limits of examined microconstituents are shown in Table 2.2. Six-liter grab samples were collected from each sampling location in pre-preserved amber glass bottles provided by MWH Laboratories for sample analysis and quality control measurements. Microconstituent concentrations in the RO influent (MBR effluent in the MBR/RO train or UF effluent in the UF/RO train) were back calculated through mass balance of microconstituent concentrations in RO effluent and RO brine and corresponding flow rates.

Table 2.2. Analysis Methods and Detection Limits of Examined Microconstituents

Microconstituent	Analysis Method	Detection Limit (ng/L)
2,6-di-*tert*-Butylphenol	USGS 4 MOD	10
4-Methylphenol	USGS 4 MOD	25
4-Nonylphenol	USGS 4 MOD	25
Acetaminophen	LC-MS-MS	1
Alpha chlordane	USGS 4 MOD	10
Amoxicillin	LC-MS-MS	1
Bisphenol A	USGS 4 MOD	25
Caffeine	LC-MS-MS	1
Caffeine	USGS 4 MOD	25
Carbamazepine	LC-MS-MS	5
Carbaryl	USGS 4 MOD	50
Chlorpyrifos	USGS 4 MOD	25
N,N-Diethyl-*m*-toluamide	USGS 4 MOD	25
Diazinon	USGS 4 MOD	25
Dieldrin	USGS 4 MOD	25
Estradiol	LC-MS-MS	1
Estrone	LC-MS-MS	1
17α-Ethinylestradiol	LC-MS-MS	5
Fluoxetine	LC-MS-MS	1
Gemfibrozil	LC-MS-MS	1
Ibuprofen	LC-MS-MS	1
Iopromide	LC-MS-MS	5

Microconstituent	Analysis Method	Detection Limit (ng/L)
Methyl parathion	USGS 4 MOD	25
Phenol	USGS 4 MOD	100
Progesterone	LC-MS-MS	1
Sulfamethoxazole	LC-MS-MS	1
Tris(1,3-dichloro-2-propyl) phosphate	USGS 4 MOD	25
Testosterone	LC-MS-MS	1
Triclosan	LC-MS-MS	5
Triclosan	USGS 4 MOD	50
Trimethoprim	LC-MS-MS	1
Triphenylphosphate	USGS 4 MOD	25
Tris(2-butoxyethyl) phosphate	USGS 4 MOD	100
Tris(2-chloroethyl) phosphate	USGS 4 MOD	25

Table 2.3 lists several quality control parameters and corresponding test procedures and purposes.

Table 2.3. Quality Control Parameters for Microconstituents

Parameters	Procedures	Purposes
Laboratory control standard (LCS)	Deionized water spiked with the analytes of interest and processed the same as a sample. Accuracy (% recovery) and precision (relative percent difference between LCS1 and LCS2) were quantified	To test method performance in a matrix-free sample
Method blank (MBLK)	Deionized water processed the same as a sample	To measure background contamination potential in a matrix-free sample and to avoid false positives due to background or due to processing
Matrix spike (MS)	Field sample spiked with the analytes of interest	To measure accuracy for a specific matrix
Matrix spike duplicate (MSD)	Same field sample spiked with the analytes of interest	To measure accuracy for a specific matrix and measure precision for a specific matrix (relative percent difference between MS and MSD)

2.5 TOXICITY TESTING

To determine if effluent was toxic to aquatic organisms, standardized aquatic toxicity assays were performed. Biomonitoring was conducted with toxicity test procedures for chronic 7-day static-renewal effluent exposures. Test organisms included the fathead minnow, *Pimephales promelas*, and cladoceran, *Ceriodaphnia dubia.* Endpoints of toxicity tests

included a chronic survival and growth test of *P. promelas* and a chronic survival and reproduction test of *C. dubia*. Five rounds of toxicity testing were conducted. The first three rounds of toxicity testing were performed by David Barber at the University of Florida, and the last two rounds of toxicity testing were performed by Golder Associates and Hydrosphere Research. Seven-gallon samples were collected from each sampling location and shipped on ice overnight to the appropriate toxicity laboratory. The RO effluent samples were stabilized prior to toxicity testing by adding salts to mimic the conductivity and chemistry of the control water (Table 2.4), using the methods of WERF Report 01-HHE-4A (Schlenk et al., 2007).

Table 2.4. RO Effluent Stabilization Recipe

Ingredient	Final Concentration (mM)
$CaCl_2$	1.72
K_2SO_4	0.267
$MgSO_4$	0.809
$NaHCO_3$	3.45
Na_2HPO_4	0.0684
Na_2CO_3	0.31

For the first sampling event, exposures for the chronic 7-day test using *P. promelas* were conducted in glass vessels filled with 250 mL of effluent. Four replicates, with each replicate containing eight *P. promelas* minnows (24 h old), were used for every treatment (effluent dilution) and control. Larval *P. promelas* minnows were purchased from MBL Aquaculture, Sarasota, FL. Test results were based upon survival at the end of 7 days. Daily feeding consisted of approximately 0.1 mL of newly hatched *Artemia*. A minimum 80% survival of the control organisms was required. Exposures for the chronic 7-day test using *C. dubia* were conducted in 250-mL glass containers filled with 50 mL of effluent. Four replicates containing three *C. dubia* neonates (less than 24 h old) were used for each effluent dilution and control. The neonates were transferred from third-brood laboratory stock cultures. Daily renewal of the tests with effluent was conducted after the first reproduction occurred. Daily feeding of the tests included 0.1 mL each of laboratory-cultured yeast, cereal, and trout chow (YCT) per test chamber. A minimum 80% survival of the control organisms was required. Test results were based upon survival and reproduction. All tests were conducted at 25±2 °C with a 16:8-h light:dark photoperiod. All control and dilution water was laboratory-constituted moderately hard water (conductivity 408, µS; hardness, 102 mg/L). The range of DO for all test chambers was consistently between 5.4 and 8.0 mg/L throughout the test duration.

For the second and third sampling events, *P. promelas* toxicity assays were conducted as above. *C. dubia* assays were conducted with 10 replicates per treatment. Each replicate contained a single individual in 30 mL of test water. Dilution water for these tests was laboratory-constituted moderately hard water with a conductivity of 1190 to 1300 µS and a hardness of 312 mg/L as based on the AWT facilities' RO effluent stabilization recipe for dilution water and control water. Control and dilution water contained selenium as recommended by U.S. EPA guidelines.

Values for survival and reproduction were obtained by using a hypothesis test approach with one-way analysis of variance and Dunnett's procedure (EPA, 1994). Tests for normality and homogeneity of variance included the Shapiro–Wilks and Bartlett's test, respectively. The

response used in the analysis was either the number of animals surviving at each test concentration or, with respect to reproduction data, the number of young produced per adult female. Reproductive success was determined by taking the total number of young produced until the time of death of the adult or the end of the experiment, whichever came first. The mean number of live young produced per adult female for each effluent concentration provided a combined measure of the effluent's effect on both mortality and reproduction (EPA, 1994).

For the fourth and fifth sampling events, the 7-day chronic static renewal definitive bioassays with *P. promelas* and *C. dubia* were conducted according to U.S. EPA standard method EPA-821-R-02-013 (EPA, 2002). The water used for acclimation, culture, and dilution during the testing was moderately hard reconstituted (MHR) freshwater prepared according to U.S EPA methods (EPA, 2002). For the *C. dubia* and *P. promelas* tests, serial dilutions were prepared by using the samples and MHR water. These dilutions were 0 (controls), 6.25, 12.5, 50, 75, and 100% samples. The *C. dubia* tests were conducted with one organism per replicate and 10 replicates per concentration. The *P. promelas* tests were conducted with 10 organisms per replicate and four replicates per concentration. Samples were stored at less than 4 °C in a cold room until test initiation. The samples were warmed to 25 °C prior to test initiation. The warmed samples were checked for total residual chlorine using a Chlorimeter (HACH DR/890), method 8167 for total chlorine, which is equivalent to U.S. EPA method 330.5 for wastewater and Standard Methods 4500-Cl G for drinking water. Similar to the first three tests, the RO effluent samples were stabilized prior by adding salts to mimic the conductivity and chemistry of the control water, as described in WERF Report 01-HHE-4A (Schlenk et al., 2007). UF samples and primary effluent samples were not altered in any fashion. The *C. dubia* and *P. promelas* tests were monitored daily for survival, reproduction (*C. dubia* only) temperature, pH, DO, and conductivity. *C. dubia* and *P. promelas* were fed prior to test initiation and at every daily renewal. *P. promelas* was fed *Artemia nauplii* twice daily, and *C. dubia* was fed YCT and the green alga *Selenastrum capricornutum* daily. All tests were conducted at 25±1 °C. The range of DO for all test chambers was consistently between 5.0 and 8.9 mg/L throughout the test duration, and the pH range was 7.6 to 8.6. Standard *F* tests and *t* tests were conducted to determine if each sample's data were significantly different from the respective control data. For both the *F* tests and *t* tests, an α value of 0.05 was used. The reference toxicant test was conducted with potassium chloride to document test organism health. All reference toxicant tests showed that the test organisms were of normal sensitivity.

2.6 E-SCREEN BIOASSAY

To complement the toxicity testing and microconstituent analysis, E-Screen bioassays were conducted to demonstrate the extent to which the advanced treated effluent possessed endocrine disrupting potential as measured by an in vitro assay. The E-Screen used MCF-7 cells, a breast cancer cell line that proliferates in responses to estrogenic activity. This bioassay is an in vitro assay and can demonstrate whether compounds in the various advanced treated effluents bind to a hormone receptor and elicit a response. All E-Screen bioassays were conducted at the Wisconsin State Laboratory of Hygiene (WSLH) by incubating MCF-7 cells in media containing extracts of the collected samples. Two 1-L samples of each advanced treated effluent were collected in amber glass bottles provided by the WSLH. MCF-7 cells were incubated in media with no sample extract as a negative control and in media dosed with estradiol as a positive control. Tests were run concurrently with samples of known estrogen concentrations. Following incubation, cell proliferation was measured by the sulforhodamine protein assay, which determines the total number of cells

through the total protein content. Each set of E-Screen bioassays was conducted alongside an estradiol standard curve, which consists of multiple concentrations of estradiol in the cell media. The cell proliferation results from the extracted treatment process samples were compared to a standard curve to determine the estradiol equivalents of the sample water. This assay does not indicate specifically what compounds are causing the estrogenic activity. The limit of detection is 0.027 ng/L, and samples below this limit are reported as not detected (ND). The limit of quantification is 0.052 ng/L, and activities below this limit but higher than 0.027 are reported as < the limit of quantification. Standard deviations reported are of the triplicate wells. Each sample is run with a positive control to ensure the sample itself is not interfering with the growth of the cells. Interference is set at <80% of the positive control growth.

2.7 YES BIOASSAY

Two in vitro assays are commonly found in the literature, the E-Screen and the YES. For this project, both assays were performed to potentially provide some correlation of the information gathered as part of this project with YES information gathered as part of other projects (particularly WRF-02-009, Linden and Salveson, 2010). In the YES assay, yeast cells were transformed to certain human estrogen receptors, and, similar to the E-Screen, could indicate potential estrogenic activity of the sample water. In this test, yeast cells that have been transfected with the human estrogen receptor and a β-galactosidase reporter plasmid were exposed to an extract of the water sample. Compounds in the water extract that bind to the estrogen receptor will cause the cell to produce β-galactosidase, which can be measured spectrophotometrically. The YES assays were conducted at the WSLH. Two 1-L samples of each process sample were collected in amber glass bottles provided by the WSLH. At the WSLH, transformed yeast cells were grown to a specific density and exposed to diluted sample extracts. Sample extracts were run concurrently with samples of known estrogen concentrations. The β-galactosidase activity of the unknown sample was compared with the activity at the known estrogen concentrations, and the results of the unknowns were reported as estradiol equivalents in nanograms per liter. This assay does not indicate specifically what compounds are causing the estrogenic activity. The limit of detection depends on the concentration of extract used and for these samples was generally 0.20 ng/L. Samples below this limit were reported as ND. Standard deviations reported are of the triplicate wells. The optical density was measured on each to ensure that the density of the yeast cells was not by the toxicity of the extract. The results from the YES bioassay allowed for comparison with results from the E-Screen and the Vtg and steroid assays.

2.8 FATHEAD MINNOW Vtg AND STEROID ASSAYS

Fathead minnow vitellogenin (Vtg) assays and steroid immunoassays were conducted to demonstrate whether the fish are potentially impacted by exogenous estrogenic substances from the various treated effluents. Vtg induction in male fathead minnows is an in vivo test that can complement the microconstituent analysis and in vitro E-Screen and YES assays. The measurement of steroid hormones in the blood of the fish, including testosterone and estradiol, also provides an in vivo measure of potential impact. The Vtg assays and steroid immunoassays were conducted by Nancy Denslow's laboratory at the University of Florida. Effluents were sent to the University of Florida for fathead minnow exposures. One 20-gal sample of each effluent was collected and hand delivered on the day of collection. Only male fathead minnows were used in the exposures. Prior to the exposures, the fathead minnows

were acclimated to the water and tanks and were fed a formulated trout diet at 1% of their body weight. The male fathead minnows were subjected to 7-day semistatic exposures in four separate tanks per exposure group. Each treatment consisted of three 12-L glass aquariums containing three adult male fathead minnows and 4 L of exposure solution. Exposures were conducted for 7 days with a 90% water change daily. The fathead minnows were also exposed to a negative control water and a positive control (5-ng/L ethinylestradiol) for each exposure set. On the 8th day of exposure, male fathead minnows were anesthetized with MS-222 (100 mg/L buffered with sodium bicarbonate). Then blood was collected from the caudal sinus into heparinized microcentrifuge tubes. Plasma was obtained by centrifuging blood samples at 1000 × *g* for 5 min. The plasma was collected and split between two tubes, one for Vtg analysis and one for steroid analysis. The plasma was stored at −80 ºC until Vtg and steroid assays were performed.

The fathead minnow plasma Vtg was measured by using the homologous enzyme-linked immunosorbent assay (ELISA) developed specifically by Nancy Denslow's lab and the University of Florida–Hybridoma Core (Denslow et al., 1999; Hemming et al., 2001). Specifically, concentrations of plasma Vtg were determined by direct enzyme-linked immunosorbent assay (ELISA) using the monoclonal antibody (MAb) 2D3 that is specific for carp but cross-reacts well with fathead minnow Vtg. The plasma samples were diluted 1:100 and 1:10,000 with 10 mM phosphate, 150 mM NaCl, 0.02% azide, and 10-KIU/mL aprotinin, pH 7.6 (PBSZ-AP). Fathead minnow Vtg standards (0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 µg/mL) containing 1:100 and 1:10,000 male plasma (in PBSZ-AP) were added to account for matrix effect. Samples and standards were loaded onto a 96-well ELISA plate in triplicate and stored overnight at 4 ºC in a humidified container. The following day, the plates were washed four times with PBSZ and then blocked with 1% bovine serum albumin (BSA) in 10 mM Tris, 150 mM NaCl, 0.05% Tween, 0.02% azide, and10-KIU/mL aprotinin, pH 7.6 (1% BSA/TBSTZ-AP) for 2 h at room temperature. The plates were rewashed with PBSZ (four times), and the MAb was loaded into wells on each plate. The lowest dilution (1:100) was probed with 1 µg of the MAb/mL and the higher dilution of 1:10 K with 0.1-µg/mL MAb. After the addition of the MAb, the plates were stored at 4 ºC overnight in the humidified container. The following day the plates were washed, and the biotinylated secondary antibody (goat anti-mouse IgG-biotin) was added to each well at a 1:1000 dilution in 1% BSA/TBSTZ-AP and incubated at room temperature for 2 h. The plates were washed, and strepavidin-alkaline phosphatase was added at a 1:1000 dilution in 1% BSA/TBSTZ-AP and was incubated for 2 h at room temperature. After a final wash of the plates, the color was developed by adding 1-mg/mL *p*-nitrophenyl phosphate in carbonate buffer (0.03 M carbonate, 2 mM $MgCl_2$, pH 9.6) and the color was measured by using an ELISA plate reader (SpectraMax Plus384; Applied Biosystems) at 405 nm. Concentrations of the unknowns were determined from the standard curves. The detection limit for fathead minnow Vtg is 0.5 mg/L. All assays were performed in triplicate and reported as the mean of the three measurements. The coefficient of variation was < 10% for all samples analyzed. Inter- and intra-assay variability was routinely measured by analyzing controls on several plates, and different runs were found to be <10% and <5%, respectively.

Steroids were quantified by radioimmunoassay as previously described (Jensen et al., 2001). For testosterone analysis, samples were thawed on ice and 10 µL of plasma was placed in 12- by 75-mm borosilicate glass test tubes. Ninety microliters of buffer (0.1 M phosphate, pH 7.6, containing 0.1% gelatin, phos-gel buffer) were added to allow efficient phase separation during extraction, and samples were vortexed briefly. Samples were extracted by adding 1 mL of *n*-butyl chloride to each tube and vortexing for 1 min. Samples were then centrifuged gently to separate organic and aqueous phases, and the upper organic phase was transferred to

a new 12- by 75-mm borosilicate glass tube. Samples were extracted a second time, and the organic phases were combined. Samples were evaporated to dryness under a stream of nitrogen and reconstituted in 100 µL of phos-gel buffer containing 0.5% radioimmunoassay-grade bovine serum albumin. Samples were capped and placed on an orbital shaker overnight at 4 °C to ensure optimal reconstitution. Recovery of testosterone by using this method is typically 90% or greater based on recovery of ^{3}H-testosterone. Testosterone analysis was performed by ELISA using a kit for testosterone manufactured by IBL America (Minneapolis, MN). Standards were prepared in steroid-free serum provided with the kit and ranged from 0.1 to 6 ng/mL. R^2 values for the standard curve were greater than 0.99. Values of testosterone in the samples were determined from the standard curve and were multiplied by 10 to account for dilution of the sample. Up to seven male fish in each treatment were analyzed. The number analyzed varied because of mortality, accidental inclusion of females, and low volumes of plasma for some fish.

2.9 RECHARGE MODELING

As detailed previously, the fate and transport of select microconstituents from a point of hypothetical discharge through surface water canals and into the aquifer were modeled by DHI Water & Environment, Inc. (DHI). Both a hydrodynamic model and a water quality model were developed. The model domain, river network, and wellfield locations are shown in Figure 2.2.

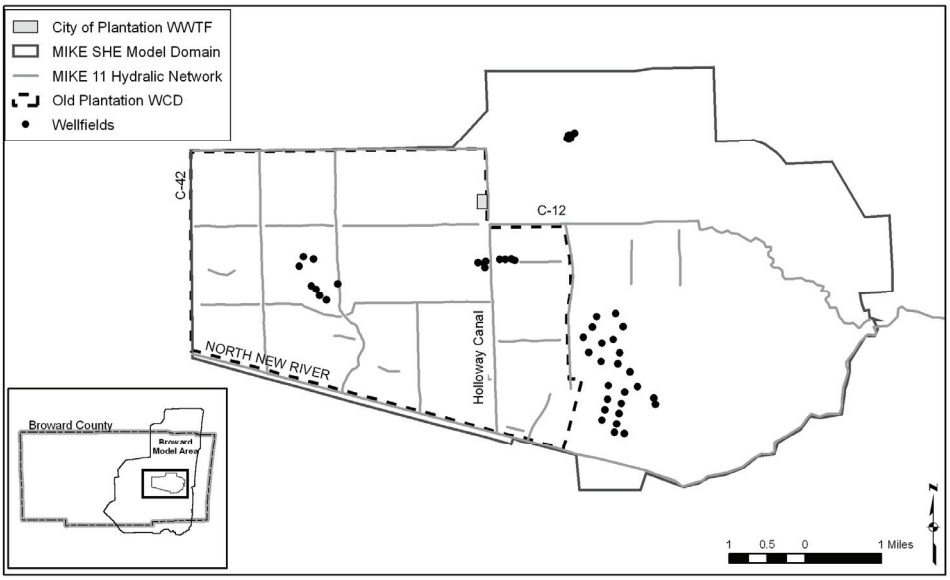

Figure 2.2. Plantation model domain, river network, and wellfield locations.

The hydrodynamic model for the City of Plantation AWT pilot study was extracted from the larger Broward County Baseline Model (BLM). The hydrodynamic model is an integrated surface-groundwater model that was consolidated in 2006 (Broward County, 2006) from smaller integrated models by Camp Dresser & McKee Inc. and DHI in 2002 and 2005 (Camp Dresser & McKee Inc., 2002; 2005a; 2005b), and revised mainly to study alternative sources of water supply for the county (DHI, 2008a). The advection-dispersion (AD) solute transport

routines in the MIKE SHE and MIKE 11 program are added to the hydrodynamic model. The MIKE SHE and MIKE 11 AD modules are capable of simulating bidirectional mass transfers between the groundwater and surface water components. The stability of this preliminary AD model was tested by using a CT, which does not undergo degradation or adsorption. This hydrodynamic model serves as a base to evaluate the potential risk of wellfield groundwater contamination from the hypothetical point source discharge of highly treated reclaimed water. The details of the hydrodynamic model are included as Appendix C.

For the water quality model, the ECO Lab template was used to simulate the various pathways of microconstituent transport through the canal water system. Three of the six microconstituents (sulfamethoxazole, phenol, and triclosan) from the literature review were selected for the water quality model, based on their properties of photodegration, sorption, and biotransformation, as well as on their detections as part of this project. The input parameters for the model were selected from the literature review and additional sources. The results obtained for the different microconstituents and for the CT were compared to evaluate the effect of different degradation/removal processes in the surface water and groundwater systems. The water quality model was carefully examined to ensure that results were reasonable. However, empirical data were not available for calibrating the water quality model.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 WATER QUALITY MEASUREMENTS

Water quality analyses showed that TSS readings in RO effluents were expectedly all below 1 mg/L and that BOD_5 readings in RO effluents were all below 2 mg/L (Figures 3.1, 3.2, and 3.3), which were all below the values found in the canal water. TDS concentrations in RO effluent were below 19 mg/L, which is one order of magnitude lower than what was found in MBR and UF effluent (namely, feed to the RO system). As shown in Figure 3.4, the average salt rejection rate (the percentage of TDS removed by the RO membrane) was 98.3%.

The pH values of RO effluent were always below 6.0, while the pH values of all other samples were near 7.0 (Figure 3.5).

Turbidities of RO effluent, MBR effluent, and UF effluent were below 0.9 NTU, as shown in Figure 3.6. The turbidity of secondary effluent was a little higher (2.61 NTU), but the turbidity of all treated samples was lower than that of canal water (7.67 NTU).

The results of PSDs are shown in Figures 3.7, 3.8, and 3.9. Most small particles in MBR effluent and DNF effluent were removed by RO, and the resulting PSDs of RO effluent were not statistically different from those of distilled water. Some RO effluent unexpectedly had more particles than UF effluent, a result that could be caused by regrowth downstream of the RO membrane or scale that could be flaking off the permeate piping or unclean sample ports. The number of particles in all effluent samples in all size ranges was significantly lower than that of canal water.

All water quality measurements suggest that the discharge of reclaimed water likely would not degrade the general water quality of surface canals.

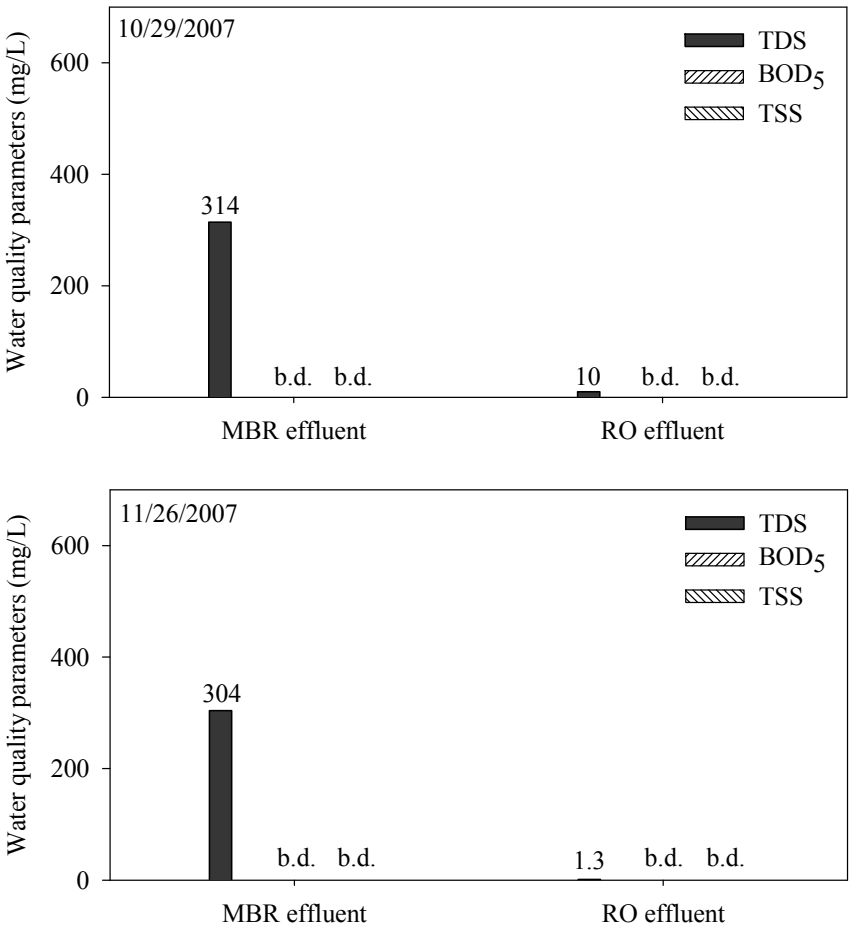

Figure 3.1. General water quality of MBR and RO effluent. b.d.: below detection limits (BOD_5 < 2 mg/L, TSS < 1 mg/L).

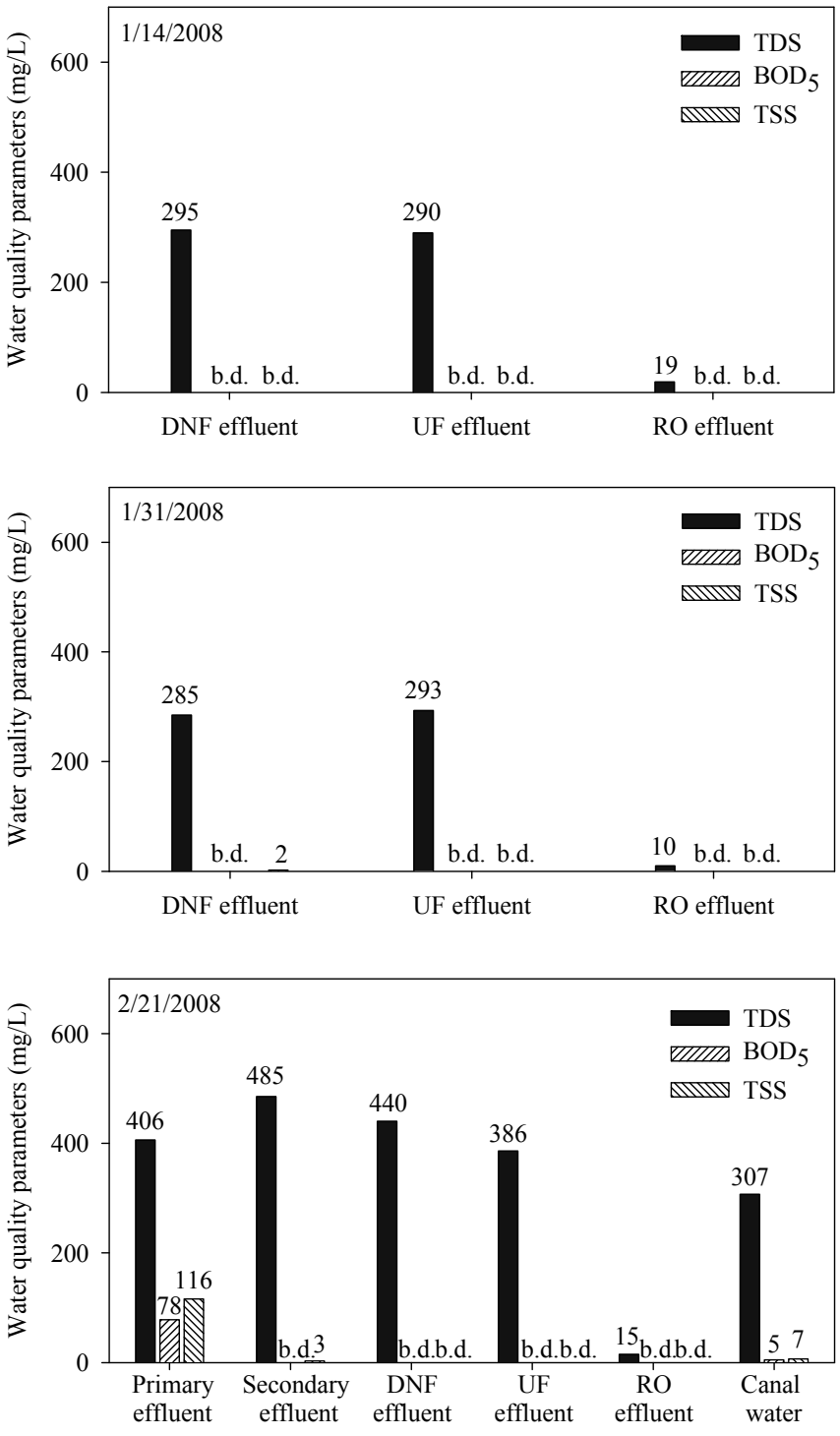

Figure 3.2. General water quality of DNF, UF, and RO effluent. b.d.: below detection limits (BOD_5 < 2 mg/L, TSS < 1 mg/L).

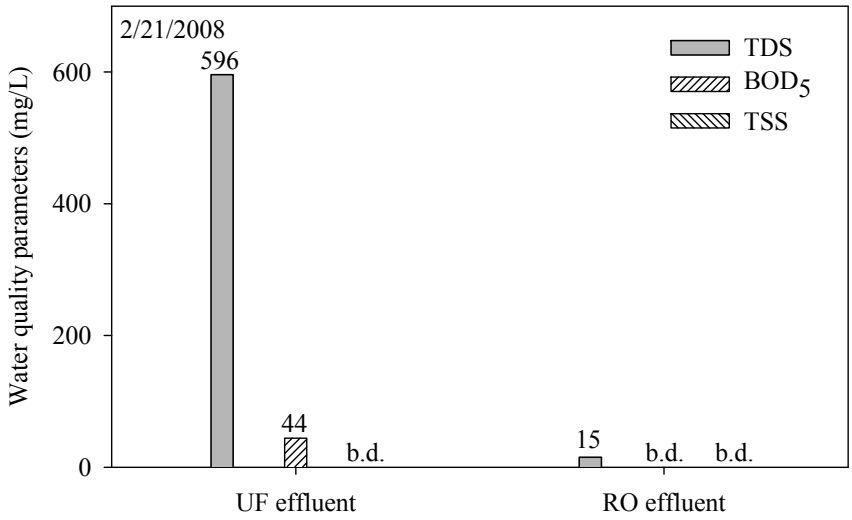

Figure 3.3. General water quality across IMANS® system.
b.d.: below detection limits (BOD_5 < 3 mg/L, TSS < 10 mg/L).

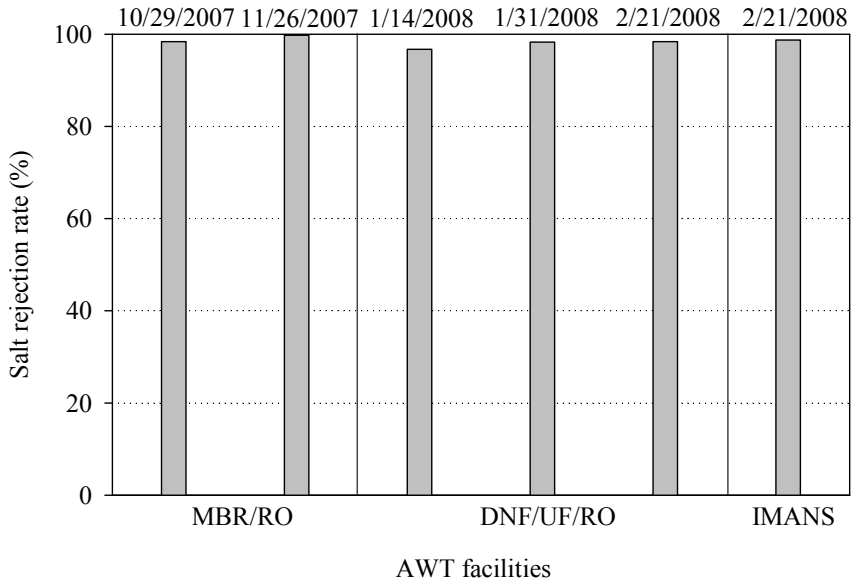

Figure 3.4. Salt rejection rates of MBR/RO system, DNF/UF/RO system, and IMANS® system.

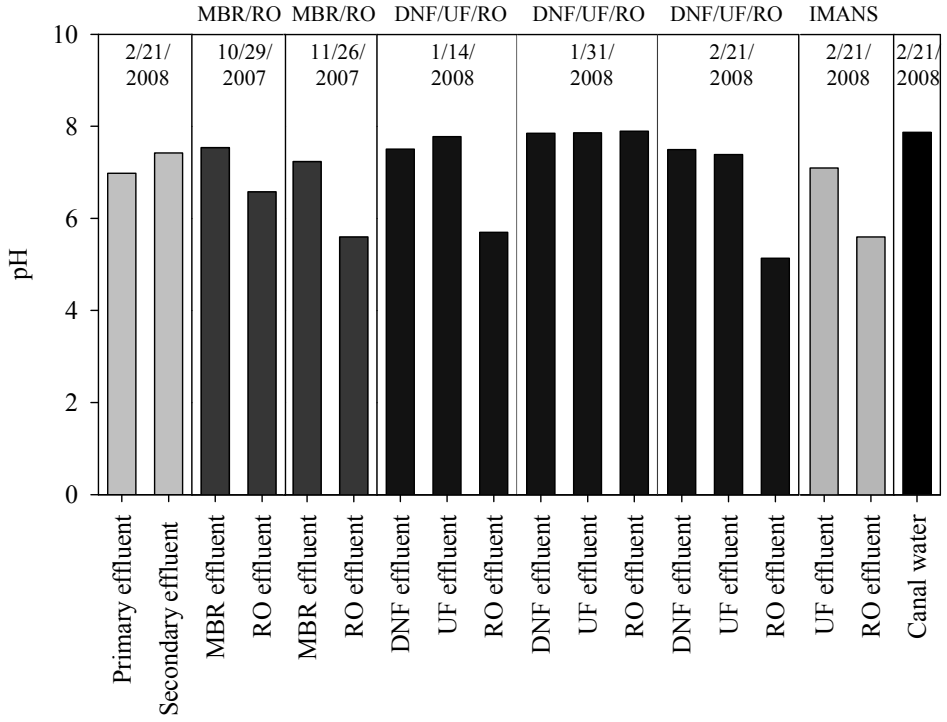

Figure 3.5. pH across MBR/RO system, DNF/UF/RO system, and IMANS® system and in canal water.

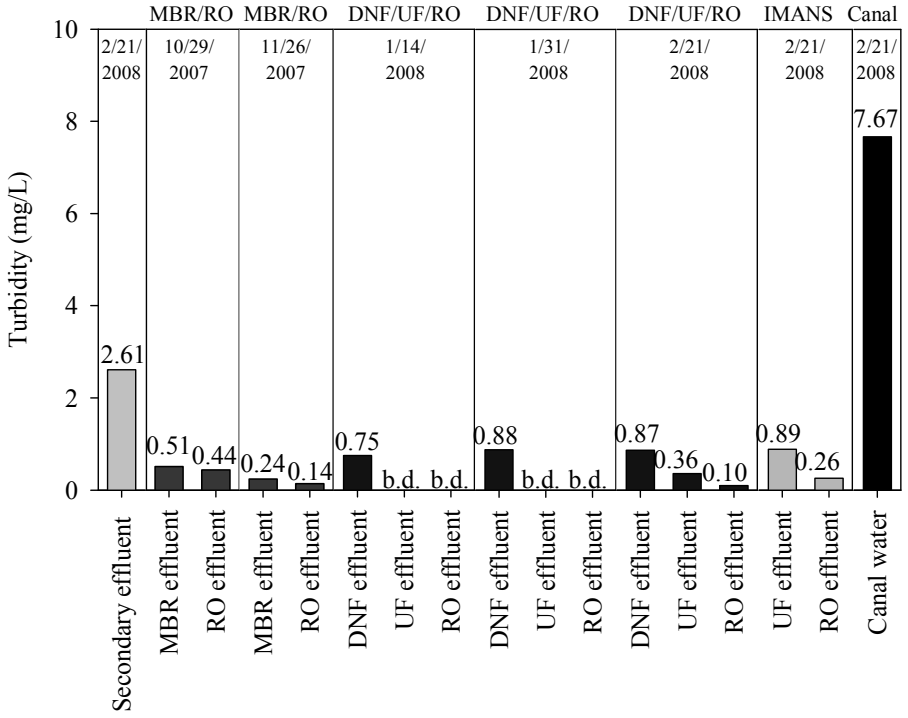

Figure 3.6. Turbidity across MBR/RO system, DNF/UF/RO system, and IMANS® system and in canal water.

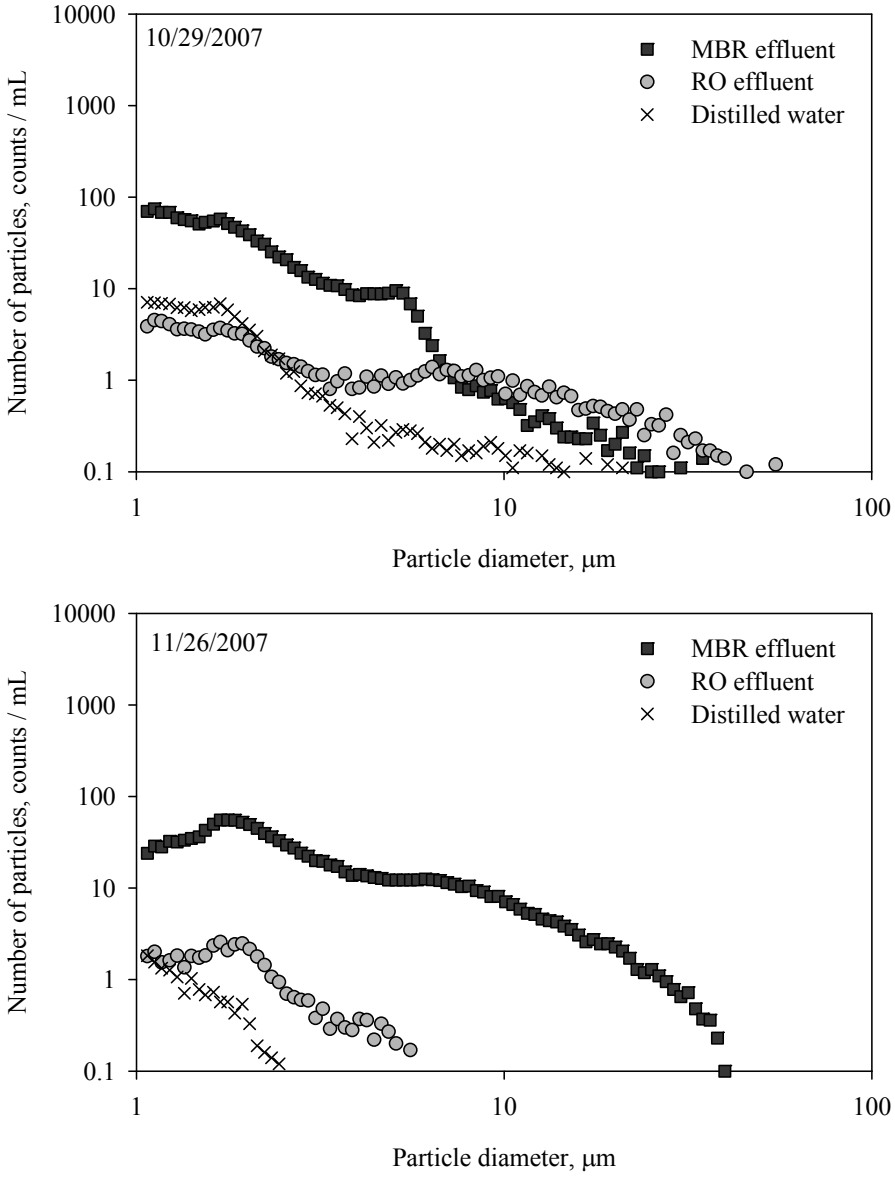

Figure 3.7. PSD in MBR and RO effluent.

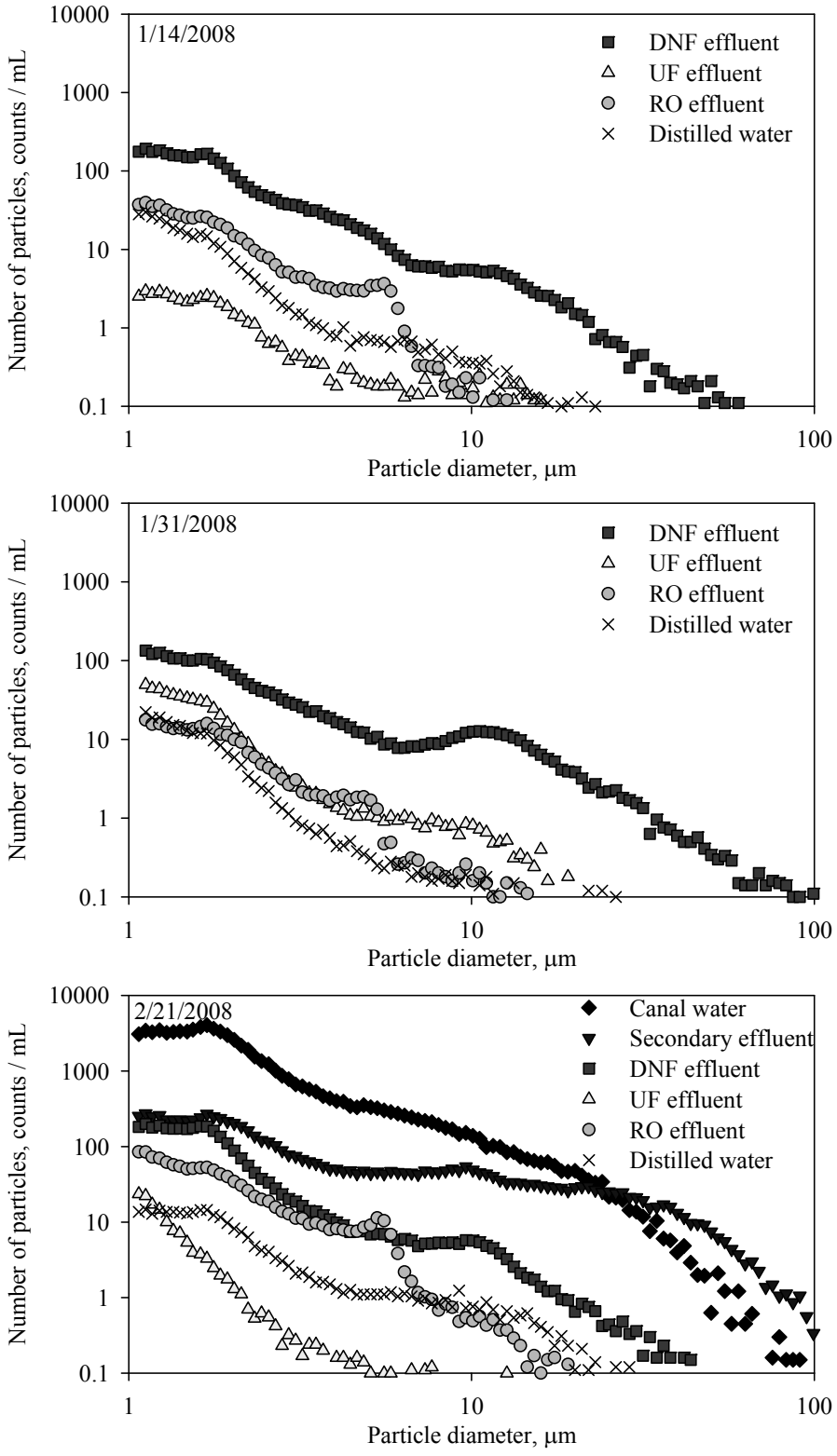

Figure 3.8. PSD in DNF, UF, and RO effluent.

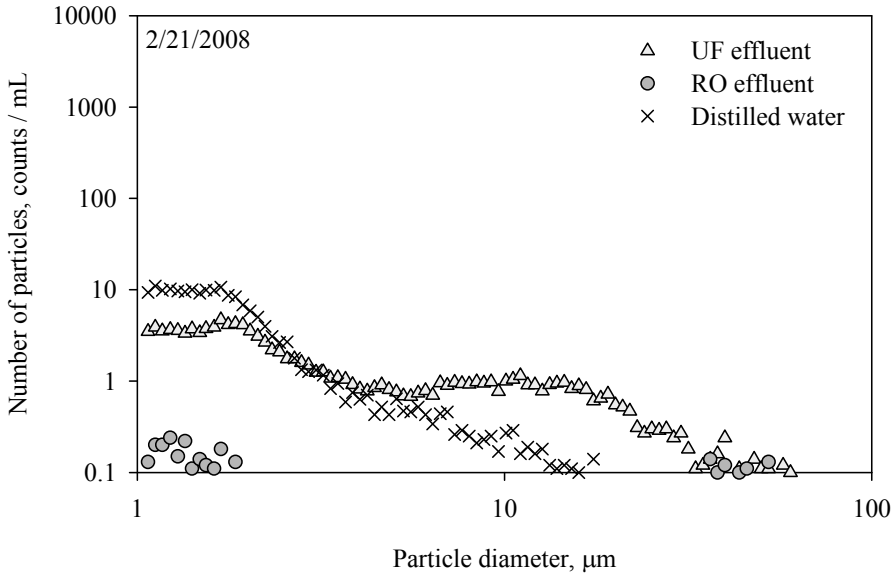

Figure 3.9. PSD across IMANS® system.

3.2 MICROCONSTITUENT TESTING

As shown in Table 3.1, 24 out of 31 microconstituents were effectively removed by more than 93.6% in the activated sludge process of the DNF/UF/RO configuration during the test on February 21, 2008, while removals of carbamazepine (67.6%), estrone (76.0%), and sulfamethoxazole (57.5%) were relatively less effective.

As shown in Table 3.1, 16 and 20 out of 31 microconstituents were detected in the RO brine in the MBR/RO system and the DNF/UF/RO system, respectively. Removals of caffeine (24.2 to 95.0%), estrone (35.9%), gemfibrozil (53.6 to 76.3%), and triclosan (28.1 to 54.8%) were observed across the UF membrane. Almost all microconstituents in RO effluent were below detection limits. The rejection rates for the RO system were greater than 98%. These results were consistent with previous results that proved the effectiveness of removing microconstituents by RO (Xu et al., 2005). During the five rounds of sample analysis, bisphenol A (57 ng/L) was detected once and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) (81 ng/L, 100 ng/L) was detected twice in the RO effluent. However, these detections were likely caused by sample contaminations. Bisphenol A is ubiquitous and even can be detected in laboratory distilled water, suggesting that the detected bisphenol A was likely from sampling or transportation. Tris(1,3-dichloro-2-propyl) phosphate is a chlorinated flame retardant that usually co-occurs with tris(2-carboxyethyl) phosphine. Tris(2-carboxyethyl) phosphine was below detection limits, while tris(1,3-dichloro-2-propyl) phosphate was detected. Tris(1,3-dichloro-2-propyl) phosphate has a chemical structure similar to that of tris(2-carboxyethyl) phosphine but is much larger and is typically well rejected (Bellona and Drewes, 2007). Similar to bisphenol A, flame retardants are ubiquitous and almost any material made out of plastic contains them.

It is notable that the RO effluent from the IMANS® process contained some microconstituents not found in the other RO effluent, including caffeine, ibuprofen, and sulfamethoxazole (Table 3.1). This property is presumably attributable to the removals of these compounds in the upstream biological treatment processes associated with the MBR/RO and DNF/UF/RO configuration. Removals of caffeine (99.9%), ibuprofen (99.9%), and sulfamethoxazole (57.5%) were observed in the activated sludge process of the DNF/UF/RO system. Though there was more breakthrough observed from the IMANS® RO membranes, the membranes still achieved greater than 99% removal of caffeine, ibuprofen, and sulfamethoxazole.

Table 3.1. Concentrations of Microconstituents

Microconstituents (ng/L)	Findings for:																						
	MBR/RO system						DNF/UF/RO system															IMANS®	
	10/29/2007			11/26/07			1/14/2008				1/31/2008				2/21/2008							2/21/2008	
	RO influent[a]	RO effluent[b]	RO brine[c]	RO influent[a]	RO effluent[b]	RO brine[c]	DNF effluent	RO influent[a]	RO effluent[b]	RO brine[c]	DNF effluent	RO influent[a]	RO effluent[b]	RO brine[c]	Primary effluent	Secondary effluent	DNF effluent	RO influent[a]	RO effluent[b]	RO brine[c]	Surface water	RO influent	RO effluent
2,6-di-*tert*-Butylphenol	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<1000	<10	<10	<10	<10	<10	<10	<10	<10
4-Methylphenol	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	**11,300**	<25	<25	<25	<25	<25	<25	**30**	NA[d]
4-Nonylphenol	<25	<25	<25	<25	<25	<25	<25	**22.5**	<25	**45**	<25	**25.5**	<25	**51**	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Acetaminophen	<1	<1	<1	<1	<1	<1	**2.9**	**2.2**	<1	**4.3**	<1	**2.5**	<1	**5**	**5400**	<1	<1	<1	<1	<1	<1	**6500**	NA[d]
Alpha Chlordane	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<1000	<10	<10	<10	<10	<10	<10	<10	<10
Bisphenol A	**33.5**	<25	**67**	**40.5**	<25	**81**	<25	**26**	<25	**52**	<25	<25	<25	**35**	**5800**	**372**	**156**	**105.1**	NA[d]	**152**	**56**	<25	<25
Caffeine	**3.1**	<1	**6.1**	**6**	<1	**12**	**15**	**19**	<1	**38**	20	<1	<1	<1	**906,000**	<1	**12**	**9.1**	<1	**18**	**152**	**61,200**	**340**
Caffeine	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	**21,000**	<25	<25	<25	<25	<25	**59**	**25,000**	**139**
Carbamazepine	**43**	<5	**86**	**62**	<5	**124**	**106**	**102**	<5	**204**	**77**	**63.5**	<5	**127**	**176**	**57**	**53**	**56.7**	<5	**112**	<5	**98**	<5
Carbaryl	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<5000	<50	<50	<50	<50	<50	<50	<50	<50
Chlorpyrifos	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
N,N-Diethyl-*m*-toluamide	**27**	<25	**54**	**77**	<25	**154**	<25	**12.5**	<25	**25**	<25	**13.5**	<25	**27**	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Diazinon	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Dieldrin	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Estradiol	**1.5**	<1	**2.9**	**1.5**	<1	**2.9**	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Estrone	**35**	<1	**70**	**0.8**	<1	**1.6**	**31**	**35.5**	<1	**71**	<1	<1	<1	<1	**50**	**12**	**39**	**2.5**	<1	**4.9**	**7**	**1.8**	<1
17α-Ethinylestradiol	<1	<1	<1	**31.5**	<5	**63**	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Fluoxetine	<1	<1	<1	**52.6**	<1	**104**	**14**	**17**	<1	**34**	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Gemfibrozil	NA[d]	NA[d]	NA[d]	**9**	<1	**18**	**5.5**	**8.5**	<1	**17**	**3.8**	**0.9**	NA[d]	**1.7**	**1020**	**26**	**11**	**5.1**	<1	**10**	<1	**43**	<1
Ibuprofen	NA[d]	<1	NA[d]	**14.6**	<1	**26**	<1	<1	<1	<1	**2.9**	**2.4**	<1	**3.7**	**7000**	**6**	**2.8**	**3.1**	<1	**6.1**	**2.7**	**8140**	**21**
Iopromide	<5	<5	<5	<5	<5	<5	**11**	**17.5**	<5	**35**	**13**	**8**	<5	**16**	<500	<5	<5	<5	<5	<5	<5	<5	<5
Methyl parathion	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<2500	<25	<25	<25	<25	<25	<25	<25	<25
Phenol	<100	<100	<100	<100	<100	<100	<100	**126**	<100	**252**	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	**258**	NA[d]
Progesterone	<1	<1	<1	<1	<1	<1	<1	**0.6**	<1	**1.2**	<1	<1	<1	<1	<100	<1	<1	<1	<1	<1	<1	<1	<1
Sulfamethoxazole	**78.5**	<1	**156**	**283**	<1	**565**	**62**	**155**	<1	**310**	**46**	**210**	<1	**420**	**854**	**363**	**28**	**22.8**	<1	**45**	**76**	**768**	**3.5**
Tris(1,3-dichloro-2-propyl) phosphate	**138.5**	<25	**277**	**212**	NA[d]	**324**	**186**	**176.5**	<25	**353**	**148**	**169.5**	NA[d]	**258**	<2500	**94**	**121**	**108.4**	<25	**214**	<25	<25	<25
Testosterone	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**75**	<1	1	<1	<1	<1	<1	**1**	<1
Triclosan	**17.5**	<5	**35**	**71**	<5	**142**	**32**	**23**	<5	**46**	**42**	**19**	<1	**38**	<500	<5	<5	<5	<5	<5	<5	<50	<50
Triclosan	**42**	<50	**84**	**52.5**	<50	**105**	<50	**34.5**	<50	**69**	<50	<50	<50	<50	**5500**	<50	<50	**46.1**	<50	**91**	<50	<5	<5
Trimethoprim	**0.6**	<1	**1.2**	**22.2**	NA[d]	**43**	**1**	**0.8**	<1	**1.5**	<1	<1	<1	<1	**36**	<1	<1	<1	<1	<1	<1	**32**	<1
Triphenylphosphate	<25	<25	<25	<25	<25	<25	**52**	**59.5**	<25	**119**	**44**	**65.5**	<25	**131**	<2500	**57**	**72**	**50.1**	<25	**99**	<25	<25	<25
Tris(2-butoxyethyl) phosphate	<100	<100	<100	**52.5**	<100	**105**	<100	<100	<100	<100	**140**	**196**	<100	**392**	<10,000	**148**	NA[d]	**97.2**	<100	**192**	**352**	<100	NA[d]
Tris(2-chloroethyl) phosphate	**71.5**	<25	**143**	**99.5**	<25	**199**	**137**	**151.5**	<25	**303**	**64**	**84.5**	<25	**169**	<2500	**93**	**118**	**95.2**	<25	**188**	<25	<10	<10

[a]Microconstituents in RO influent were calculated based on their concentrations in RO effluent and RO brine and corresponding flow rates.
[b]RO effluent is the effluent water after RO treatment.
[c]RO brine is rejected RO influent with highly concentrated salts.
[d]NA: not available because of low sample recovery caused by matrix effect or because spikes exceeded acceptance limits.

3.3 TOXICITY TESTING

The survival and growth of *P. promelas* and the survival and reproduction of *C. dubia* were used to evaluate the toxicity of various effluent streams in the AWT facility and canal water. Toxicity test samples were collected on October 29, 2007; November 26, 2007; January 14, 2008; January 31, 2008; and February 21, 2008.

The survival results from the October 29, 2007, sample indicate that RO effluent could result in 100% mortality of the test organism, *C. dubia*. Because microconstituents in the RO effluent were all below detection limits, the observed toxic effects were likely caused by other compounds added to the RO system. Additional tests showed that the observed toxicity was not caused by RO stabilization chemicals, DO, pH, or trace minerals. Further evaluation of the RO system indicated that ammonia, chloramine, and antiscalant used for maintaining the RO system might contribute to the observed toxicity. Therefore, tests in which the RO effluent samples were quenched with sodium thiosulfate (thus reducing the combined chlorine to below detection limits) were performed for the second round of testing on November 26, 2007. Chloramine quenching reduced and delayed toxicity but did not eliminate it. To further diagnose the cause of toxicity, all chemical additions (ammonia, chloramine, and antiscalant) were stopped prior to the January 14, 2008, sampling event. The results showed that RO effluent did not produce any significant toxicity, and the survival of *P. promelas* and of *C. dubia* significantly increased. The fourth and fifth tests were used to determine if the previously observed toxicity was caused by chloramine or antiscalant. For the fourth round of testing on January 31, 2008, only chloramine was added to the system and no antiscalant was used. For the fifth round of testing on February 21, 2008, only antiscalant was added to the system and no chloramine was used. These tests showed that chlorinated compounds (chloramines) most likely caused the observed toxicity.

Detailed toxicity results are shown in Figures 3.10 through 3.17 and are discussed in the following sections.

3.3.1 Toxicity of MBR and UF Effluent

The survival of *P. promelas* and of *C. dubia* in MBR or UF effluent is shown in Figures 3.10 and 3.11. The growth of *P. promelas* and reproduction of *C. dubia* in MBR or UF effluent are shown in Figures 3.12 and 3.13.

No significant survival differences in MBR and UF effluent above control (deionized water) were observed for *P. promelas* (Figure 3.10) and *C. dubia* (Figure 3.11) on October 29, 2007, except that the survival rate of *C. dubia* was low in 100% MBR effluent. No significant growth differences in MBR and UF effluent above control (deionized water) were observed for *P. promelas* (Figure 3.12). Similarly, no significant reproduction differences in MBR or UF effluent above control (deionized water) were observed for *C. dubia* (Figure 3.13). These results suggest that MBR effluent and UF effluent did not have significant toxic effects on the survival and growth of *P. promelas* and survival and reproduction of *C. dubia*. Notice that the chloramines and antiscalant are added *after* the MBR/UF membranes and thus that there are no chloramines in the MBR/UF effluent for any of the tests performed here.

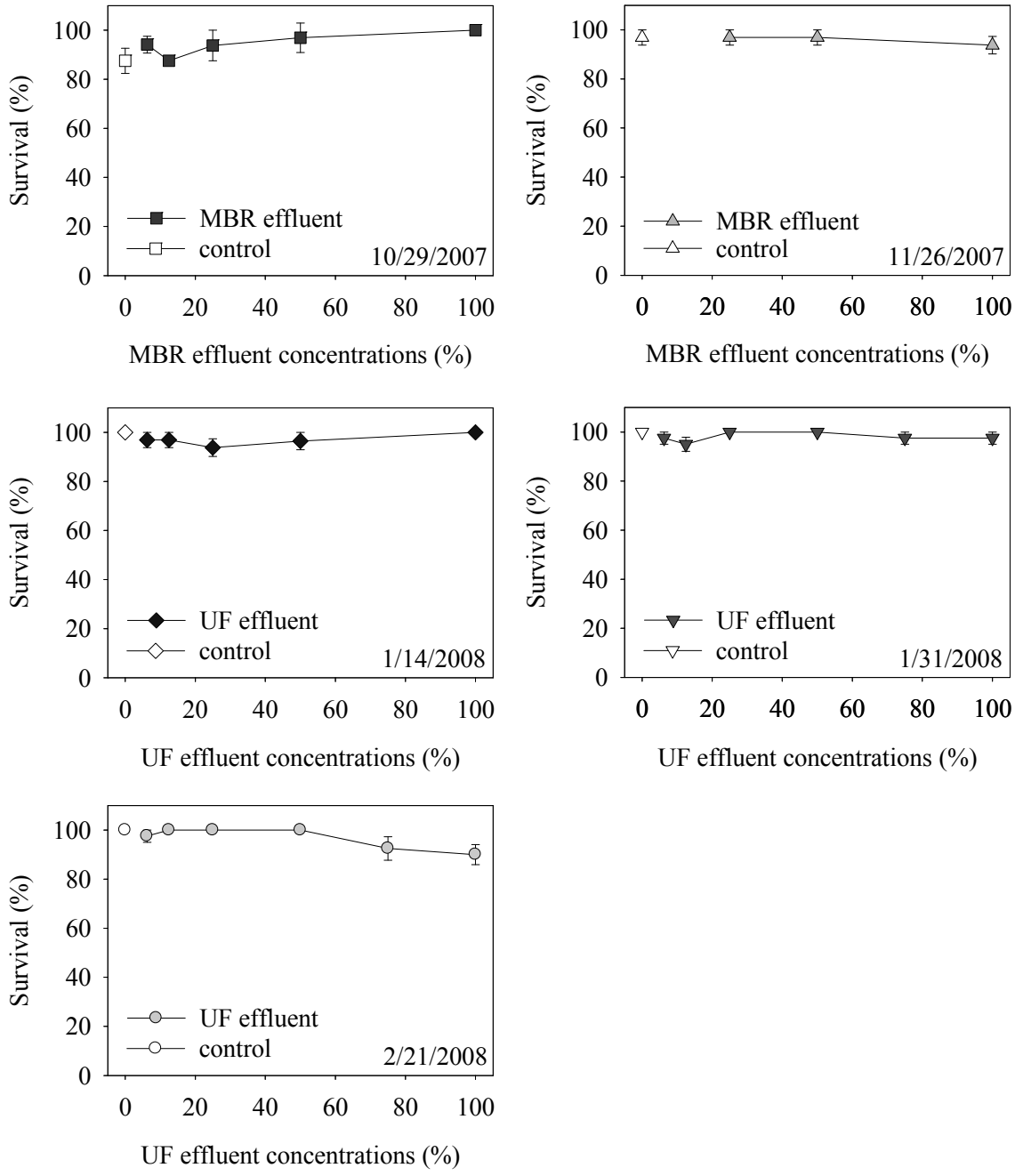

Figure 3.10. Survival of *P. promelas* in MBR effluent and UF effluent.

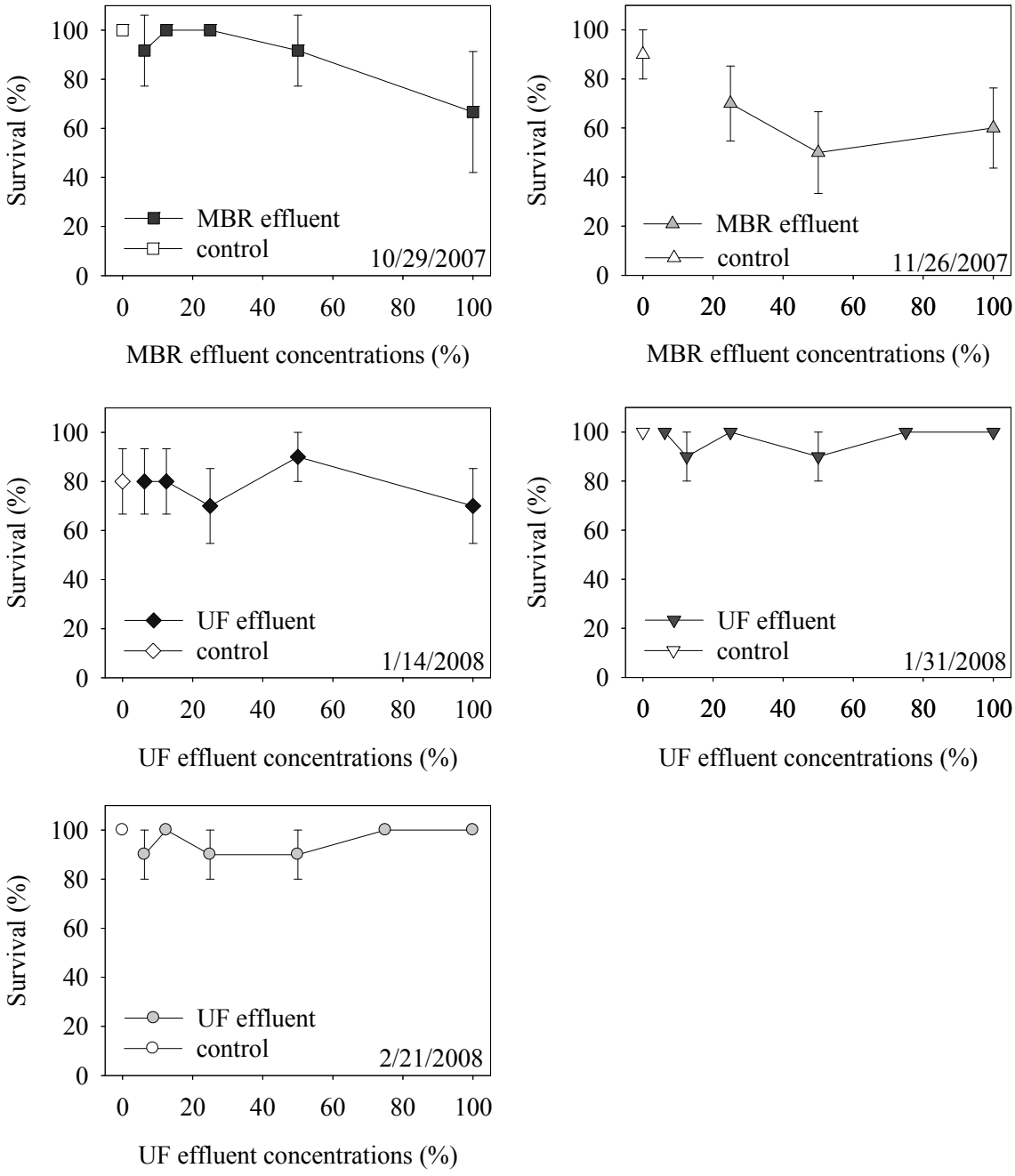

Figure 3.11. Survival of *C. dubia* in MBR effluent and UF effluent.

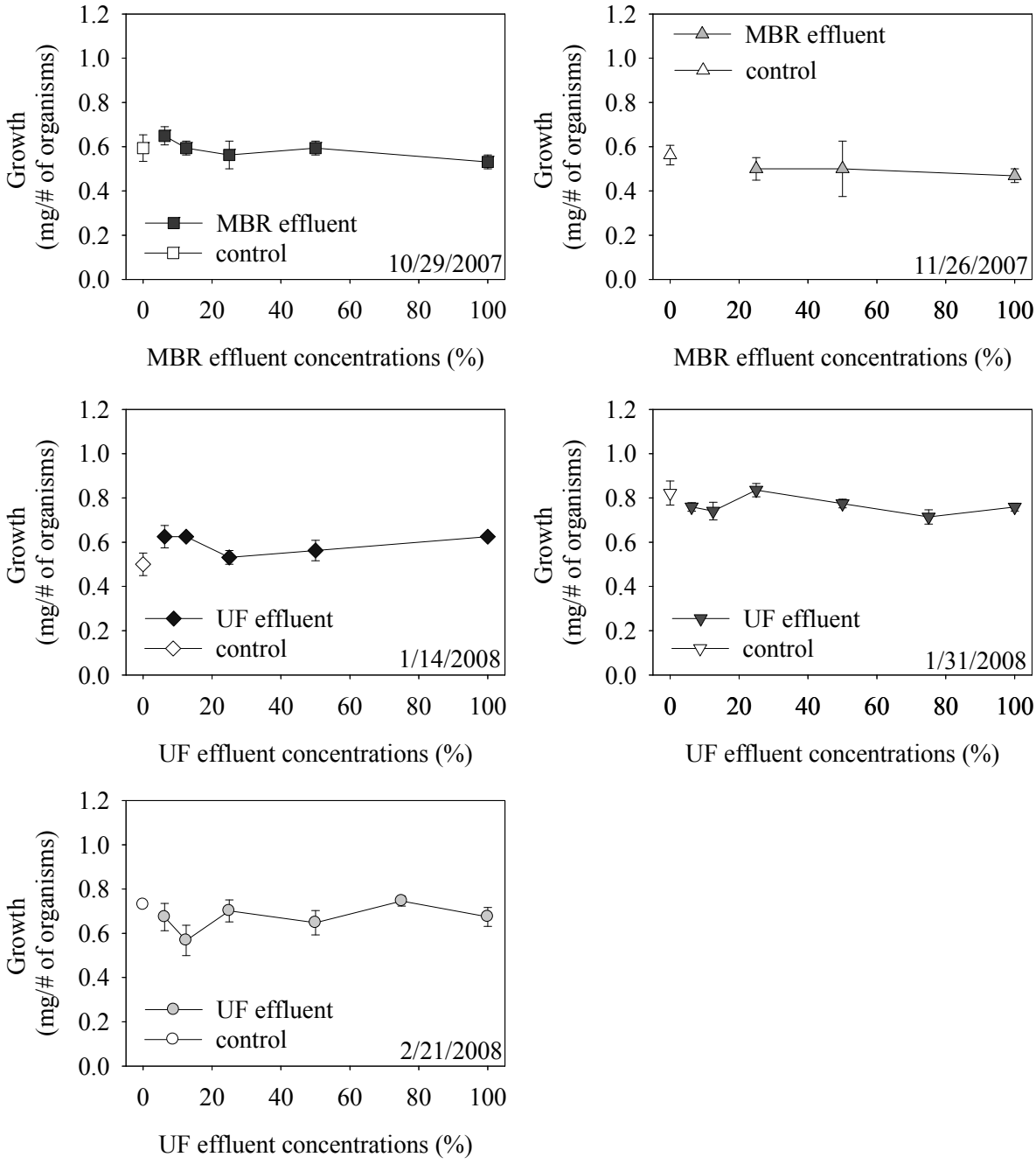

Figure 3.12. Growth of *P. promelas* in MBR effluent and UF effluent.

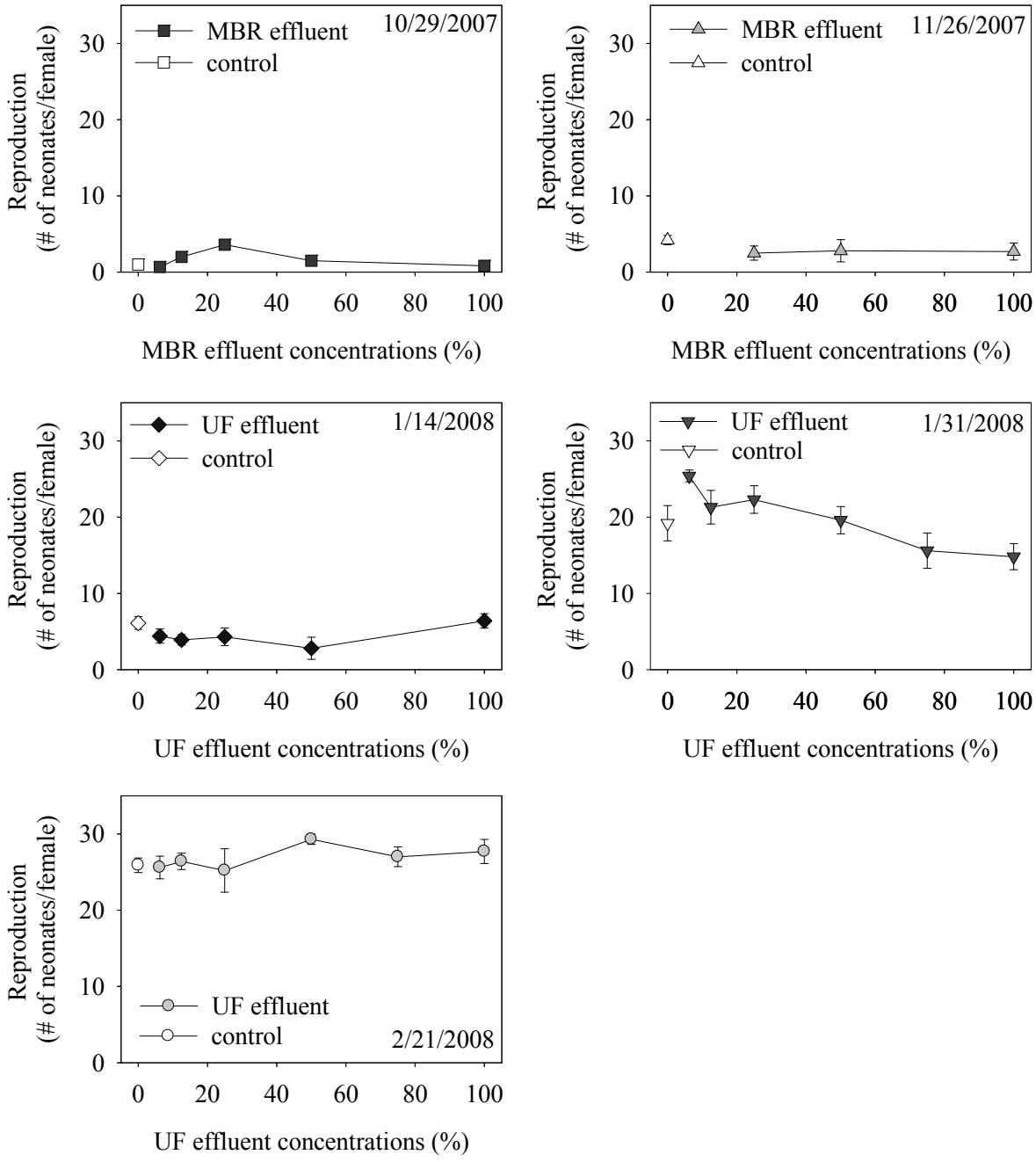

Figure 3.13. Reproduction of *C. dubia* in MBR effluent and UF effluent.

3.3.2 Toxicity of RO Effluent and Canal Water

The survival of *P. promelas* and *C. dubia* in RO effluent is shown in Figures 3.14 and 3.15. The growth of *P. promelas* and reproduction of *C. dubia* in RO effluent are shown in Figures 3.16 and 3.17.

The survival rate of *P. promelas* and of *C. dubia* in RO effluent was low on October 29, 2007, with 100% mortality of *C. dubia* and some mortality of *P. promelas* potentially caused by chloramine in RO effluent. Therefore, RO effluent samples were quenched with sodium thiosulfate, reducing the combined chlorine to below detection for the second round of testing on November 26, 2007. The survival rate of *P. promelas* and *C. dubia* in RO effluents significantly increased after quenching (dechlorination). No significant survival differences above control were observed in *P. promelas* after dechlorination, which suggests that toxicity was completely removed after dechlorination. Conversely, the survival of *C. dubia* in less diluted (> 25%) RO effluent, which contained antiscalant and quenched chloramine, was still low after dechlorination. Further experiments on January 14, 2008, without chloramine and antiscalant showed no survival differences between RO effluent and control and significant increases in the reproduction of *C. dubia*. No significant survival differences above control were observed in *P. promelas.* The experiment on January 31, 2008, with only quenched chloramine showed a significant increase in the *C. dubia* survival rate in RO effluent compared to the survival rate in unquenched chloramine, but toxicity was only partially reduced after quenching, a result that was probably caused by a trace amount of ammonia in the water resulting from dechlorination of samples. No significant survival differences above control were observed in *P. promelas.* The final batch of experiments on February 21, 2008, with only antiscalant indicated that there were no significant survival and growth differences of *P. promelas* in RO effluent and control (deionized water) and that there were no significant survival and reproduction differences of *C. dubia* in RO effluent and control (deionized water). These results suggested that antiscalant did not have toxicity effects on *C. dubia* and that the observed toxicity was likely caused by chloramine.

Surface (canal) water toxicity was also tested. No significant differences in the survival and growth of *P. promelas* and survival and reproduction of *C. dubia* were observed between canal water and control, suggesting that canal water did not pose any toxic threat to the survival and growth of *P. promelas* or to the survival and reproduction of *C. dubia.*

Given that *P. promelas* and *C. dubia* had no survival differences in MBR effluent and UF effluent compared to controls and that the observed toxicity to *C. dubia* from RO effluent was delayed and eliminated after chloramine was removed, it can be concluded that microconstituents did not contribute to the toxicity of AWT facilities. Instead, these results suggest that chloramines or ammonia in these systems may contribute to the toxicity to *C. dubia* and should be removed prior to discharge. To facilitate surface water augmentation, the toxicity of chloramine for maintaining AWT facilities requires further investigation.

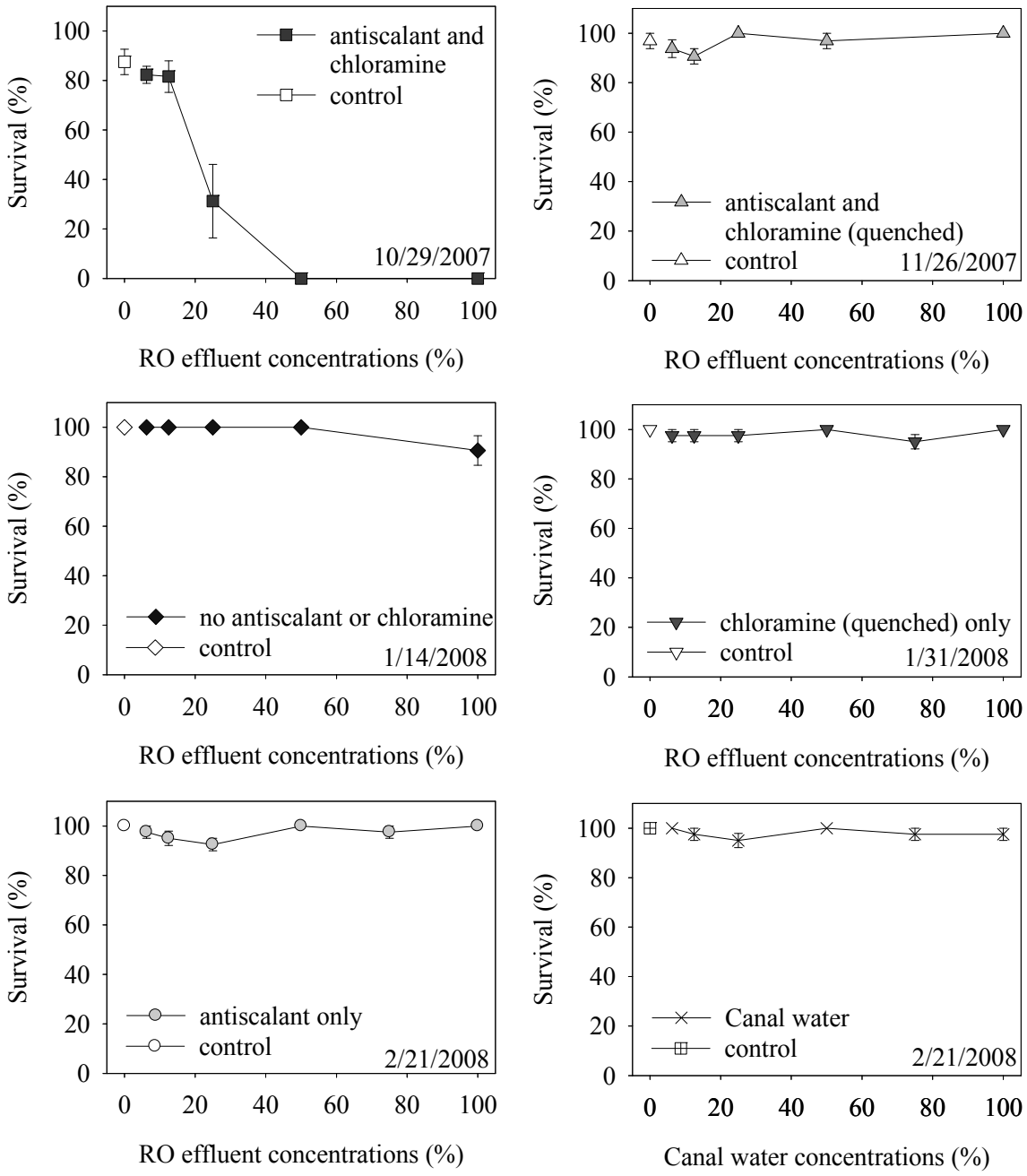

Figure 3.14. Survival of *P. promelas* in RO effluent and canal water.

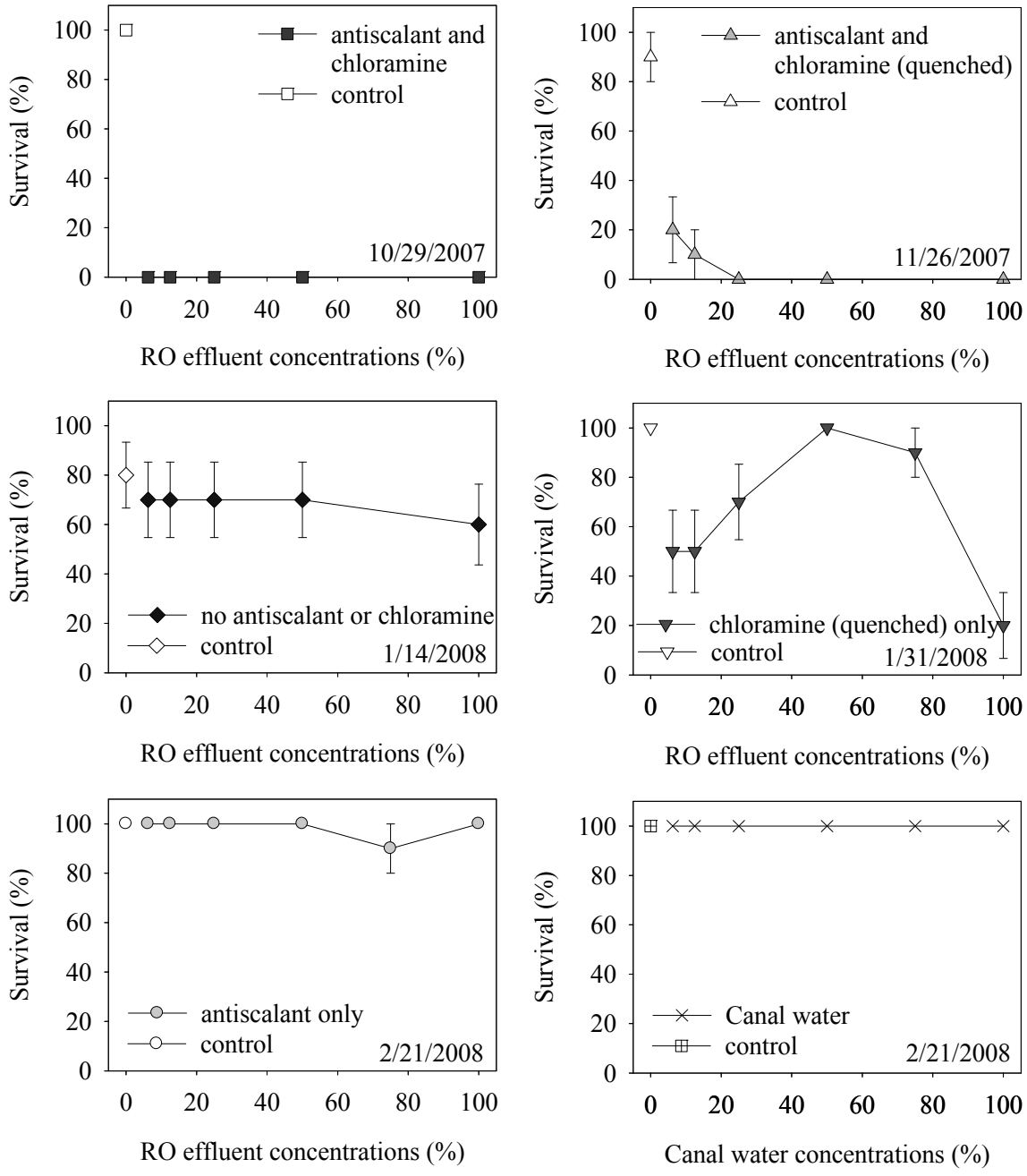

Figure 3.15. Survival of *C. dubia* in RO effluent and canal water.

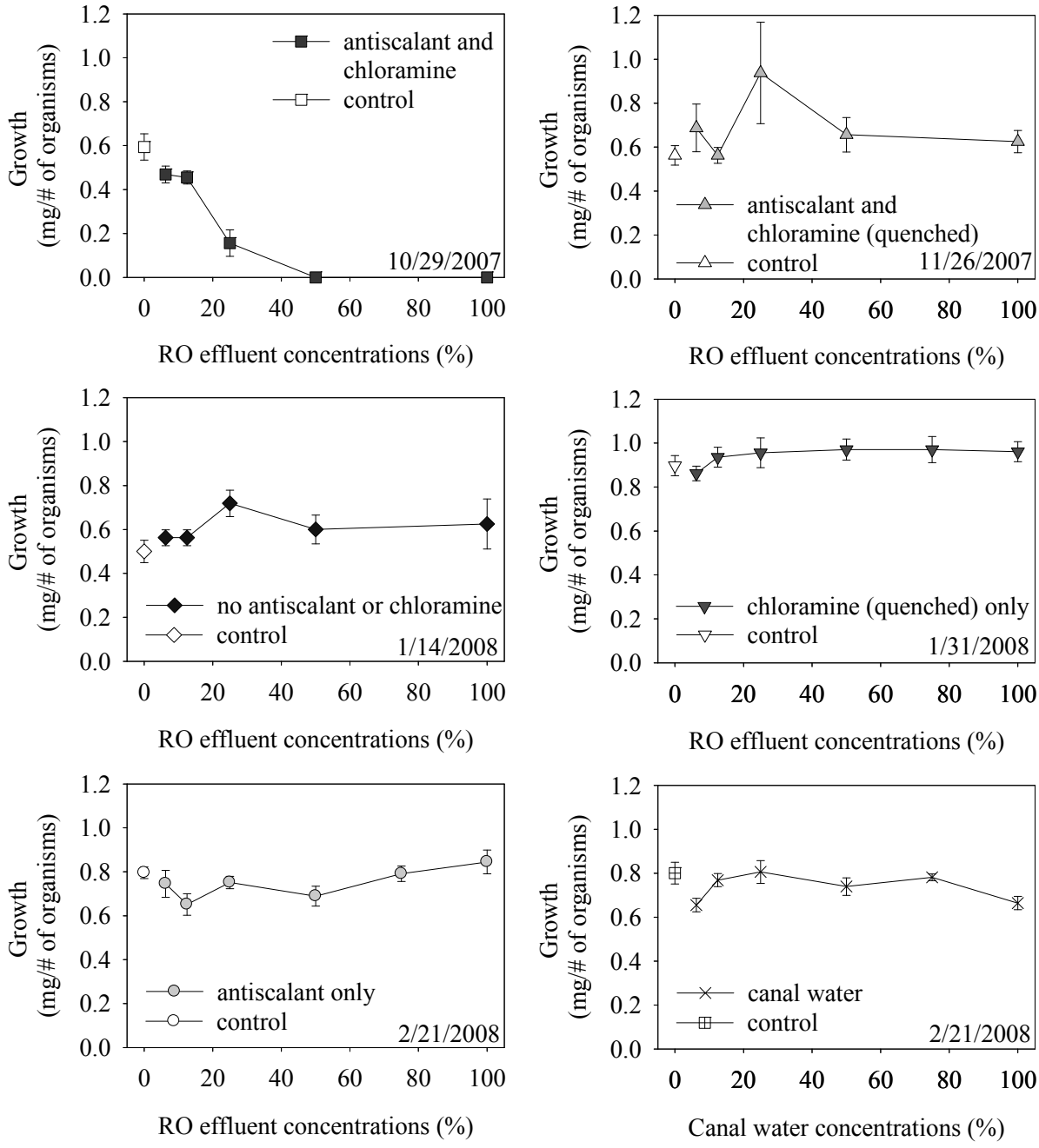

Figure 3.16. Growth of *P. promelas* in RO effluent and canal water.

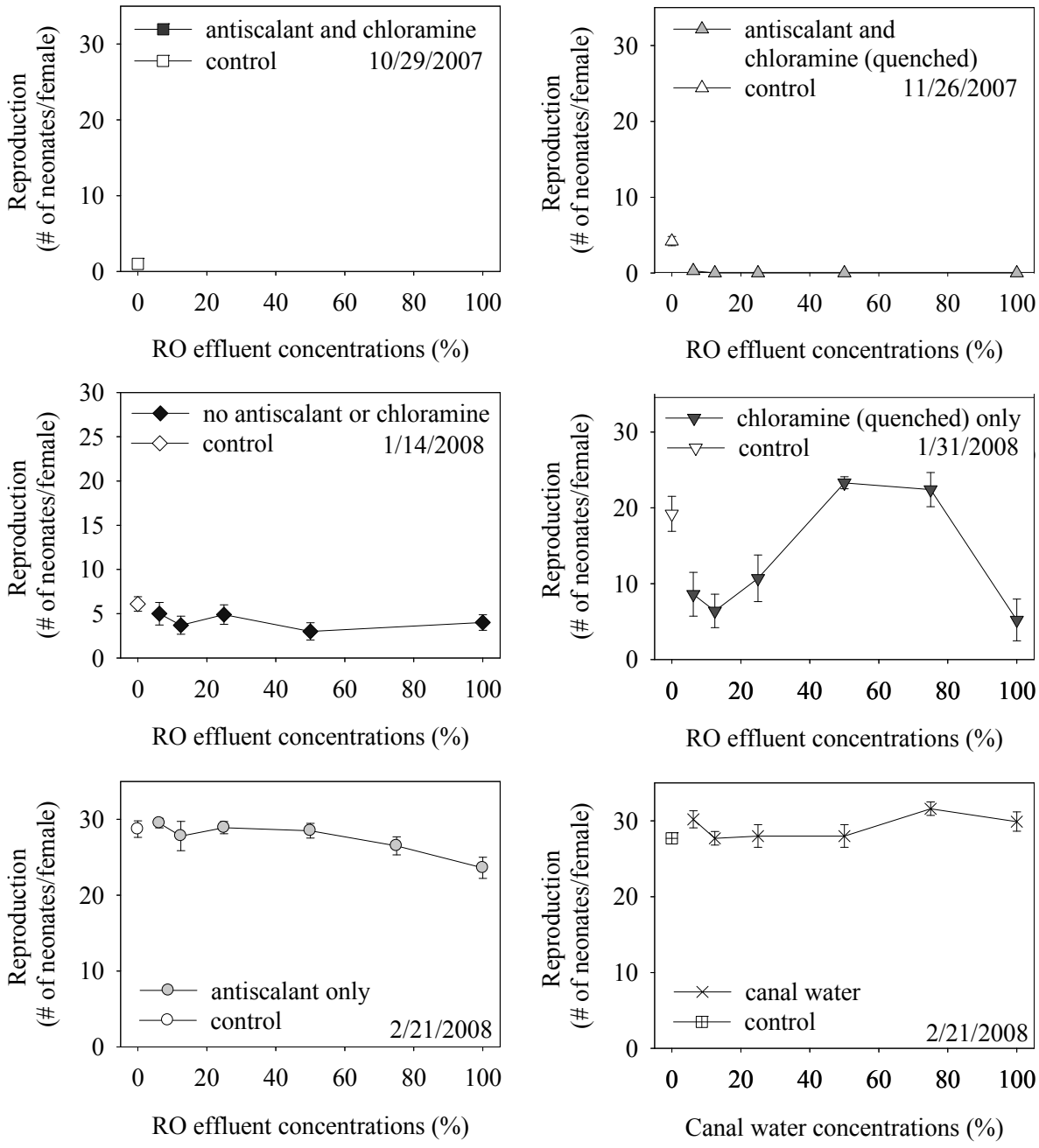

Figure 3.17. Reproduction of *C. dubia* in RO effluent and canal water.

3.4 E-SCREEN BIOASSAY

The results of E-Screen bioassays are shown in Figure 3.18. Although estradiol equivalents were detected in secondary effluent, DNF effluent, MBR effluent, and UF effluent, estradiol equivalents in all RO effluent samples were below detection. The results of the E-Screen bioassay indicate that RO effluent produced a significant response in MCF-7 cells.

3.5 YES BIOASSAY

The response of yeast cells to the sample extracts was compared to a YES assay standard curve to determine the estradiol equivalents of effluent samples. The results of the YES assays are shown in Figure 3.19. Although estradiol equivalents were detected in secondary effluent and DNF effluent, estradiol equivalents in MBR effluent, UF effluent, and RO effluent were below detection. YES bioassay testing also indicated that MBR effluent and RO effluent did not possess endocrine disrupting potential.

The differences in detected estradiol equivalents with E-Screen bioassays and YES assays are likely caused by the difference in their detection limits and target cells. The detection limit of E-Screen bioassays is 0.03 ng/L, and the detection limit of YES assays is 0.2 ng/L. Therefore, some estradiol activities detected with E-Screen bioassays could not be detected by YES assays. In addition, the expected estradiol equivalents in MCF-7 cells and in yeast cells are different, depending on the composition of estrogens and xenoestrogens in tested samples. For example, estriol is about 25% as potent as 17β-estradiol in the E-Screen bioassays but only 0.75% as potent as 17β-estradiol in the YES assays. Thus, the detected estradiol equivalents in MCF-7 cells and in yeast cells are likely different because of the complex composition of field samples.

3.6 FATHEAD MINNOW Vtg AND STEROID ASSAYS

Results of the fathead minnow Vtg assays of the MBR/RO system are shown in Figure 3.20. The positive 17α-ethinylestradiol and negative controls worked as predicted for the MBR/RO system. None of the effluent samples tested from the MBR/RO system showed an increase of plasma Vtg in male fish, indicating that they are not exposed to estrogenic components at the required concentrations for this effect.

The results of the fathead minnow Vtg assays of the UF/RO system also are shown in Figure 3.20. Effluent from DNF and RO processes shows estrogenic effects by increasing plasma Vtg to 6 and 5 mg/L respectively, though both are considered to be very low concentrations of plasma Vtg. The 5-ng/L 17α-ethinylestradiol positive control was less potent than expected, and this result was attributable to lower actual concentrations in the control test water: about 2 ng/L rather than the target 5 ng/L. However, the 17α-ethinylestradiol positive control did produce a positive result, showing that the assay worked. Please note that the limit of detection of the assay is 0.5 mg/L and that negative control values in male fish are normally below 1 mg/L. Male fish that have a positive response to an estrogenic substance usually show a concentration above 10 mg/L; thus, none of these fish exhibited a true positive response.

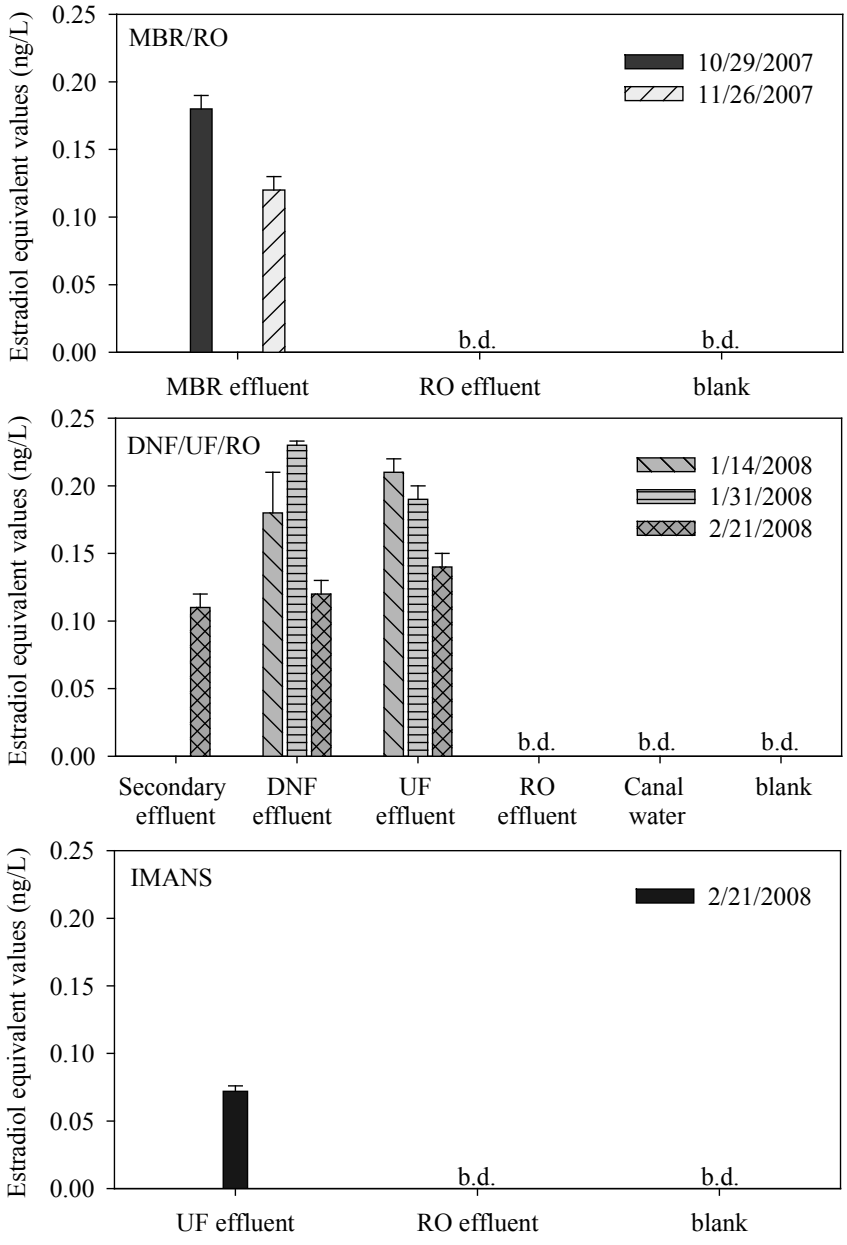

Figure 3.18. Results of E-Screen bioassay.
b.d.: below detection limits (estradiol equivalent < 0.03 mg/L).

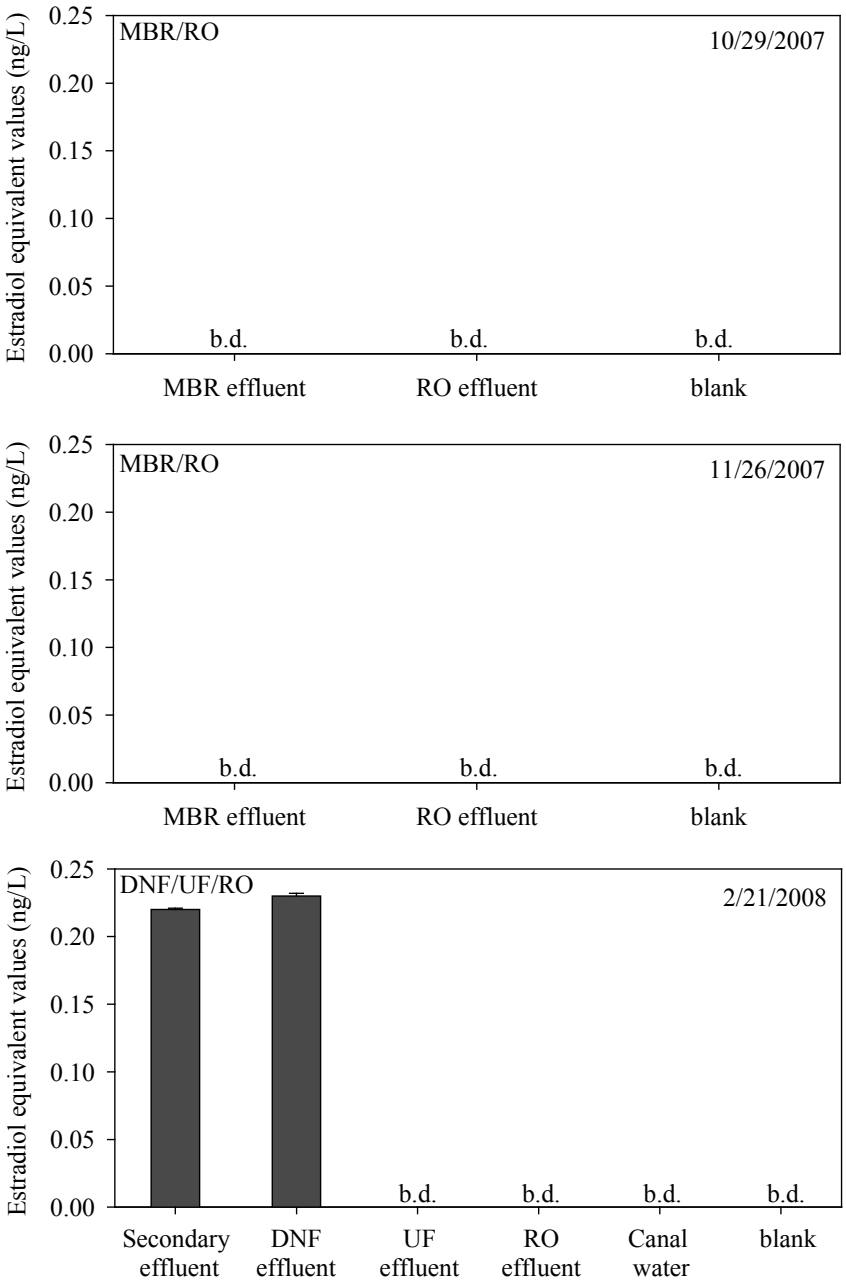

Figure 3.19. Results of YES assay.
b.d.: below detection limits (estradiol equivalent < 0.20 ng/L).

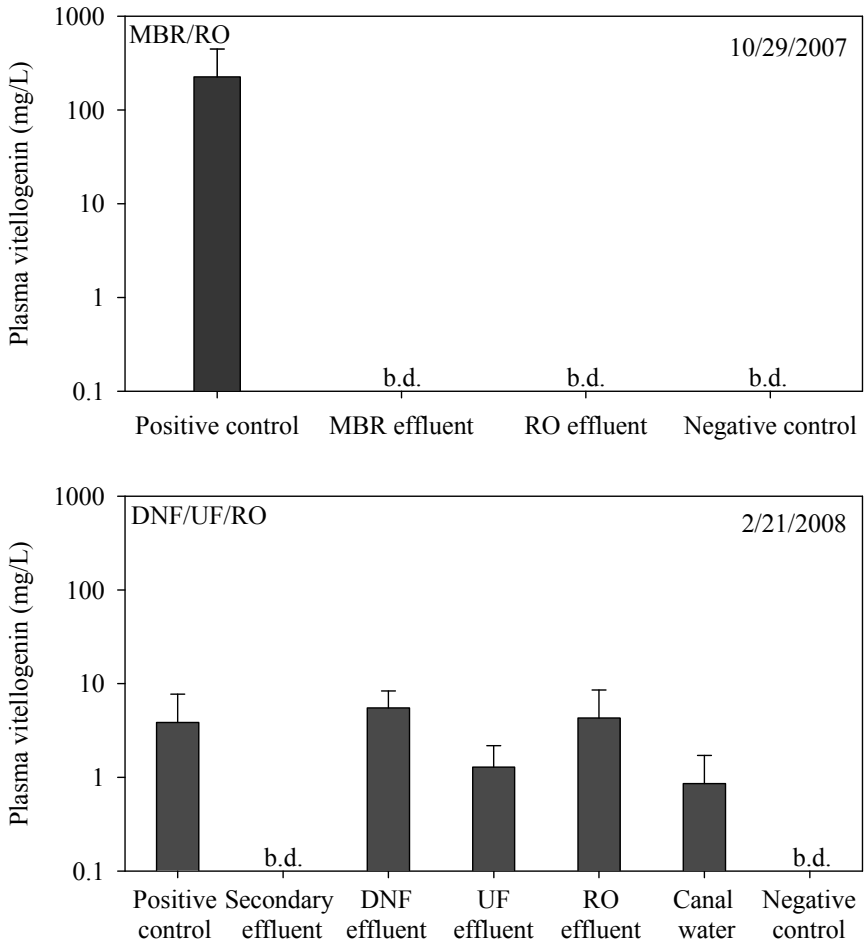

Figure 3.20. Results of fathead minnow Vtg assay.
b.d.: below detection limits (plasma Vtg < 0.5 mg/L).

The results of fathead minnow steroid assays are shown in Figure 3.21. Plasma samples obtained from male fathead minnows were extracted and analyzed for testosterone by ELISA. Testosterone concentrations in all treatments were similar to those in the negative control group. The mean values of testosterone in UF effluent and canal water as well as of 17α-ethinylestradiol (5 ng/L) tended to be higher than controls, though this result was driven by one or two individual fish with very high levels of testosterone. The reason for the high levels of testosterone in these fish is unclear but may be related to behavioral dominance (alpha males) or other causes. Dominant males have significantly higher testosterone levels than do subordinate males. There is no correlation of high testosterone values with Vtg induction, suggesting that the testosterone values are not attributable to estrogenic effects of the effluent samples. All of these results suggest that RO effluent was not estrogenic.

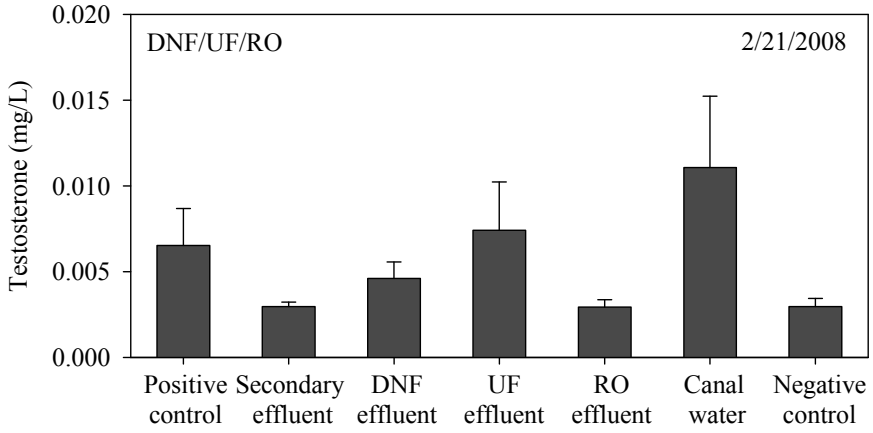

Figure 3.21. Results of steroid assay.

3.7 RECHARGE MODELING

The main objective of the modeling work was to estimate the fate and transport of three microconstituents and one CT from its hypothetical source (point of reclaimed water discharge), through a canal network, and through the surficial aquifer system. In doing so, the project team examined open channel and groundwater hydraulics, along with chemical transport in the surface water and groundwater. The three microconstituents were sulfamethoxazole, phenol, and triclosan.

3.7.1 Hydrodynamic Model

The water elevation and discharge rate predicted by the model in the Holloway canal at the WWTP effluent location are shown in Figure 3.22. To show the effect of the reclaimed water discharge, the case of no discharge from the WWTP effluent is also included. For the purpose of this model, a reclaimed water discharge rate of 5 ft^3/s was assumed. In the wetter months (May to October), water levels at that site are commonly between 3.5 and 4.5 ft. The upper limit is controlled by downstream pumps that release water if the upstream water levels are higher than 4.5 ft. Canals in MIKE 11 receive runoff from overland flow and groundwater drainage and lose water because of infiltration. Evaporation losses directly from the river network are considered only in the model in the primary canals (North New River and C-12). Infiltration losses are evident in the drier months (November to April), when the water levels are around 3 and 3.5 ft. Note that in the case of no discharge from the WWTP, the water levels for the dry season are approximately 0.25 ft lower. The flow rates in the Holloway canal at the WWTP effluent location also show a seasonal dependence, as seen in Figure 3.22. During the wet season, the direction of the flow predicted by the model is positive, which means a flow from north to south. However, during the drier months, the magnitude of the flow is lower and the direction may change more frequently.

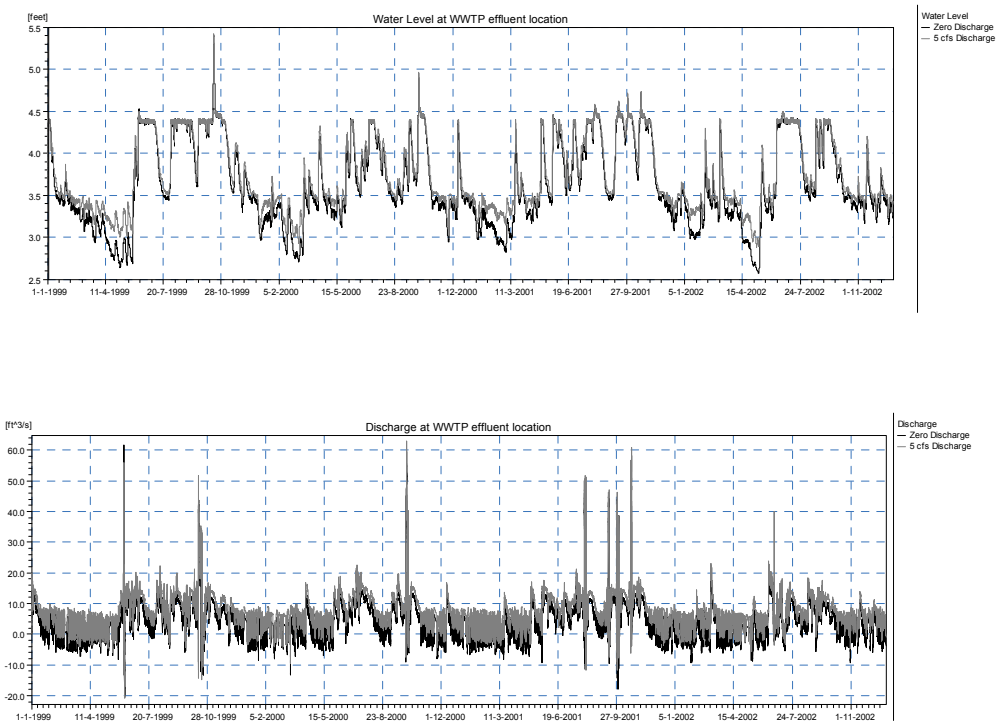

Figure 3.22. Water levels and discharge rate in the Holloway canal at WWTP effluent location as predicted by the model.
Gray and black lines represent the cases with an effluent discharge of 5 ft^3/s and without it, respectively.

Potable water supply wells are extracting water mostly from the groundwater (computational) layers 3, 4, and 5 of the model.

The spatial distribution of the head in the upper layer (layer 3) is shown in Figure 3.23. Notice that the head decreases in general from west to east. However, the extraction at some wellfields causes a head drawdown that modifies that regional pattern. The groundwater flow is driven by the head differences from high to low values.

A sketch of the average annual water budget for the 4 years considered (1999–2002) is presented in Figure 3.24. The figure shows that the well extraction from layer 3 is the largest, followed by layer 4.

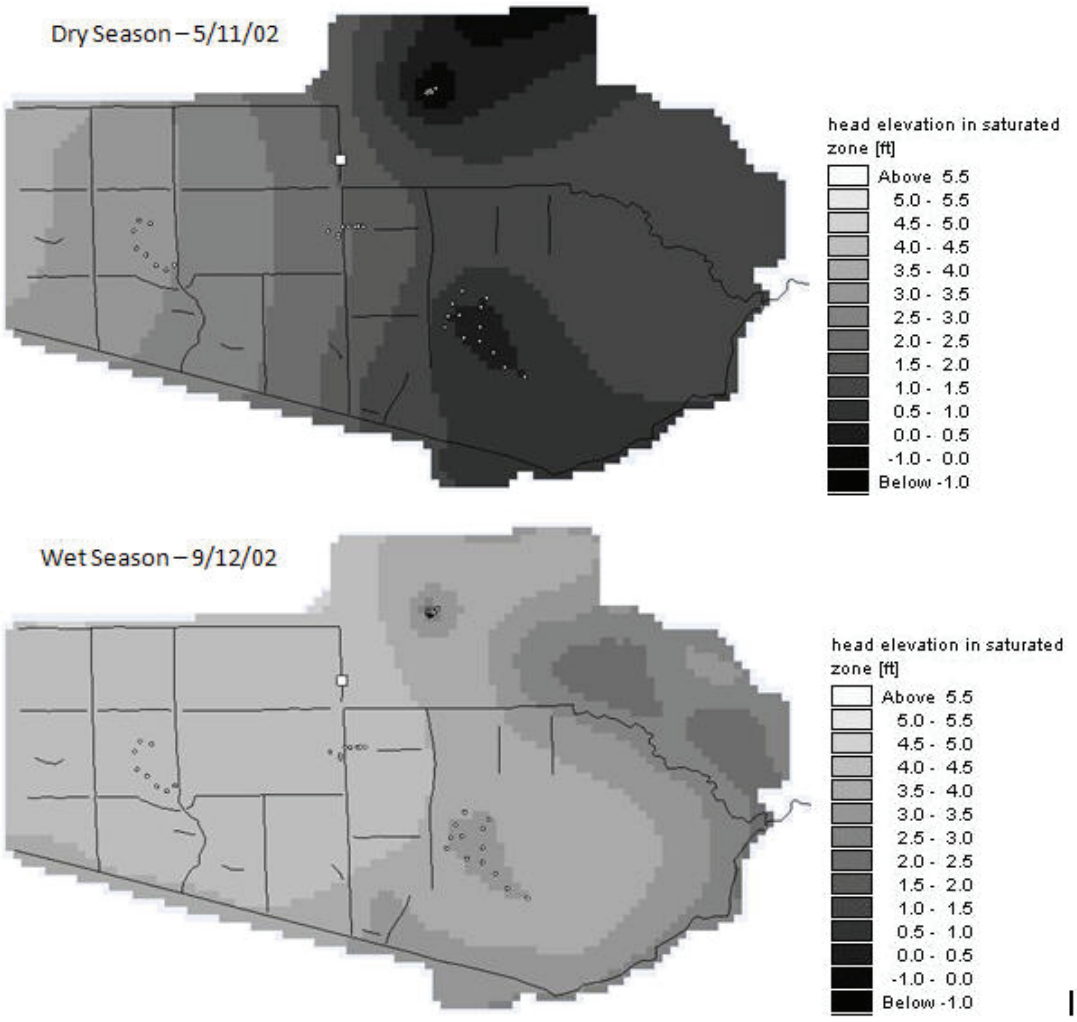

Figure 3.23. Head elevation in groundwater (computational) layer 3 at the end of the dry and wet seasons of 2002 in ft NGVD29.
The white square represents the WWTP effluent location, and the small white squares represent extraction wells.

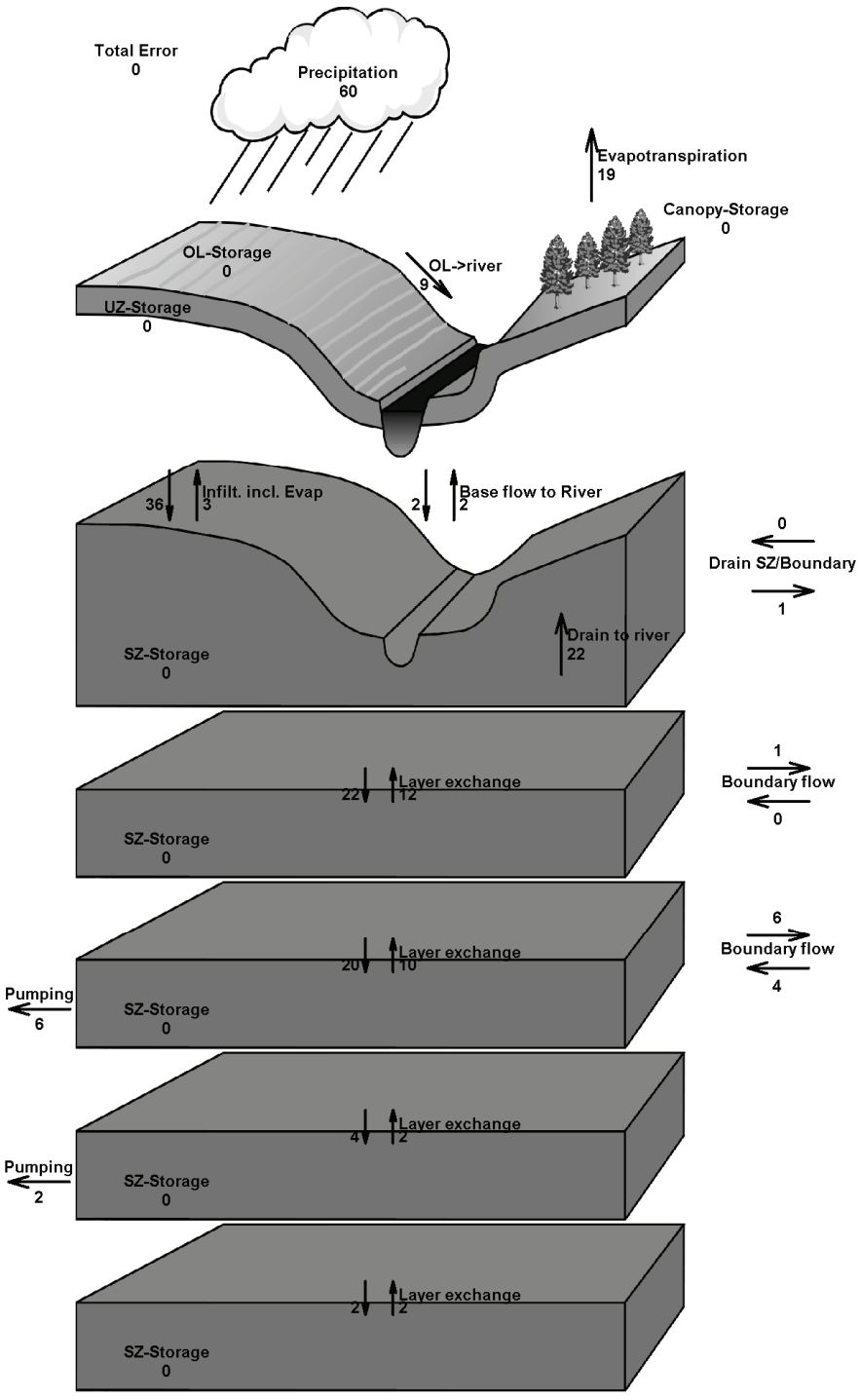

Figure 3.24. Annual average water budget for the whole hydrodynamic MIKE SHE model domain area.
Numbers are depths (volume per unit of horizontal area) in inches per year. OL stands for overland flow, UZ for unsaturated zone, and SZ for saturated zone.

The model was run for a 2-year period by using historical data in 2001 and 2002. This period falls within the Broward model calibration period (1999–2002), and it represents a period of average rainfall conditions. Some simulated surface water and groundwater results with the observed data are shown below. In general, the groundwater results follow the observed data closely (Figure 3.25). The surface water results are very sensitive to the structure operations (Figure 3.26), which tend to differ in practice from the written protocols. As shown below, the S-33 gates in the model are operating to maintain the control elevation for the C-12 basin (3.5 ft).

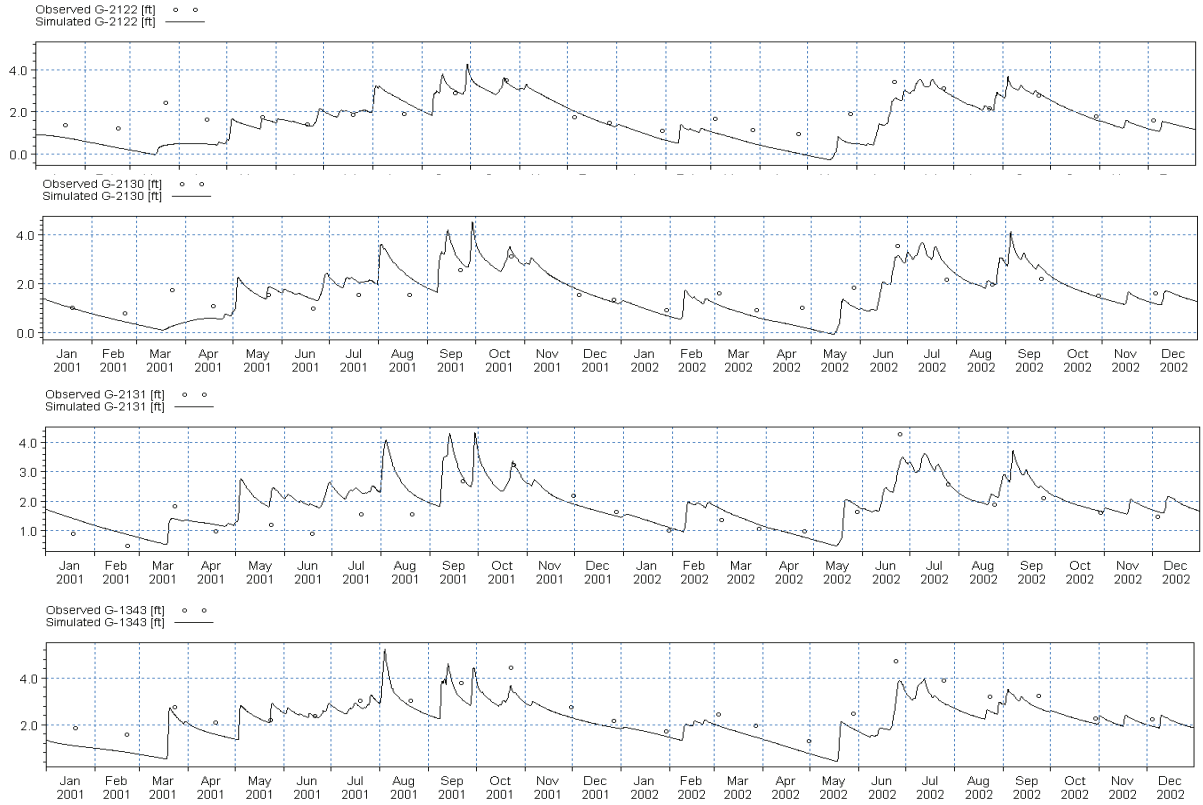

Figure 3.25. Groundwater plots.

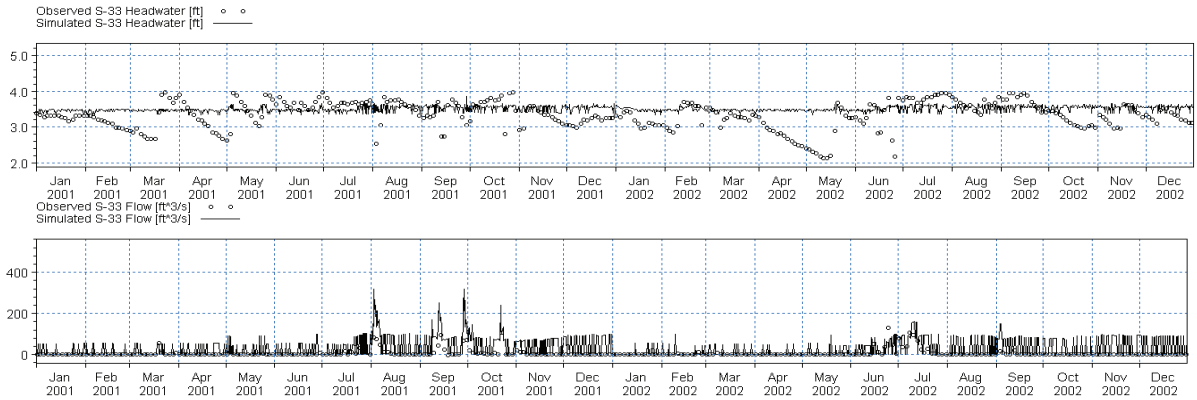

Figure 3.26. Surface water plots.

3.7.2 Water Quality Model

The water quality section is divided into two subsections; the first shows the transport of suspended sediment, and the second shows the transport of the CT and the three microconstituents considered.

3.7.2.1 Sediment transport

The results for sediment transport in canals at the hypothetical reclaimed water discharge location are shown in Figure 3.27. In general, the suspended-particle concentration fluctuates around 1 mg/L, which corresponds to the equilibrium concentration when water speed is approximately 0.4 cm/s (0.013 ft/s). During the wet season, the higher water velocities cause higher resuspension and therefore a higher concentration of suspended particles. In heavy rainfall events, the concentration may reach 5 mg/L. During the dry season the water velocities in the canal network are lower, and so are the resuspension and the suspended-particle concentration.

The graph for the suspended-particle concentration looks similar every time the water movement data are recycled (4 years), except by the effect of the initial conditions assumed at the beginning. However, the mass of the sediment layer at the hypothetical reclaimed water discharge location increases initially and then decreases. This result may indicate that the predicted changes in the sediment layer thickness continue after 20 years. A view of this variable in the whole canal network at the end of the simulation is shown in Figure 3.28. The locations of larger masses of sediment roughly correspond to the locations of higher flow rates shown in the model. However, since the resuspension rate depends directly on the water velocity and not on the volumetric flow rate, the final mass of sediment also depends on the cross-sectional area of the canals.

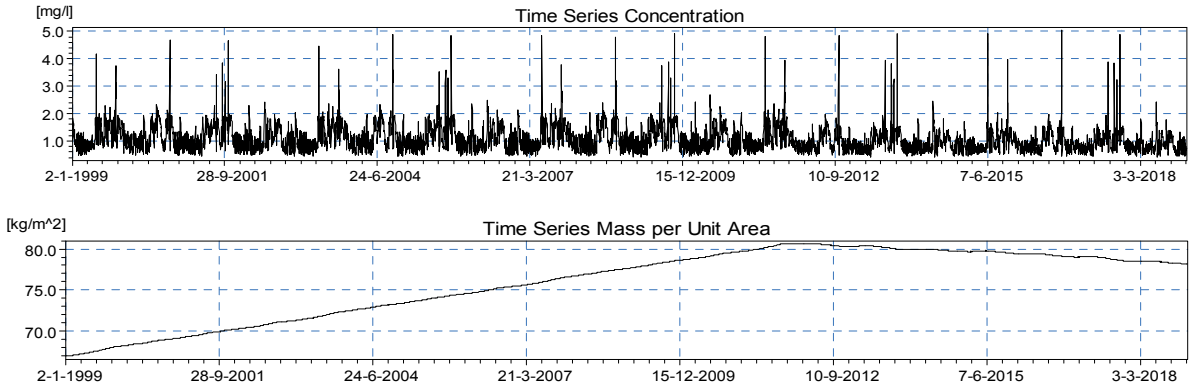

Figure 3.27. Simulated concentration of suspended particles and the mass of sediment layer in the Holloway canal at the WWTP for the whole simulation period (20 years).

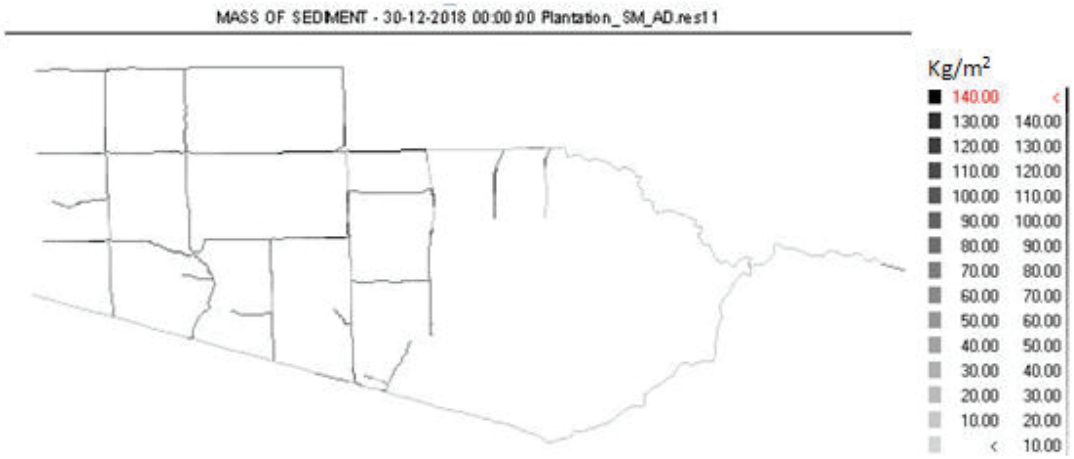

Figure 3.28. Simulated mass of sediment layer in the canal network at the end of the simulation period.

3.7.2.2 Microconstituent transport

Figure 3.29 shows the concentrations for the three microconstituents and the CT in the Holloway canal at the hypothetical reclaimed water discharge location for the period of 1999–2002. For sulfamethoxazole, phenol, and CT, the concentration stabilizes after a short period. However, for triclosan the concentration in the water column takes several years to reach asymptotic values from the zero-concentration initial condition as shown in Figure 3.30. The adsorption coefficient of triclosan is more than 10 times higher than the assumed adsorption coefficient in the other microconstituents considered, which makes the stabilization of the concentration a slower process.

The dissolved concentration divided by the concentration at the WWTP effluent gives a relative concentration, which serves to compare the effect of different processes (adsorption, biotransformation, photolysis, and evaporation) on the microconstituent concentrations. Moreover, the results expressed as relative concentration are independent of the effluent concentration (because of the linearity of the processes involved) and they can be extrapolated to other assumed effluent concentrations.

The relative sulfamethoxazole, phenol, triclosan, and CT concentrations in the canal at the hypothetical reclaimed water discharge location are shown in Figure 3.31 for the four cases considered in the model and for the entire water quality simulation period. The concentrations of the microconstituent with the highest adsorption coefficient (TS) show fewer fluctuations, which is likely a consequence of the adsorbed mass in the sediment layer acting as a buffer. The relative variation of the relative concentration in the last modeled year is plotted in Figures 3.32 and 3.33. The relative variation decreases as the organic-carbon partitioning coefficient increases. Clearly, the value of the adsorption coefficient is a significant factor in determining how fast the concentrations change in the river network.

The total degradation rate of microconstituents computed by ECO Lab is similar to the one used for the overland flow (Appendix C, Table C.2), except for the correction of the photolysis rate for the water depth and different wind velocities that take place when one is

calculating the evaporation rate. The assumption that no biotransformation occurs in this model is very conservative. Thus, further efforts can be directed to a better estimation of the related parameters such as biotransformation rate constants for microconstituents. According to Figure 3.31, the concentration at the hypothetical reclaimed water discharge location stabilizes around a value that is correlated to the total degradation rate estimated for overland water in Table C.2. This dependence is better observed by plotting the mean annual value of the relative concentration and the total decay rate, as shown in Figures 3.32 and 3.33. As expected, the results show that the stabilized concentration of the canal water column at the hypothetical reclaimed water discharge location is lower for microconstituents with a higher total decay rate from all the degradation processes (reference Appendix C for further degradation process details).

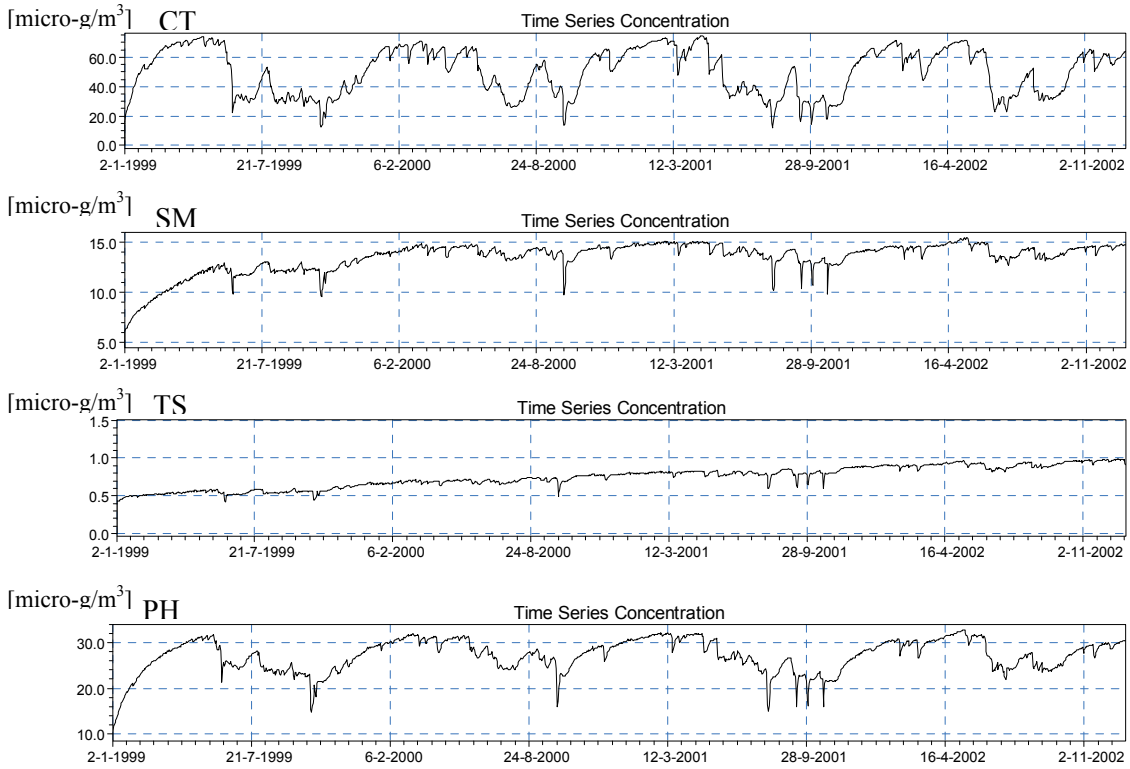

Figure 3.29. Simulated concentrations of dissolved microconstituents in the Holloway canal at the WWTP effluent location for the period of 1999–2002. SM, sulfamethoxazole; TS, triclosan; PH, phenol.

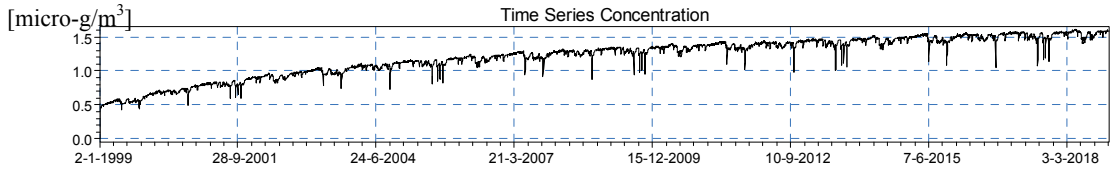

Figure 3.30. Simulated concentrations of dissolved triclosan in the Holloway canal at the hypothetical reclaimed water discharge location for the whole simulation period.

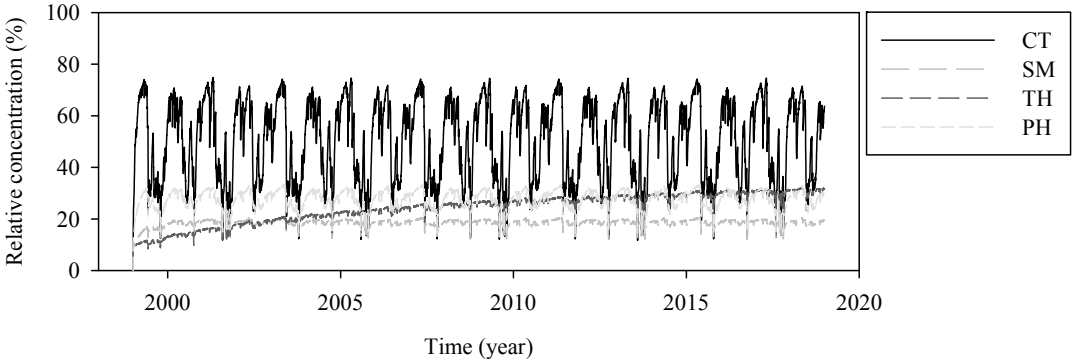

Figure 3.31. Simulated relative concentrations for all dissolved microconstituents in the Holloway canal at the hypothetical reclaimed water discharge location.

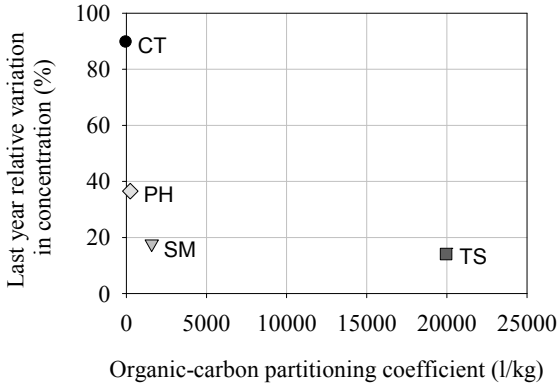

Figure 3.32. Annual relative variation of the concentration (maximum minus minimum, all divided by the mean value) as a function of the adsorption coefficient. The parameters were computed from last year's relative concentrations in the Holloway canal at the hypothetical reclaimed water discharge location presented in Figure 3.31.

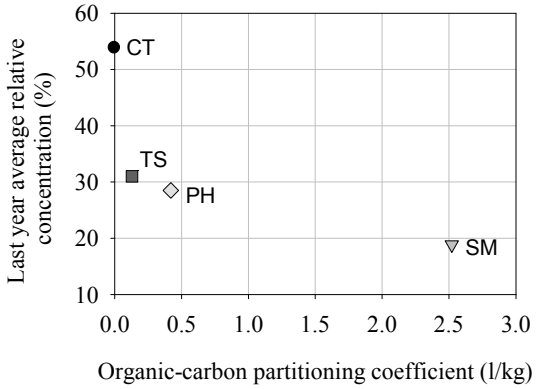

Figure 3.33. Relative concentration (maximum minus minimum, all divided by the mean value) as a function of the decay rate. The parameters were computed from last year's relative concentrations in the Holloway canal at the hypothetical reclaimed water discharge location presented in Figure 3.31.

Figures 3.34, 3.35, and 3.36 show the concentrations of microconstituents adsorbed in suspended particles, dissolved in the pore water of the sediment layer, and adsorbed in the sediment layer, respectively.

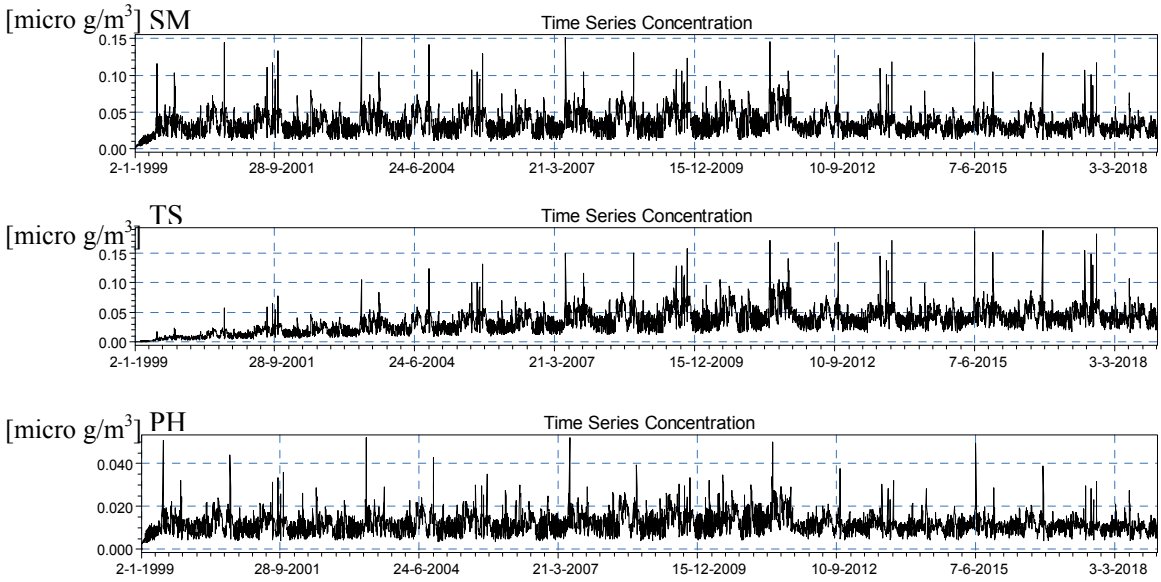

Figure 3.34. Simulated concentrations of adsorbed microconstituents in suspended sediments in the canal at the hypothetical reclaimed water discharge location. SM, sulfamethoxazole; TS, triclosan; PH, phenol.

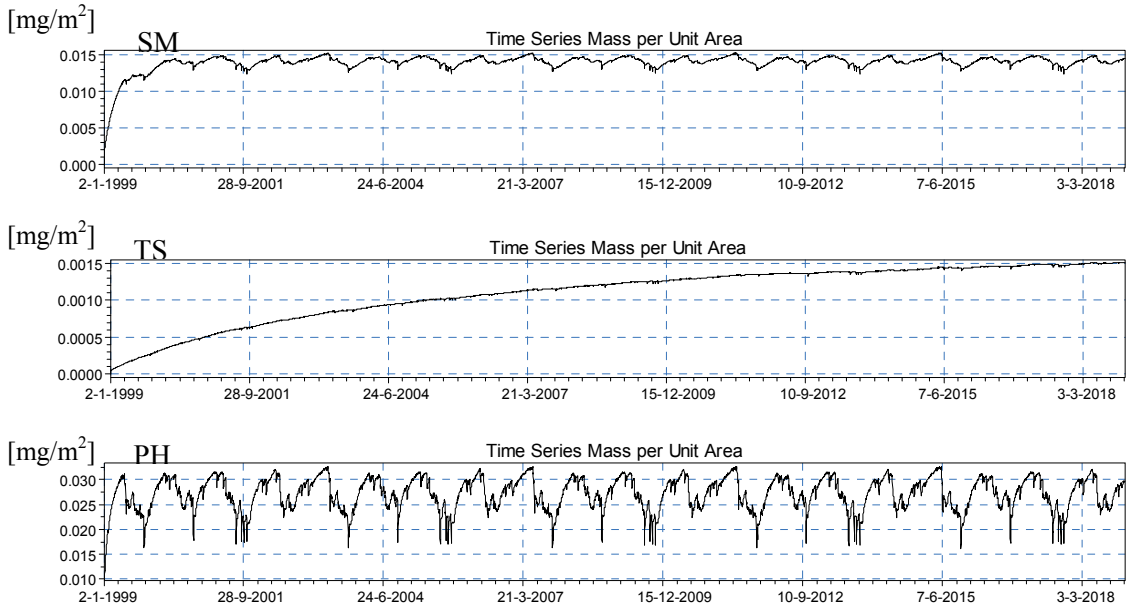

Figure 3.35. Simulated mass of dissolved microconstituents per unit area in the sediment layer pore water in the canal at the hypothetical reclaimed water discharge location. SM, sulfamethoxazole; TS, triclosan; PH, phenol.

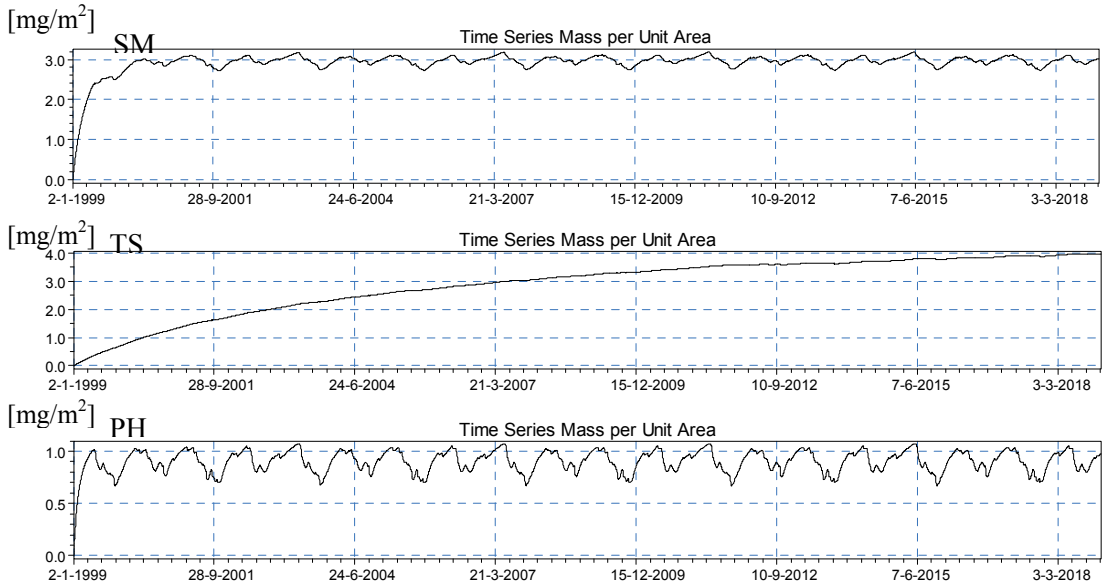

Figure 3.36. Simulated mass of adsorbed microconstituents per unit area in the sediment layer in the canal at the hypothetical reclaimed water discharge location. SM, sulfamethoxazole; TS, triclosan; PH, phenol.

The concentration of the dissolved microconstituents predicted by the model at the hypothetical reclaimed water discharge location decreases for deeper groundwater layers, as shown in Figure 3.37. In that figure, a logarithmic scale was used in order to display the low concentrations found in groundwater. It is clear from those graphs that adsorption plays an important role in the vertical variation of the concentration. Since the model assumes no degradation in groundwater layers, the mass of dissolved contaminants in cells with no extraction wells can be transported only by AD processes and also adsorbed onto the soil's porous surface, depending on its adsorption coefficient value. Starting from a zero-concentration model causes the concentrations to increase systematically in groundwater cells. Thus, adsorption represents a sink in the dissolved mass balance equation and a higher adsorption coefficient causes a slower spreading of the contaminant in the groundwater layers. As a result, the groundwater concentration at a given time is higher for the CT and lower for other microconstituents as the adsorption coefficient increases. For the microconstituents in the model, the adsorption coefficient increases in the following order: phenol, sulfamethoxazole, and triclosan.

Groundwater microconstituent transport in the horizontal direction is illustrated in Figure 3.38. This figure shows the spatial distribution of the concentration for the CT and the three microconstituents for groundwater layer 3 at the end of the 20-year simulation period. The results are shown for layer 3 because it is where most of the groundwater extraction occurs in the model. Notice that a linear color scale for the concentration was used for the CT and logarithmic ones for the others. Similar to the vertical direction, the adsorption is important in the horizontal spreading of microconstituents. In the case of no adsorption (CT), the model predicts a wide plume shifted to the east from the WWTP effluent location and covering three of the four wellfields. However, for the other three microconstituents, the higher concentrations are detected mostly below the canal branches and they are several orders of magnitude lower than the WWTP effluent concentration.

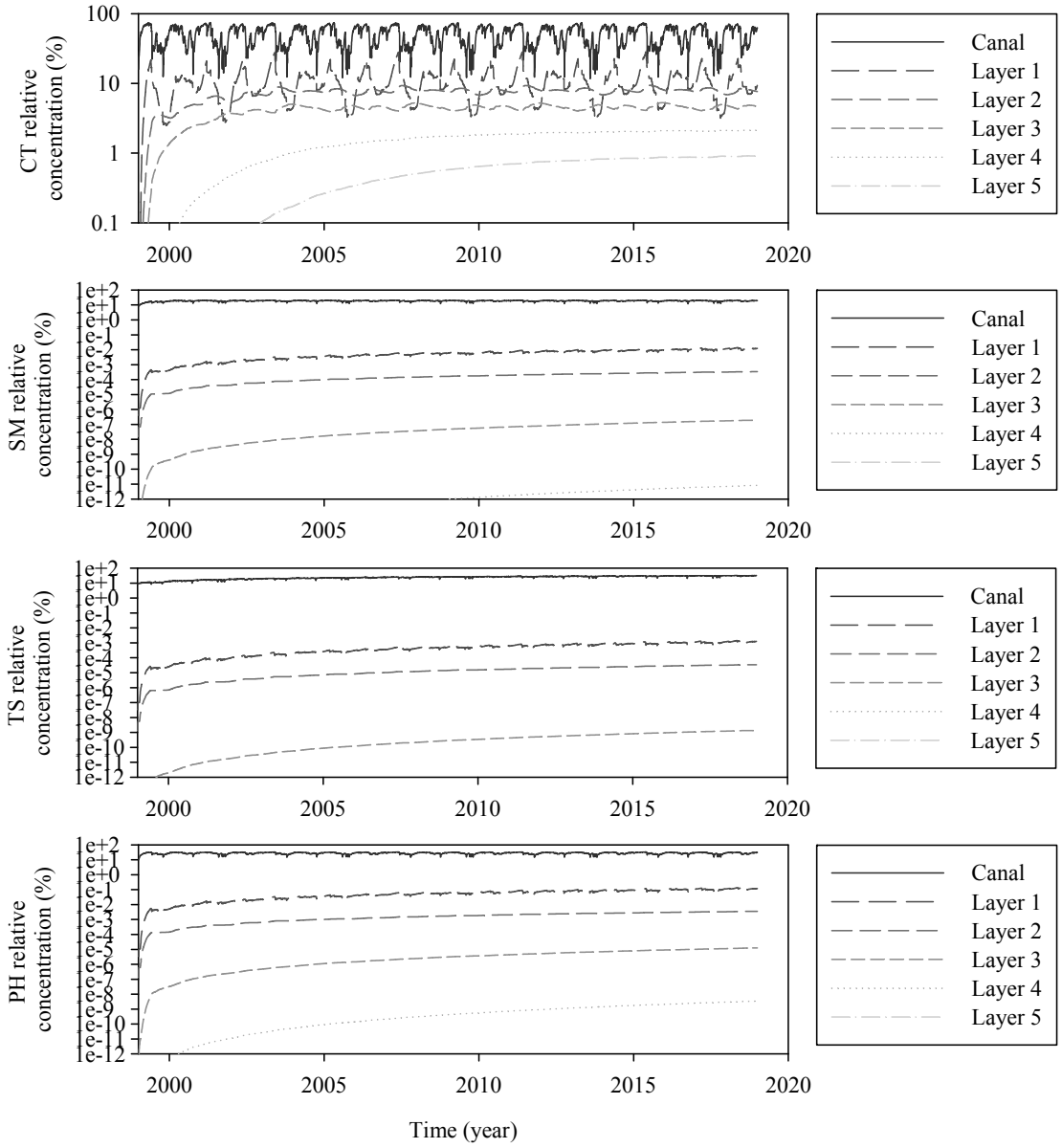

Figure 3.37. Evolution of the relative concentration at the hypothetical reclaimed water discharge location for the canal water and the different groundwater (computational) layers. SM, sulfamethoxazole; TS, triclosan; PH, phenol.

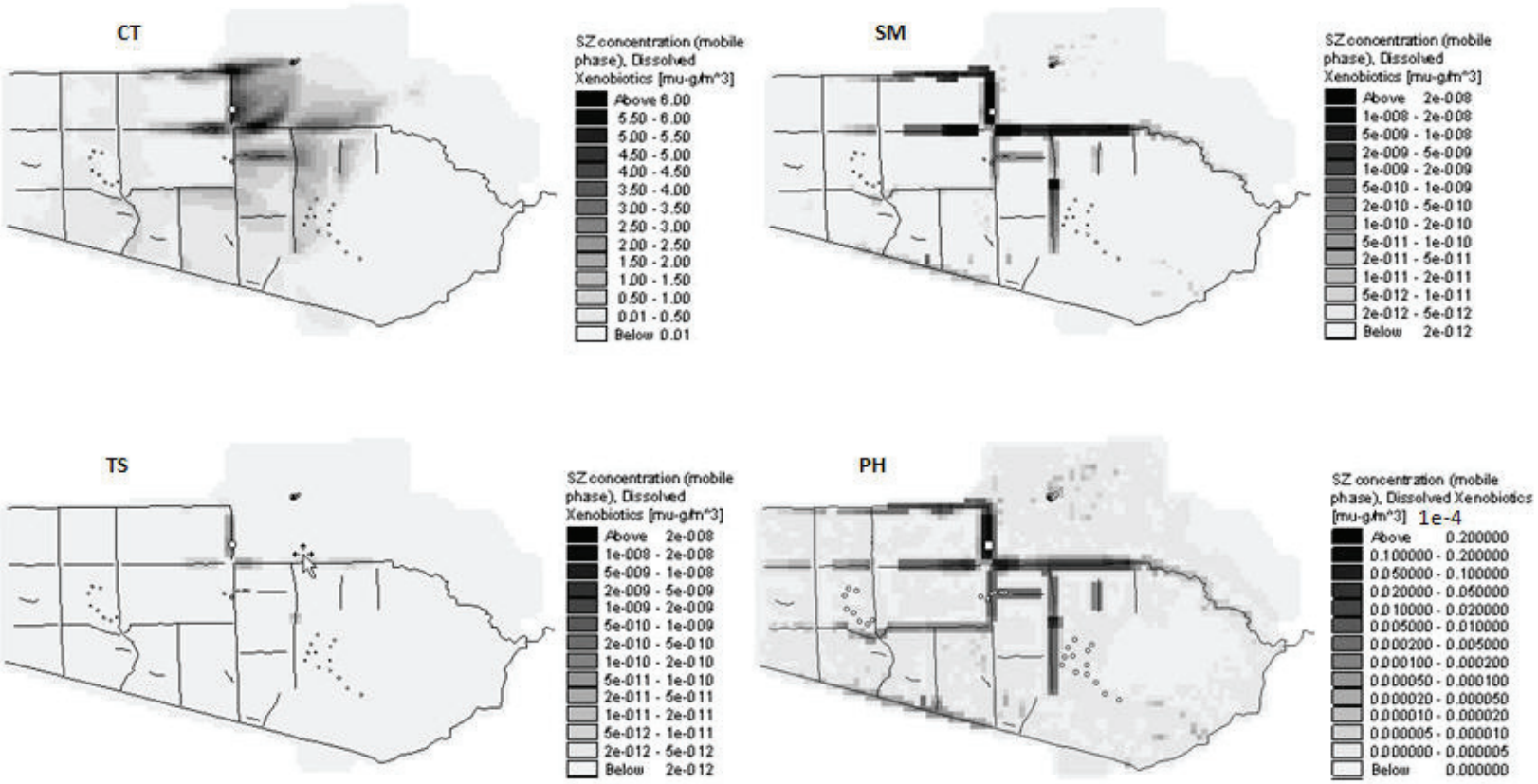

Figure 3.38. Simulated concentration of microconstituents in groundwater layer 3 at the end of the 20-year simulation period. The white square represents the WWTP effluent, and the small white squares represent the extraction wells. SM, sulfamethoxazole; TS, triclosan; PH, phenol; SZ, saturated zone.

Finally, the distribution of the concentration of the different microconstituents in the river network is presented in Figures 3.39 to 3.43.

Two dates at the end of the dry and the wet season of the last year of the simulation period were selected. The graphs illustrate that there are bigger differences in the concentration between the two dates for the CT case, where the adsorption coefficient is assumed negligible. Moreover, the spreading of the microconstituents in the river network is higher for CT and decreases for phenol, sulfaxmethoxazole, and triclosan, in that order. This finding suggests that the spreading in the canal network is more influenced by the adsorption coefficient than by the total decay rate in the model conditions and within the simulation period (20 years). In other words, this finding is a sign that the model still may be transiting from the zero-concentration conditions to stable concentration values. This statement is true at least for the triclosan.

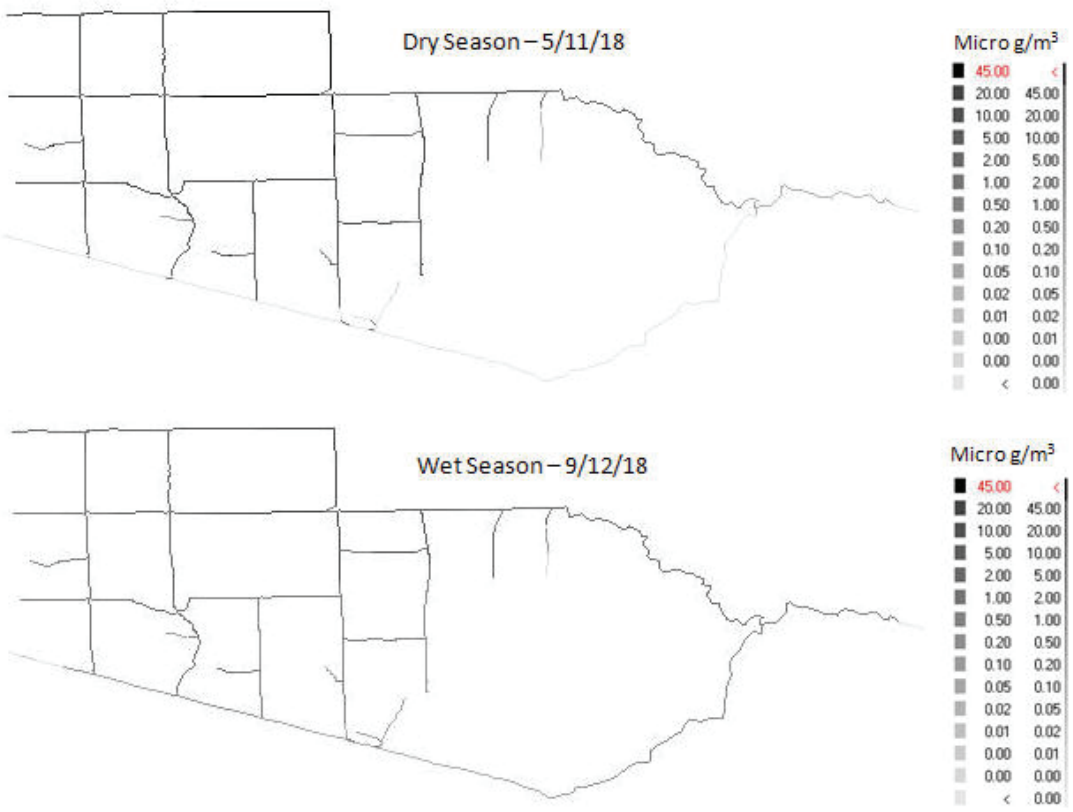

Figure 3.39. CT concentration in the canal network on two dates during the last year of the simulation period.

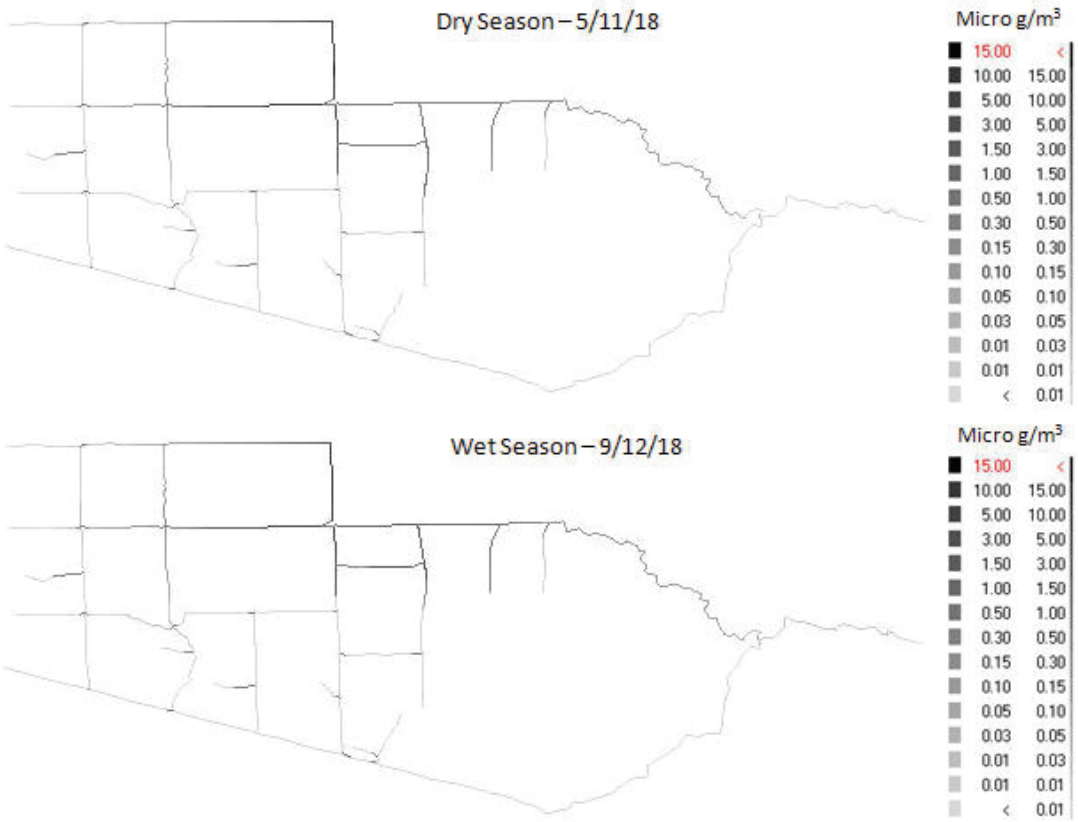

Figure 3.40. Sulfamethoxazole concentration in the canal network on two dates during the last year of the simulation period.

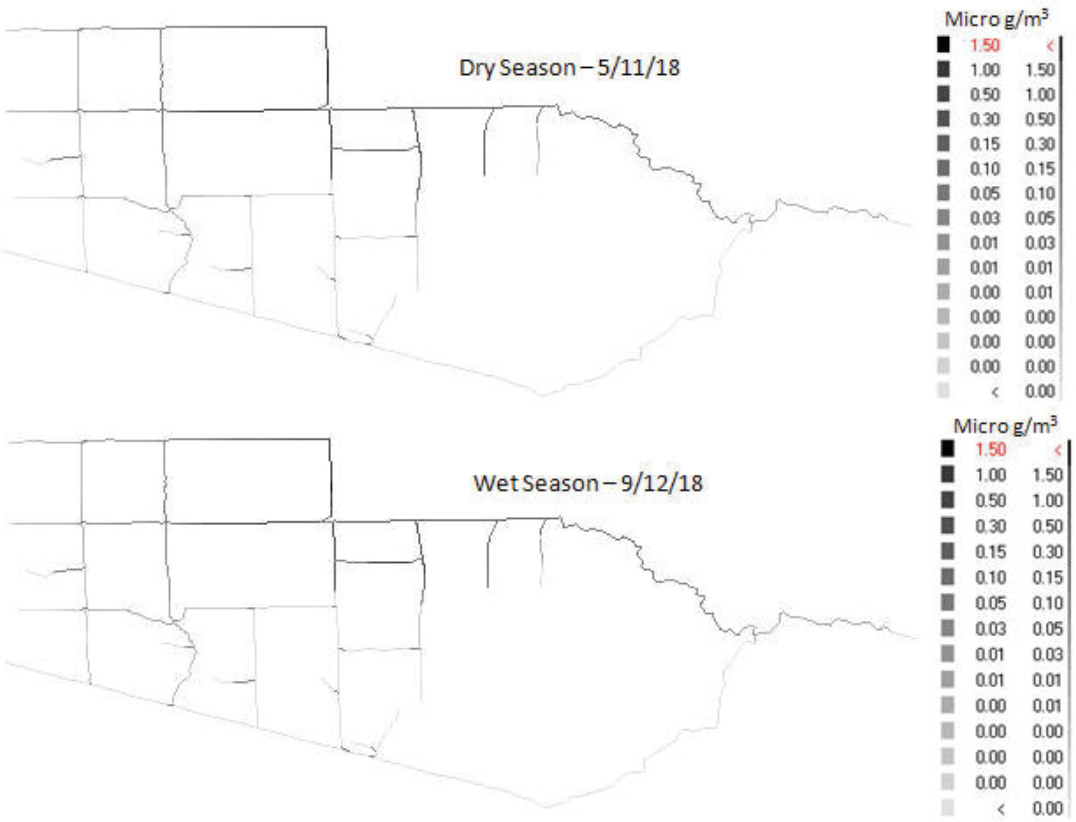

Figure 3.41. Triclosan concentration in the canal network on two dates during the last year of the simulation period.

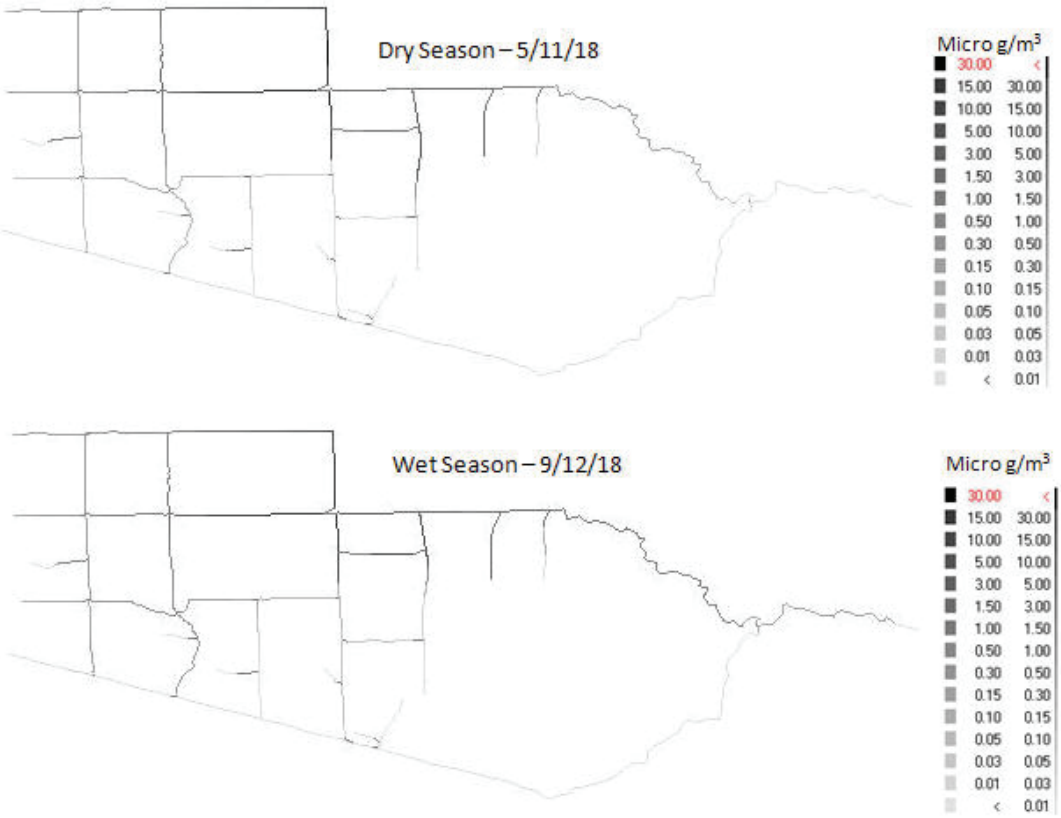

Figure 3.42. Phenol concentration in the canal network on two dates during the last year of the simulation period.

Finally, a sketch of the mass balance for the entire MIKE SHE model domain for the last year of the simulation period is presented in Figure 3.43. The mass balance for CT reveals that the mass is more distributed in the model, causing that 2.39% of the mass discharged from WWTP to be extracted in potable water supply wells. However, in the case of the other microconstituents, this mass fraction is negligible. Another difference is that the mass stored in groundwater layers during that period is dissolved for CT but mostly adsorbed for the other three cases, where the dissolved amount is negligible. Finally, notice that the amount adsorbed in the groundwater layer represents a mass fraction from 0.12% to 2.41% and that it is correlated to the adsorption coefficient for those three microconstituents.

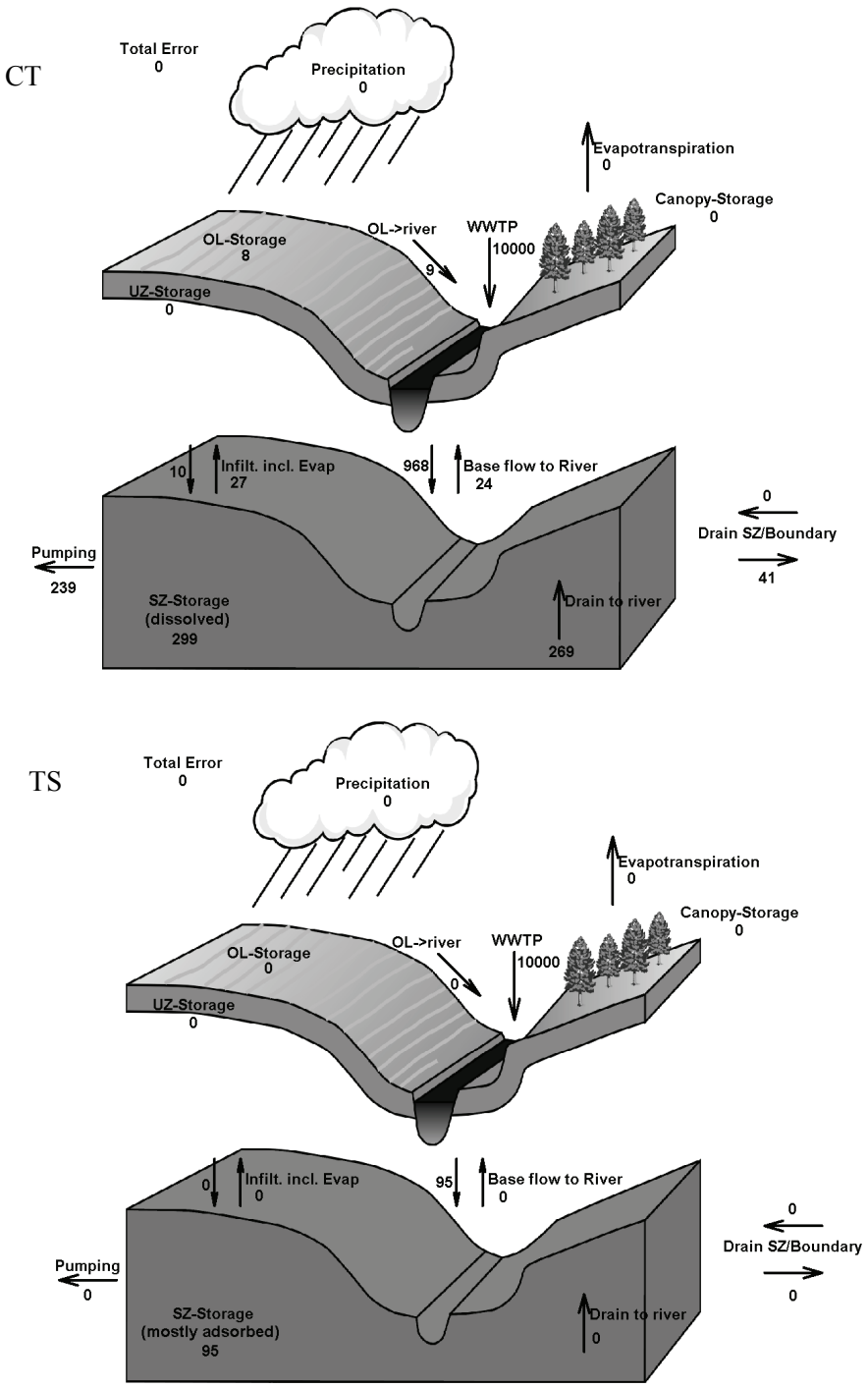

Figure 3.43. Mass balance for the CT and microconstituent models during the last year of the simulation.

Values are in relative mass units assuming a value of 10,000 discharged from the WWTP into the river network during that period. PH, phenol; OL, overland layer; UZ, unsaturated zone; SZ, saturated zone; SM, sulfamethoxazole; TS, triclosan.

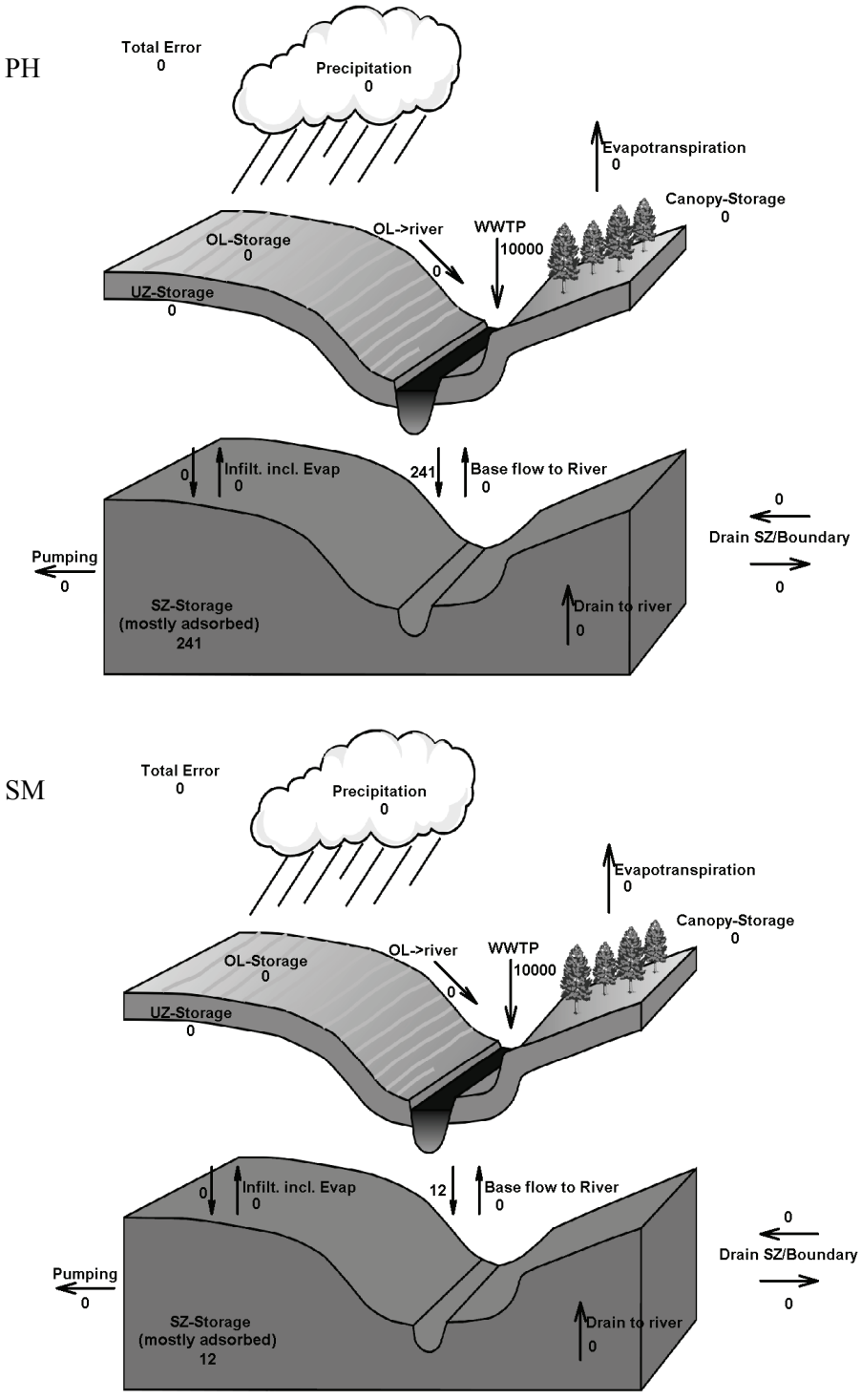

Figure 3.43. ***Continued.***

3.7.3 Summary of Recharge Modeling and Future Work

A water quantity and quality model was built to study the transport of the microconstituents discharged from the City of Plantation AWT in the surface water canals and the Biscayne Aquifer. The water quality model developed predicts that adsorption plays an important role in the transport of the microconstituents in the canal network as well as in the aquifer system. The model species sorted from lower to higher adsorption coefficients are the CT, phenol, sulfamethoxazole, and triclosan. A higher adsorption coefficient decreases the fluctuations in the dissolved concentration in the canals, which is likely a consequence of the adsorbed mass in the sediment layer acting as a buffer. For triclosan, which has the highest adsorption coefficient, stable concentrations were reached in the Holloway canal (at the WWTP effluent location) at the end of the simulation. These results confirm that the value of the adsorption coefficient influences how fast the dissolved concentration changes in the river network.

The spreading of the contaminant in the river network was found higher for lower adsorption coefficients. This finding is an indication that the river network may be still transiting from the zero-concentration condition to stable concentration values.

In groundwater, adsorption also plays an important role in the vertical and horizontal spreading of the contaminant. A higher adsorption coefficient causes a slower spreading of the microconstituents in the groundwater layers. For the microconstituents where adsorption is not neglected (phenol, sulfamethoxazole, and triclosan), the concentration decreases in orders of magnitude from one groundwater layer to a deeper one in the 20-year simulation period. In the horizontal direction, the higher concentrations were obtained mainly below some of the canal branches. Even so, the concentrations at extraction well depths (groundwater layer 3 of the model or below) are several orders of magnitude lower than the one assumed from the WWTP effluent.

While the adsorption process reduces the speed of the concentration changes, the total degradation rate determines the typical concentration values obtained in the canal at the WWTP effluent at the end of the simulation period. In other words, the higher the total degradation rate at the surface water caused by biotransformation, photolysis, and evaporation, the lower the typical concentration of the microconstituent in the canal network obtained after the period where adsorption rules the transition from the initial conditions.

The water quality model is not calibrated, and a future effort should be focused on collecting the data necessary to perform calibration. It would be useful to obtain measurements of the water discharge rates from the WWTP as well as the concentration of the microconstituents of interest. In addition, measurements of the microconstituent concentrations in surface water canals and in groundwater observation and supply wells, the dissolved fraction, and the suspended particle concentration at various canal locations and at different times would be also valuable for model calibration.

The model results indicate that adsorption is the dominant process in the microconstituent spreading. Please note that the most conservative case for biotransformation is evaluated and that the biodecay rate is considered to be zero for all six microconstituents except for phenol. Thus, further efforts can be directed to a better estimation of the related parameters such as biotransformation rate constants and the mass organic fraction and bulk density in groundwater layers and in the sediment layer.

Finally, the current model does not consider the suspended sediment transport in the water flow from the overland surface and drain features into the canals. Thus, surface runoff in the model provides sediment-free water to the canals, neglecting overland erosion. This limitation can be removed by estimating time-dependent sediment particle concentrations from the overland water inflow rates to the river network and setting them as boundary conditions in MIKE 11.

CHAPTER 4

PROJECT CONCLUSIONS

The objectives of this study were to evaluate the removal of microconstituents through AWT facilities, investigate the potential impact of microconstituents to aquatic organisms, and examine the fate and transport of select microconstituents from a hypothetical canal discharge location to a drinking water aquifer with a hydrodynamic and water quality model.

The results indicate that almost all microconstituents were effectively removed by RO in AWT facilities and that RO effluent posed no hormonal threat to tissue cultures and live fish. The observed toxicity to aquatic organisms was likely caused by chloramines, which are used to prevent membrane fouling, and not by the presence of microconstituents. Furthermore, toxicity was significantly reduced after quenching (dechlorination) of chloramine. Hydrodynamic models and water quality models can help us evaluate the fate and transport of microconstituents and the impact of discharged reclaimed water.

4.1 AQUATIC AND HUMAN HEALTH IMPACT POTENTIAL

Microconstituents can originate from numerous sources; enter the environment by many routes; and are present in WWTP effluent, surface water, groundwater, reuse water, and drinking water (usually at concentrations in the nanograms-per-liter range). Some microconstituents occurring at or above 0.1 ng/L may cause endocrine disruption in fish and other aquatic life (Purdom et al., 1994; Vanderford, 2003), but there is little evidence to suggest that typical low-level environmental exposures to microconstituents cause any adverse human health effects (Damstra et al., 2002). The long-term human health impact of trace levels of microconstituents deserves further investigation.

4.2 MICROCONSTITUENT REMOVAL

The results of treatment testing showed that, although select microconstituents may pass through RO membranes at very low levels, most microconstituents are completely removed by RO membranes. For an additional barrier to microconstituent breakthrough, additional processes can be considered, including conventional activated sludge, coagulation, activated carbon adsorption, MBR processes, O_3/H_2O_2/UV oxidation, chlorination, membrane filtration, enzymatic treatment, and ferrate(VI) oxidation. Most of these processes can effectively remove microconstituents, for example, advanced oxidation technologies are well proven to destroy microconstituents that may pass through RO systems.

All three systems (MBR/RO, DNF/UF/RO, and IMANS®) tested during this project effectively removed microconstituents and reduced BOD_5, TSS, TDS, and turbidity. The BOD_5 values of most MBR effluent samples and UF effluent samples were below detection limits (2 mg/L), and the BOD_5 values of all RO effluent samples were below detection limits. The TSS values of MBR effluent, UF effluent, and RO effluent were all below detection limits (1 mg/L). The TDS values of MBR effluent, UF effluent, and RO effluent were all below 0.88 NTU. The water quality of RO effluent in AWT facilities was higher than that of canal water. The TSS and BOD_5 values and turbidities in RO effluent samples were all below

1 mg/L, 2 mg/L, and 0.44 NTU, respectively. These numbers were much lower than those of the canal water (TSS: 7.0 mg/L; BOD_5: 5.27 mg/L; turbidity: 7.67 NTU). In addition, the PSDs of RO effluent were not significantly different from those of distilled water according to the Student *t* test. All of these results suggest that the discharge of reclaimed RO water would not degrade the water quality of surface canals and that any of the three tested systems can be used to remove microconstituents to improve the quality of reclaimed water for surface water augmentation.

4.3 TOXICITY TESTING

The chronic toxicity tests included chronic survival and growth tests for *P. promelas* and chronic survival and reproduction tests for *C. dubia*. The survival of *P. promelas* and *C. dubia* in RO effluent was low during the first toxicity test, a result likely caused by chloramine in RO effluent. Additional tests on RO effluent samples that were quenched with sodium thiosulfate significantly reduced toxicity and increased the survival of *P. promelas* and *C. dubia* in RO effluent. The final batch of toxicity experiments without chloramine indicated that there was no significant difference in RO effluent and control (deionized) water for the survival and growth of *P. promelas* and survival and reproduction of *C. dubia*. Similarly, there were no significant differences in surface (canal) water and control (deionized) water for the survival and growth of *P. promelas* and survival and reproduction of *C. dubia*. This result suggests that discharge of reclaimed water (RO effluent that is properly stabilized) would have no adverse toxic effect on aquatic organisms, provided that chloramine was not used or was properly quenched. However, unquenched chloramines or trace levels of ammonia in AWT facilities may contribute to the toxicity to *C. dubia* and should be removed by break point chlorination followed by dechlorination, advanced oxidation, or another quenching method.

4.4 IN VIVO AND IN VIVO TESTING

The endocrine disrupting potential of microconstituents in RO effluent was evaluated with an E-Screen bioassay, YES assay, fathead minnow Vtg assays, and steroid immunoassays. The results of E-Screen bioassays showed that estradiol equivalents in all RO effluent samples were below detection, while estradiol equivalents were detected in secondary effluent, DNF effluent, MBR effluent, and UF effluent. The results of the E-Screen bioassay indicate that RO effluent did not provoke a significant response in MCF-7 cells. The YES bioassay showed that estradiol equivalents of RO effluent were below detection, while estradiol equivalents were detected in secondary effluent and DNF effluent. Vtg assays and steroid immunoassays did not show an increase of plasma Vtg in male fish. Steroid immunoassays showed that the testosterone response in samples from all treatment processes was similar to those in the negative control group and that there was no significant difference in plasma testosterone between any of the treatments and negative controls. All of these results suggest that RO effluent was not estrogenic.

Although the effluent of the nonbiological membrane process (IMANS®) contained a few microconstituents, their impact on endocrine disrupting potential was negligible. Therefore, biological processes (as part of secondary treatment) may not be necessary for the removal of microconstituents and estrogenic activity, as long as there is a RO step in the process.

4.5 MODELING RESULTS

Three compounds (sulfamethoxazole, triclosan, and phenol) were selected as representative microconstituents for model development based on their physicochemical properties. Hydrodynamic and water quality models were developed to examine the fate and transport of these simulated microconstituents from the AWT facilities through surface canals. The hydrodynamic model was run for a 2-year period by using historical data in 2001 and 2002, and the results indicated that the groundwater results follow the observed data closely. The hydraulic model includes the primary and secondary canals and main hydraulic structures (weirs, culverts, pumps, and gates) for these canals. It was shown that the surface water results are very sensitive to the structure operations. The water quality model predicted that adsorption plays a dominant role in the transport of the microconstituents in the canal network as well as in the aquifer system. While less significant, various pathways of decay do impact the fate and transport of microconstituents. In this study, biotransformation was not considered (biodecay rate: 0). Therefore, the modeling prediction is conservative and dominated by adsorptive processes.

Transport of microconstituents in the canal network was found to be lower for compounds with higher adsorption coefficients. The higher adsorption coefficient reduces the fluctuations in the dissolved concentration in the canals, an occurrence that is likely a consequence of the adsorbed mass in the sediment layer acting as a buffer. The water quality model was not calibrated; future efforts should focus on collecting the data necessary to perform this calibration. Additional work can be done to better estimate related parameters such as microconstituent biotransformation rate constants and the mass organic fraction and bulk density in groundwater sediment layers.

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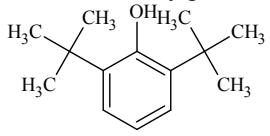
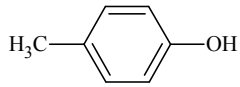
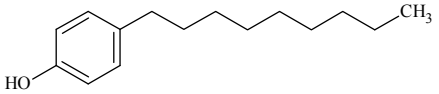
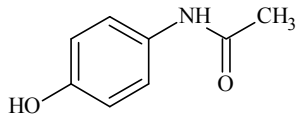
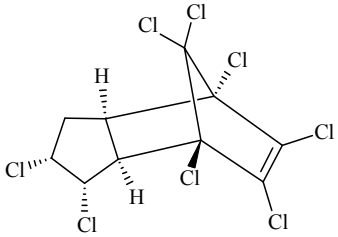
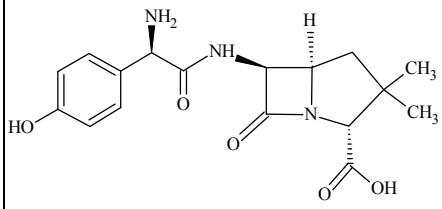
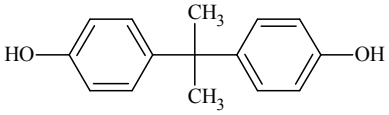
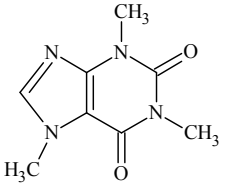
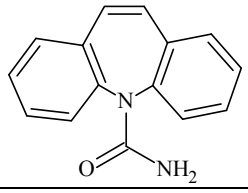
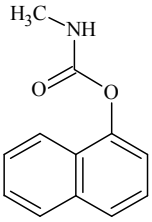
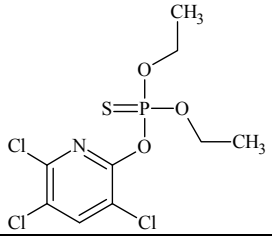
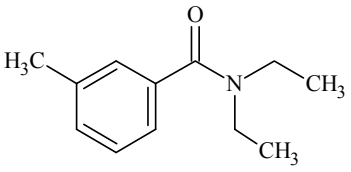
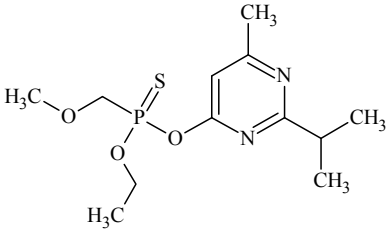
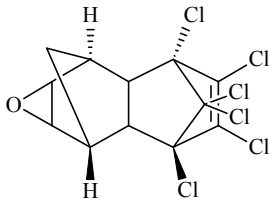
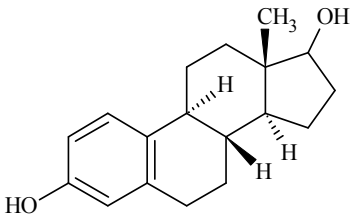
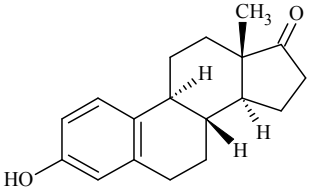
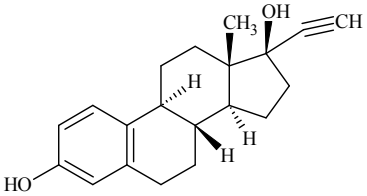
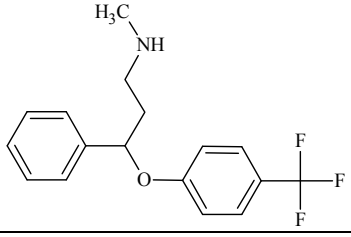
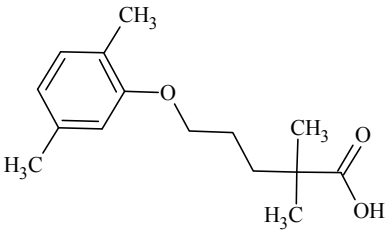
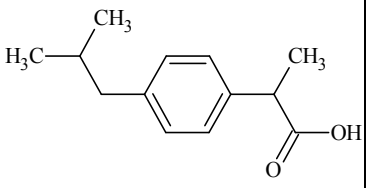
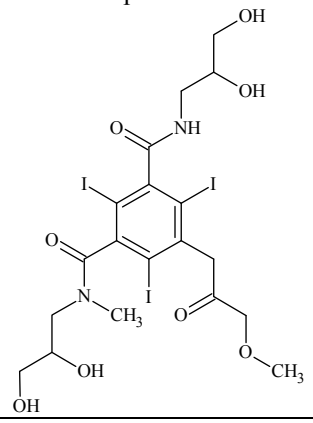
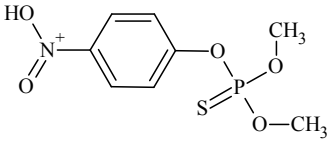
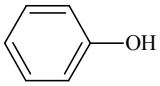
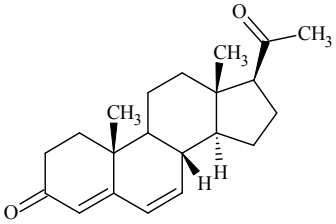
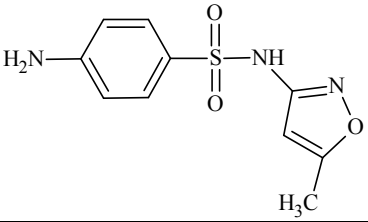
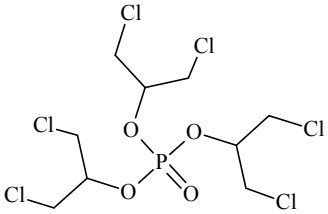
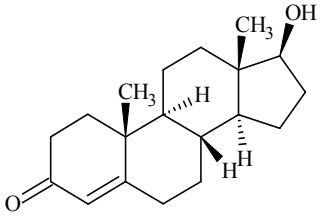
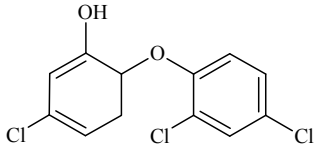
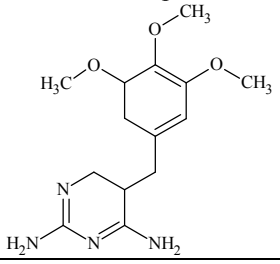
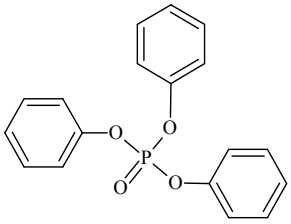
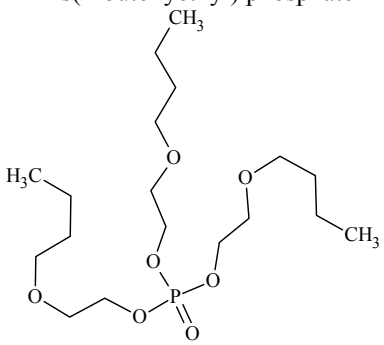
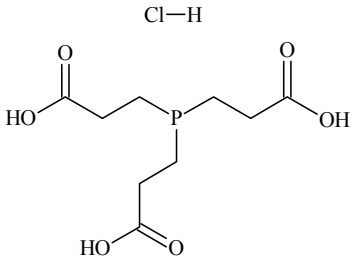
APPENDIX A

CHEMICAL STRUCTURES OF EXAMINED MICROCONSTITUENTS

2,6-di-*tert*-Butylphenol 	4-Methylphenol 	4-Nonylphenol 
Acetaminophen 	Alpha chlordane 	Amoxicillin 
Bisphenol A (BPA) 	Caffeine 	Carbamazepine 
Carbaryl 	Chlorpyrifos 	*N,N*-Diethyl-*m*-methylbenzamide (DEET) 
Diazinon 	Dieldrin 	Estradiol (E3) 
Estrone (E1) 	17α-Ethinylestradiol (EE2) 	Fluoxetine 

Gemfibrozil 	Ibuprofen 	Iopromide 
Methyl parathion 	Phenol 	Progesterone (PS) 
Sulfamethoxazole 	Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) 	Testosterone 
Triclosan 	Trimethoprim 	Triphenyl phosphate 
Tris(2-butoxyethyl) phosphate 	Tris(2-chloroethyl) phosphate 	

PubChem Project, 2010.

APPENDIX B

MICROCONSTITUENT PROPERTIES FOR RECHARGE MODELING

Compound	Sulfamethoxazole	
CAS Number	723-46-6	
Aerobic degradation	Sulfamethoxazole is biodegradable under aerobic conditions in an adapted activated sludge culture. Lag period before initiation of degradation was 4 days (Drillia et al., 2005). Thirty-two to 49% was removed during secondary treatment. Tertiary treatment by sand filtration (hydraulic retention time, 25 min) did not affect the concentration (Göbel et al., 2007). In lab studies no significant biotransformation was found in pond water over a period of 30 days (Lam et al., 2004). A field investigation showed that 4 of 54 studied PPCPs were found below a treated sewage infiltration site (45 years of operation). Three meters below the groundwater table (unsaturated zone, 1.5 to 2 m), sulfamethoxazole concentrations were between 0% and 20% of input concentrations (Ternes et al., 2007).	
Anaerobic degradation	NA[a]	
Photolysis degradation	Sulfamethoxazole (SMX) in its nonionized form in aqueous solution has UV adsorption that is maximal at 268 nm but extends through the UV B region (Moore and Zhou, 1994). Half-lives in synthetic field water are between 2.7 and 6.6 h depending on the DOM content (Lam and Mabury, 2005). Mean half-life in 12-m^3 microcosms with fish, aquatic plants, zooplankton, phytoplankton, macrophytes, and bacteria was 19 days (Lam et al., 2004).	
Hydrolysis	NA[a]	
Chemical behavior	K_d	NA[a]
	K_{oc}	NA[a]
	Log K_{ow}	0.89[b]
	H	NA[a]
	pK_a	6[b]

[a]NA: not available.
[b]HSDB, 2008.

Compound	Triclosan	
CAS Number	3380-34-5	
Aerobic degradation	Aerobic biotransformation in soil, 17.4- to 35.2-day half-life (Morrall et al., 2004). A study designed to determine the die-away rate of triclosan released into a river as part of the sewage treatment plant effluent matrix determined a first-order loss rate from measured data of 0.06 h^{-1}. Mathematical modeling indicated that sorption and settling accounted for approximately 19% of total triclosan loss over 8 km. When sorption and settling were removed, the remaining amount of triclosan had an estimated first-order loss rate of 0.25 h^{-1} (Morrall et al., 2004).	
Anaerobic degradation	Triclosan is not readily or inherently degradable in standardized screening tests like OECD 301C (MITI I) or OECD 302C (MITI II). The negative results in these tests may be a consequence of the bacterial toxicity of triclosan at the high substrate concentration required for these biodegradability screening tests (Samsøe-Petersen et al., 2003).	
Photolysis degradation	Aqueous photolysis, 41-min half-life at pH 7 and 25 °C (Samsøe-Petersen et al., 2003). Environmental abiotic degradation: The rate constant for the vapor phase reaction of triclosan with photochemically produced hydroxyl radicals has been estimated as 1.6×10^{-11} cu. cm/molecule-s at 25 °C if one uses a structure estimation method. This value corresponds to an atmospheric half-life of about 8 h at an atmospheric concentration of 5×10^5 hydroxyl radicals per cu. cm. A direct photolysis rate of 0.07/day was measured by using a water sample from Greifensee, Switzerland, tested under laboratory conditions, corresponding to a photolysis half-life in water of 10 days; the elimination rate sum of different transport and transformation processes in this lake is 0.03/day, corresponding to a half-life of 21 days.[a]	
Hydrolysis	Triclosan is stable against hydrolysis in the environment because of its stability against strong acids and bases.[b]	
Chemical behavior	K_d	NA[b]
	K_{oc}	47,454 mL/g (Morrall et al., 2004)
	Log K_{ow}	4.8 (Morrall et al., 2004)
	H	NA[b]
	pK_a	7.9[a]

[a]HSDB, 2008.
[b]NA: not available.

Compound	Ibuprofen	
CAS Number	15687-27-1	
Aerobic degradation	OECD Guideline 301B "Ready Biodegradability" Modified Sturm test (CO_2 evolution) degraded after 28 days. Aerobic; activated sludge, 20 mg/L: 10 to 60.[a] A half-life of 20 days was determined from a study using water samples from Lake Greifensee, Switzerland, that were incubated at room temperature for 37 days with 200 ng of racemic ibuprofen/L.[c] A field investigation showed that 4 of 54 studied PPCPs were found below a treated sewage infiltration site (45 years of operation). Three meters below the groundwater table (unsaturated zone, 1.5 to 2 m), ibuprofen was undetectable. Input concentrations were in the range of 0.1 µg/L (Ternes et al., 2007).	
Anaerobic degradation	NA[b]	
Photolysis degradation	Ibuprofen is not expected to directly photolyze because of the lack of adsorption in the environmental UV spectrum (>290 nm).[a] The rate constant for the vapor phase reaction of ibuprofen with photochemically produced hydroxyl radicals has been estimated as 1.2×10^{-11} cu. cm/molecule-s at 25 °C. This finding corresponds to an atmospheric half-life of about 32 h at an atmospheric concentration of 5×10^5 hydroxyl radicals per cu. cm.[a]	
Hydrolysis	Carboxylic acids are generally resistant to hydrolysis. Therefore, hydrolysis is not expected to be an important process for removal of ibuprofen from water systems.[b]	
Chemical behavior	K_d	NA[b]
	K_{oc}	9,333[c]
	Log K_{ow}	3.94 at 37 ºC[a], 3.97[d]
	H	NA[b]
	pK_a	4.54 at 25 ºC[a], 4.91–5.2[d]

[a]ESIS, 2010.
[b]NA: not available.
[c]Interactive PhysProp Database Demo, 2010.
[d]HSDB, 2008.

Compound	4-Nonylphenol	
CAS Number	104-40-5	
Aerobic degradation	Biotransformation of *p*-nonylphenol will occur rapidly in aerobic soils but is inhibited under anaerobic soil conditions.[a] Degradation of 4-nonylphenol has been investigated in the laboratory by using sediment and groundwater from an aquifer in Bolivar, South Australia. 4-nonylphenol degraded quickly under aerobic conditions with a half-life of 7 days (Ying et al., 2003).	
Anaerobic degradation	See above	
Photolysis degradation	Environmental abiotic degradation: *p*-nonylphenol should not be susceptible to direct photolysis based upon its lack of adsorption of light at wavelengths of >290 nm.[a] Nonylphenol is susceptible to indirect photolysis. The rate depends on initial concentration; pH; temperature; and concentrations of H_2O_2, Fe^{3+}, and DOM. Half-lives in samples of the River Rhine and Hohloh Lake irradiated in a solar UV simulator were 30 and 178 days (Neamtu and Frimmel, 2006). Sunlight phototransformation of nonylphenol was performed in quartz tubes, which were suspended in a shallow flat-bottomed container filled with tap water or in Chriesbach Creek. Half-lives of 10 to 15 h under continuous clear sky, noon, and summer sunlight were found in the surface layer of natural waters were found. At a depth of 20 to 25 cm, half-lives were 1.5 times longer (Ahel et al., 1994).	
Hydrolysis	NA[b]	
Chemical behavior	K_d	NA[b]
	K_{oc}	575,440[c]
	Log K_{ow}	5.76
	H	3.4×10^{-5} atm-cu. m/mol[a]
	pK_a	NA[b]

[a]HSDB, 2008.
[b]NA: not available.
[c]Interactive PhysProp Database Demo, 2010.

Compound	Methyl parathion	
CAS Number	298-00-0	
Aerobic degradation	Half-lives in river sediments between 3 and 6 days. Studies of five different soils showed half-lives between 3.5 days and 18 days. The same soils when waterlogged, indicating anaerobic conditions, showed half-lives between 2.3 and 22 days in four soils and 275 days in the fifth soil.[a]	
Anaerobic degradation		
Photolysis degradation	Direct photolysis does not appear to be a significant transformation process in soils. Photolysis studies of methyl parathion have been reported. A study examining the photodegradation of methyl parathion in river water and seawater at variable temperatures showed the half-lives to be 11 and 34 days, respectively. In a photolysis study of methyl parathion in freshwaters of Portugal, a half-life of 3 days in groundwater and a half-life of 4 days in river water were observed.	
Hydrolysis	Methyl parathion is rapidly degraded in natural water systems. The degradation of methyl parathion occurs much more rapidly in alkaline (pH 8.5) than in neutral (pH 7) or acidic (pH 5) conditions (Badawy and el-Dib, 1984). A hydrolysis half-life of 72 to 89 days was calculated for freshwater at 25 ºC and pH < 8 (EPA, 1978; Mabey and Mill, 1978), compared with about 4 days at 40 ºC and pH 8 (EPA, 1978).[b] The degradation of methyl parathion by hydrolysis and biotransformation was studied in four types of water (ultrapure water, pH 6.1; river water, pH 7.3; filtered river water, pH 7.3; and seawater, pH 8.1) maintained at 6 and 22 ºC in the dark. The half-lives of methyl parathion at 6 ºC in the four water types were determined to be 237, 95, 173, and 233 days, respectively, and the half-lives at 22ºC were determined to be 46, 23, 18, and 30 days, respectively. The study shows that degradation rates increase with pH and temperature and are highest in river water.[b]	
Chemical behavior	K_d	NA[c]
	K_{oc}	2.7[b]
	Log K_{ow}	2.86[b]
	H	6.2×10^{-6} to 4.4×10^{-7} atm m^3/mol[b]
	pK_a	3.8[d]

[a]HSDB, 2008.
[b]ATSDR, 2008.
[c]NA: not available.
[d]EXTOXNET, 2010.

Compound	Phenol	
CAS Number	108-95-2	
Aerobic degradation	Available data indicate that phenol biodegrades in soil under both aerobic and anaerobic soil conditions. The half-life of phenol in soil is generally < 5 days (Baker and Mayfield, 1980), but acidic soils and some surface soils may have half-lives of up to 23 days (Shiu et al., 1994). Mineralization in an alkaline, parabrown soil under aerobic conditions was 45.5, 48, and 65% after 3, 7, and 70 days, respectively.[a]	
Anaerobic degradation	While degradation is slower under anaerobic conditions, evidence presented in the literature suggests that phenol can be rapidly and virtually completely degraded in soil under both aerobic and anaerobic conditions.[a] Anaerobic degradation to carbon dioxide or methane also occurs (IPCS, 1994).	
Photolysis degradation	Phenol does not absorb light in the region of 290 to 330 nm; therefore, it should not photodegrade directly in the atmosphere.[a] Although phenol does not absorb light at wavelengths of >290 nm, phenols react rapidly to sunlit natural water via an indirect reaction with photochemically produced hydroxyl radicals and peroxyl radicals; typical half-lives for hydroxyl and peroxyl radical reactions are on the order of 100 and 19.2 h of sunlight, respectively (Canonica et al., 1995; Mill and Mabey, 1985). These reactions require dissolved natural organic materials that function as photosensitizers (Canonica et al., 1995). The estimated half-life for the reaction of phenol with photochemically produced singlet oxygen in sunlit surface waters contaminated by humic substances is 83 days.[a]	
Hydrolysis	No hydrolytic degradation is to be expected because of the chemical structure of the substance.[b]	
Chemical behavior	K_d	NA[c]
	K_{oc}	1.21–1.96[a]
	Log K_{ow}	1.46[a]
	H	0.022 Pa × m^3/ mol at 20 ºC[b]
	pK_a	10[a]

[a]ATSDR, 2008.
[b]European Union, 2006.
[c]NA: not available.

APPENDIX C

MODEL DEVELOPMENT

The hydrodynamic model and water quality were completed by DHI. The Plantation submodel was extracted from the Broward County model, which included the surface water and groundwater features as they have a direct hydraulic connection to the proposed discharge location, the East Holloway canal. Boundary conditions for the model area were extracted from the Broward model results for all of the groundwater and the surface water boundaries in the Plantation submodel. Three representative microconstituents (sulfamethoxazole, phenol, and triclosan) were selected for the water quality model based on their properties in photodegradation, sorption, and biotransformation, as well as for their detections as part of this project.

C.1 MIKE SHE/MIKE 11 HYDROLOGIC MODEL

The MIKE SHE/MIKE 11 model includes components that represent the important processes of the land phase of the hydrologic cycle. MIKE SHE/MIKE 11 can represent physical processes using a variety of numerical methods that range from conceptual subbasin-based lumped parameter approaches to physics-based and spatially distributed approaches. Processes that can be simulated with MIKE SHE/MIKE 11 include rainfall, evapotranspiration, overland flow, channel flow and hydraulic routing, infiltration, unsaturated zone flow, irrigation, and groundwater flow. The processes that can be simulated with MIKE SHE/MIKE 11 are conceptually shown in Figure C.1.

Because the important land-based hydrologic and hydraulic processes can be represented with MIKE SHE/MIKE 11, it can be used as a planning and management tool to address a wide range of water resources and environmental problems.

In addition, MIKE SHE/MIKE 11 includes comprehensive AD transport modules that were used in this project to evaluate the movement of microconstituents in the surface water and groundwater. The MIKE SHE and MIKE 11 AD models are fully coupled and are capable of simulating bidirectional mass transfers between the groundwater and surface water components in addition to transport within individual components.

DHI incorporated the appropriate algorithms in the water quality model (ECO Lab) coupled with MIKE 11 to simulate the fate and transport of the selected microconstituents in the canals and rivers. The fate and transport of microconstituents in the overland zone, unsaturated zone, and saturated zone (SZ) can be simulated in the groundwater and surface water bodies with MIKE SHE/MIKE 11. The MIKE SHE fate and transport modules allow conservative and simple reactive processes to be simulated, including:

- **AD** — basic AD solute transport module
- **Sorption/Degradation** — equilibrium/nonequilibrium adsorption and first-order degradation
- **Biotransformation** — advanced biological degradation

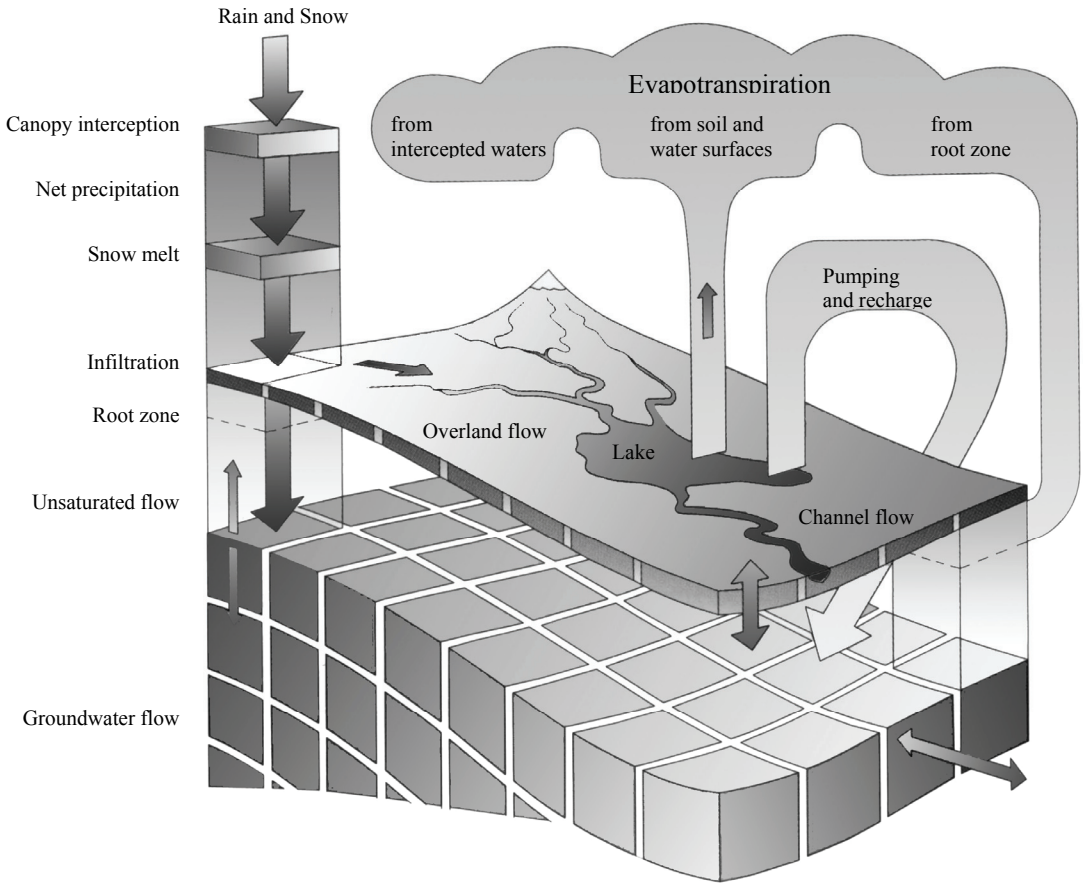


Figure C.1. Land-based hydrologic and hydraulic processes simulated with MIKE SHE/MIKE 11.

C.2 HYDRODYNAMIC MODEL

The Plantation hydrodynamic model maintains the same approach as the Broward County model. The MIKE SHE hydrologic model uses a 500-ft cell discretization, which pertains to the topography, the land use-based and soil-based parameters, and the hydrogeologic properties. The MIKE 11 hydraulic model includes the primary and secondary canals and main hydraulic structures (weirs, culverts, pumps, and gates) for these canals. The urban tertiary system is conceptually represented in both the MIKE SHE and MIKE 11 models, as explained below.

In the Broward model, each Water Control District (WCD) subbasin is represented as a runoff/drainage unit where a certain control elevation and a common drainage outlet(s) are defined. The subbasin outlets are typically the secondary canals located within the subbasin controlled by structures that maintain the control elevation for the basin. In the absence of a secondary system, the runoff and subsurface drainage for the subbasin are routed directly to the primary canals. Within the subbasin, runoff, evapotranspiration, infiltration, irrigation, groundwater pumpage, and groundwater flow are simulated for every 500-ft cell in the subbasin. The forces that drive these processes depend on the topographic gradients, the land use-based and soil-based parameters, and the hydrogeologic properties defined for each cell of the model.

In order to better handle the runoff of urban areas in the Broward model, the MIKE SHE Paved Area Runoff Module is used instead of the Overland Flow Module. Each subbasin is spatially represented in MIKE SHE by using a surface water-routing map that assigns a routing code for each grid cell in a WCD subbasin. Areas that are hydraulically connected are represented through the use of the same routing code value. A land use-based runoff coefficient is specified for each grid cell. The runoff coefficient is a fractional value that indicates the fraction of water on the overland flow plane that is routed directly as paved area runoff to areas defined by the specified surface water routing map. In general, the paved area runoff coefficients increase as the degree of urbanization increases.

Rainfall that falls on each WCD subbasin can move to a secondary or primary canal based on the water level gradient and the specified runoff coefficient. The water that does not leave the subbasin via a MIKE 11 canal is available for evapotranspiration, infiltration, and groundwater pumpage and flow after infiltration. Outflow from a WCD subbasin to a primary canal system is controlled by using either a pump(s) or, if the subbasin is connected by gravity, a conceptual fixed weir to maintain water levels in the subbasin at the defined control elevations. For subbasins controlled by a pump, the actual pump capacity is used in the model. For subbasins with gravity connections to the secondary system, the drainage criterion, where known, was used to develop the maximum drainage rate for the subbasin. Figure C.2 illustrates the exchange of flows in the MIKE SHE/MIKE 11 model. All significant primary and secondary canals in the Broward model area are represented in MIKE 11 using a level of detail sufficient to accurately simulate the dynamics of the primary and secondary canal system. The surface water-routing map discussed above is used to route runoff from each grid cell to a defined location in the canal system simulated by using MIKE 11.

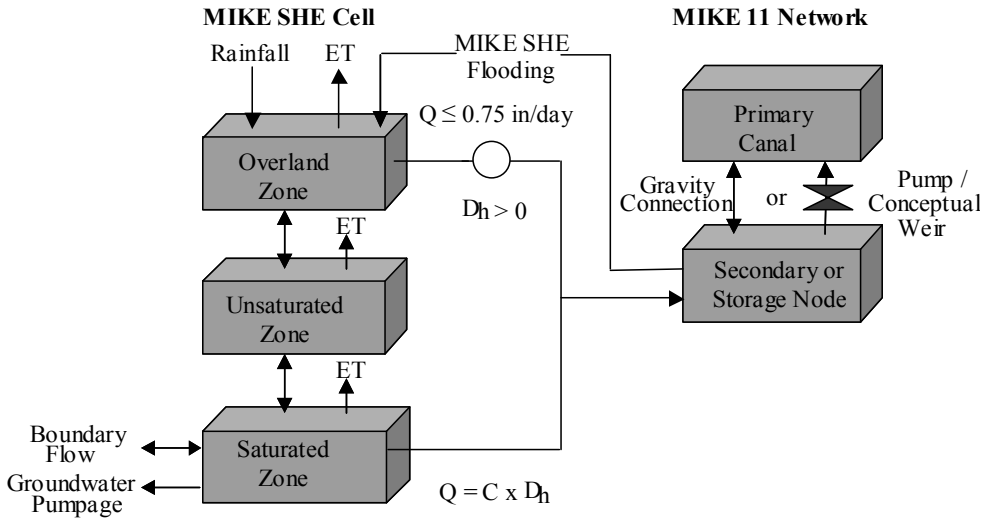


Figure C.2. Conceptualization of interaction between MIKE SHE and MIKE 11 for individual cells in a WCD subbasin. ET, evapotranspiration.

In addition to the dynamics of the secondary system described above, there are components of the tertiary system such as swales, ditches, and exfiltration trenches that have connections to the groundwater and to the secondary canals. These features are conceptually represented in MIKE SHE using the drainage option. The same surface water-routing map used for the paved area runoff module is used to route the drainage water. If the groundwater level

exceeds the specified drainage level, it is then directly routed to the MIKE 11 canals at a specified drainage rate. This rate is a function of the height of the groundwater above the drainage level and a calculated drainage conductance developed from a specified leakage coefficient for a cell and the cell area. In the Broward model, the drainage level has been set based on the control elevation for each WCD subbasin.

Although internal basin storage is well represented as a result of using topographic data derived from Broward County's light detection and ranging (LIDAR) data, the model also accounts for all significant storage, such as subdivision lakes, present in the interconnected surface water system in each WCD subbasin. The internal surface water storage capacity of a subbasin is physically represented in the topographic data used by MIKE SHE and conceptually in MIKE 11.

Internal subbasin surface water storage is conceptually represented in MIKE 11 using a conceptual surface water storage node branch that contains all the surface water storage volume capacity in a subbasin (namely, the total volume of all the lakes that are connected to the secondary drainage system in a subbasin). In general, there is a MIKE 11 surface water storage node for each WCD subbasin and each of these surface water storage nodes is appropriately connected to a secondary canal branch in that particular subbasin. To control discharge from the surface water storage nodes to the secondary canal network, a conceptual weir has been defined at the outlet point. The weir crest elevation for each surface water storage node is based on the WCD subbasin control elevation.

Water contained in the MIKE 11 surface water storage nodes is spatially distributed in MIKE SHE by using the area inundation option (namely, flood codes). Use of flood codes allows MIKE SHE to map water simulated in MIKE 11 to the landscape based on simulated MIKE 11 stages and model topography. This mapping allows groundwater seepage and evapotranspiration to be spatially represented in a realistic way. To ensure realistic results, the total area defined with flood codes in a subbasin corresponds to the area simulated in the MIKE 11 surface water storage node (Figure C.3).

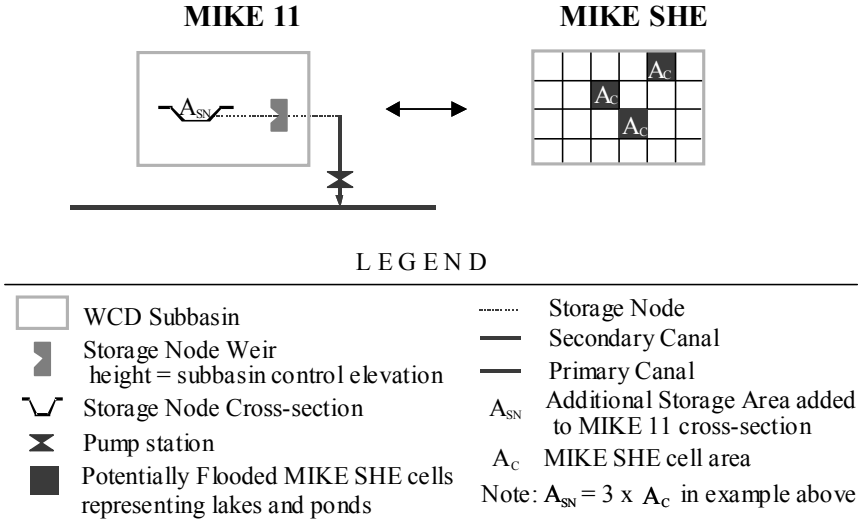


Figure C.3. Conceptualization of WCD storage nodes in MIKE 11 and MIKE SHE.

For WCD basins with surface water storage nodes, all paved area runoff for the subbasin is routed to the surface water storage node to ensure that the dynamics of stage storage relationships are accurately simulated. In addition, a lake may receive subsurface inflows from surrounding areas, which contribute to the water level in the storage node. MIKE SHE accounts for the evapotranspiration in the storage nodes for all lakes where the MIKE 11 storage node water level exceeds the bottom elevation of the lake.

The focus of the modeling effort for this report is to trace the hypothetical wastewater effluent discharge to the Holloway canal on the nearby surface water and groundwater system; thus, the Plantation submodel extracted from the Broward County model includes only the surface water and groundwater features that would have a direct hydraulic connection to the Holloway canal. For the initial phase of the project, the spatial resolution was left the same as the Broward model (500-ft cell size). In later phases of the project, the model can be refined to represent the area more accurately if necessary.

The model area was determined by taking into account both the surface water basin divides and the groundwater capture areas. The model area and key features are shown in Figure C.4. The primary surface water basins included in the model are the C-12 and the eastern North New River Basins. The eastern North New River basin is defined by the areas east of the C-42 canal, which include the Old Plantation WCD (OPWCD) and the area east of the G-54 gates. The western subbasins (Plantation Acres ID subbasin and the areas west of it) were considered to be hydraulically disconnected and were excluded. The entire C-12 basin is included in the model area, but the secondary canals north of the C-12 canal were not included. Flows into and out of the C-12 canal from these secondary canals were taken from the Broward County model results and are represented as boundary conditions.

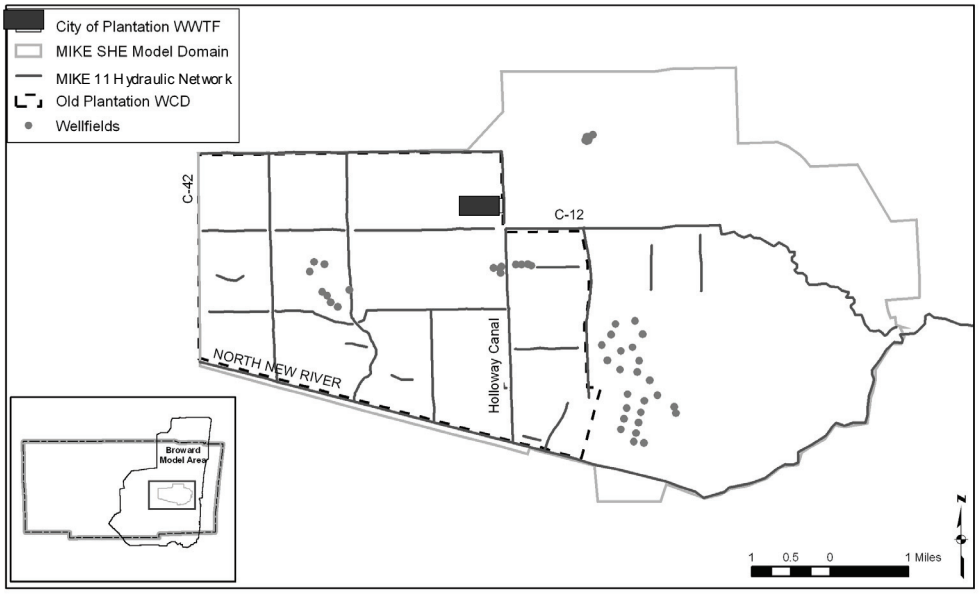


Figure C.4. Plantation model domain, river network, and wellfield locations.

In addition, a preliminary study of the ground age was performed to determine the capture zone of the wellfields in the vicinity of the Holloway canal by running a simple AD transport

model for the Broward model. For this simulation, a CT and a decaying tracer were used. The groundwater age was estimated by using the following equation (Delhez et al., 2003):

$$T = (-\frac{1}{k}) \ln(\frac{C_{decay}}{C_{conservative}})$$

Where

k is the first-order decay rate

C_{decay} is the concentration of the decaying tracer, and

$C_{conservative}$ is the concentration of the CT

The results show groundwater ages ranging from 1 to 10 years in the urban areas of the county. A groundwater capture zone for the wellfields in the proximity of the Holloway canal was delineated from the differences in age. This area is shown in Figure C.5.

Boundary conditions for the model area were extracted from the Broward model results for all of the groundwater and the surface water boundaries in the Plantation submodel. The northwest surface water boundary is the connection between the C-42 canal and the 3L3W secondary canal in the OPWCD. The southwest surface water boundary is the North New River just upstream of Canal No. 3. Both of these boundaries were set as water level boundaries. The eastern surface water boundary is the S-33 gate tailwater tidal signal.

The groundwater model for Broward County is composed of five hydrogeologic layers that represent the surficial aquifer system. All of these groundwater layers were also included in the Plantation submodel. For each groundwater layer, the head elevation results from the Broward model were extracted and were used as temporally and spatially distributed boundaries all along the outer boundary of the Plantation submodel.

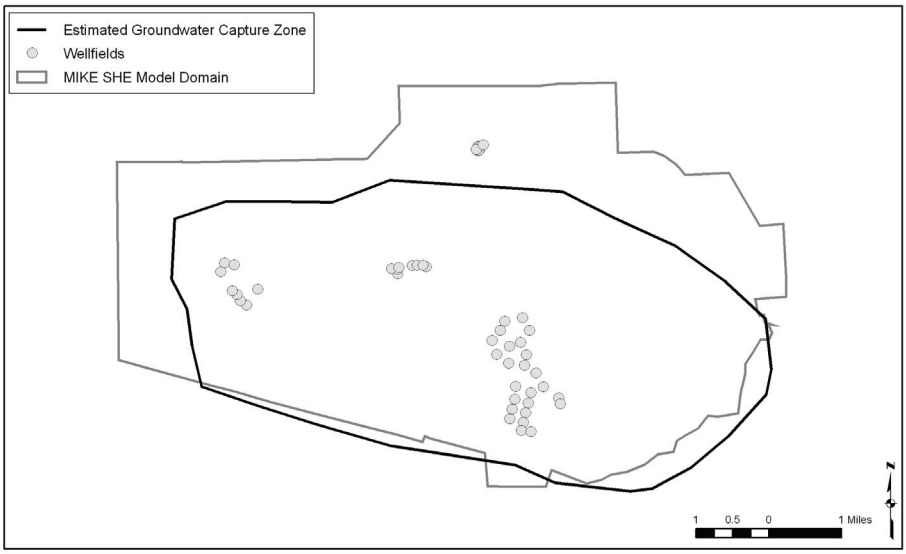


Figure C.5. Estimated groundwater capture area.

C.3 WATER QUALITY MODEL

In this section, the parameters introduced in the water quality model (fate and transport) are presented as well as their literature sources and the assumptions involved. The ECO Lab-related parameters are described first, followed by the ones used in MIKE SHE AD and MIKE 11 AD modules. Finally, a description of the simulation is also included.

The MIKE 11 Water Quality module is known as ECO Lab. ECO Lab is integrated with the AD module of MIKE 11 and works dynamically with the hydrodynamic computations of MIKE SHE to simulate the fate and transport of water quality and biological constituents in the stream network. ECO Lab can handle a wide range of water quality processes, ranging from simple first-order decay to fully dynamic eutrophication processes. ECO Lab also has several standard templates of predefined ecosystem descriptions ready to be used for ecological modeling or serve as a starting point for more customized modeling.

A modification of the ECO Lab template designed for microconstituents was used to model the water quality processes for the Plantation model (DHI, 2008c). The constants used in the template for each species are listed in Table C.1, and the source of the parameters and of other assumptions is described next. The description is divided according to the processes where the parameters are involved. In general, when a range of parameters was reported, the more conservative limit was selected. In other words, the parameters that would cause the least degradation of the microconstituents were used in the model.

C.3.1 Adsorption onto soil particles (Table C.1, No. 1–5)

Adsorption and desorption of the dissolved species are considered in the microconstituent template for suspended and deposited sediment particles. The six examined microconstituents are mostly bound to the organic fraction (DHI, 2008c), and the corresponding partition coefficient in equilibrium is available from EPI suite software (EPA, 2008). The equilibrium between dissolved and adsorbed species is reached according to the desorption rates assumed in Table C.1, which are considered higher in open water than in sediment. Preliminary tests shown that in the cases with a higher adsorption coefficient, desorption rates in the sediment layer must be set even lower in order to avoid numerical oscillations in the pore water concentration.

C.3.2 Diffusive transport at sediment-water interface (Table C.1, No. 6–9)

The transport of the dissolved species between the sediment and the open water layer is modeled in the microconstituent template as a diffusive process. The sediment layer depth is assumed initially as 20 cm, and a thickness of water film much lower than that value would not affect the diffusive flux. On the other hand, the diffusion layer thickness in the sediment layer is assumed to be half of the layer thickness.

The diffusion coefficient for the microconstituent molecules in water is found in the template from their molecular weights. The factor for diffusion due to bioturbation, vertical convection, etc. relates the effective diffusion coefficient with the molecular diffusion one. The effective diffusion coefficient may be 4 orders of magnitude higher (Harvey et al., 2005; Langevin, 2001).

Table C.1. Input Parameters Assumed in the ECO Lab Template

No.	Description	Unit	Values for Microconstituent[a]					
			SM	TS	IB	4NP	MP	PH
1	Organic-carbon partitioning coefficient	l/kg	1585	19,953	398	63,096	501	251
2	Desorption rate in water	1/day	1					
3	Desorption rate in sediment	1/day	0.1	0.02	0.1	0.01	0.1	0.1
4	Fraction of organic carbon in suspended solids	—	0.328					
5	Fraction of organic carbon in sediment	—	0.328					
6	Thickness of water film	mm	0.1					
7	Ratio between thickness of diffusion layer in sediment and sediment thickness	—	0.5					
8	Factor for diffusion due to bioturbation, convection, etc.	—	10,000					
9	Molecular weight of the microconstituent molecule	g/mol	253.3	287.5	206.3	220.4	263.2	94.1
10	ECO Lab time step, controlled by MIKE 11	S	120					
11	Density of dry sediment	kg/m^3 bulk	334.5					
12	Porosity of sediment	m^3 H_2O/m^3 bulk	0.83					
13	Settling velocity of suspended solids	m/day	18.6					
14	Particle production rate	gdw/m^2/day	1.37					
15	Resuspension rate at velocities below or equal to ucrit	gdw/m^2/day	3.42					
16	Critical current velocity for sediment resuspension	m/s	0					
17	Factor for the resuspension rate term that is proportional to the water speed (above ucrit)	gdw/m^2/day *s/m	3330					
18	Minimum value for X_{SED}. Below, resuspension = 0	gdw/m^2	16,725					
19	Biodecay rate water, max	1/day	0	0	0	0	0	0.14
20	Biodecay rate sediment, max	1/day	0	0	0	0	0	0.14
21	Half-saturation constant biodecay water	gXE/m^3	10^{-9}					
22	Half-saturation constant biodecay sediment	gXE/m^2	10^{-9}					
23	Arrhenius temperature coefficient for biotransformation	—	1					
24	Background concentration air	gXE/m^3	0					
25	Light attenuation water column	1/m	2					
26	Photolysis rate at surface	1/day	2.52	0.07	0.00	1.11	0.09	0.01
27	Henry's constant	Pa m^3/(mol × K)	9.69×10^{-8}	5.06×10^{-12}	1.54×10^{-3}	3.45	1.70×10^{-3}	$3.37 \times 10^{-}$
28	Is the compound an acid [0/1]	—	0					
29	Is the compound a base [0/1]	—	0					
30	Dissociation constant acid ['pH units']	—	10					
31	Dissociation constant base ['pOH-units']	—	3					
32	Hydrolysis constant, acid	10^{-3}/day	0	0	0	0	7.79	0
33	Hydrolysis constant, neutral	10^{-3}/day	0	0	0	0	7.79	0
34	Hydrolysis constant, alkaline	10^{-3}/day	0	0	0	0	7.79	0
35	Universal gas constant	m^3 air Pa/(mol × K)	8.3144					

[a] SM: sulfamethoxazole, TS: triclosan, IB: ibuprofen, 4NP: 4-nonylphenol, MP: methyl parathion, PH: phenol.

C.3.3 Sediment transport (Table C.1, No. 11–18)

The microconstituent template includes the mass of suspended solids (X_{SS}) and mass of sediment (X_{SED}) as variables. The mass balance of those variables involves the following processes: production of suspended particles, resuspension (or erosion), and settling (or deposition).

The original template (DHI, 2008c) considers a constant settling velocity and rate of resuspension, which are applied if the current water speed is lower and higher than a critical value, respectively. This approach was improved, considering that deposition always occurs and that resuspension above a critical speed (ucrit) increases linearly with the current speed (cspd) as shown in the following equation:

$$\text{ressa} = \begin{cases} \text{resrat} & \text{cspd} \le \text{ucrit} \\ \text{resrat} + \text{fresrat}\,(\text{cspd} - \text{ucrit}) & \text{cspd} > \text{ucrit} \end{cases}$$

Where ressa is the resuspension rate per unit area, resrat is its value below ucrit and fresrat is the factor to account for the speed dependence above ucrit.

A more complex treatment of the erosion-deposition terms can be found in Tsujimoto (1999) and Xu et al. (2005).

Since there are no measured data available to calibrate the transport of suspended sediments in the canals; the model uses parameters from measurements conducted in the Water Conservation Areas (WCAs) and the Everglades in South Florida. The density of the dry sediment (or bulk density) and the organic matter mass fraction presented in Table C.1 were estimated from the median value of the measurements conducted in the WCA canals by Diaz et al. (2006). Grain densities of 2.56 g/cm^3 for inorganic and 1.288 g/cm^3 for organic matter were found from the measurements on suspended particles in the Everglades reported by Bazante et al. (2006). The porosity of the sediment layer was computed from these values as

$$\text{Porosity} = 1 - \text{bulk density/average grain density}$$

The settling velocity of the suspended particles was estimated as the quotient between the average deposition rate and the average concentration. The values for average deposition rate and the average concentration reported for the Everglades marsh were 12.3 gdw/m^2/day by Leonard et al. (2006) and 1 mg/L by Bazante et al. (2006). The particle production rate is assumed as a typical leaf litter production rate in Everglades marsh areas adopted from the range reported by Ewe et al. (2006).

The resuspension rate was estimated from the deposition rates measured at different velocities by Leonard et al. (2006) at the Everglades marsh. In equilibrium the deposition rate is equal to the production plus the resuspension rates. The deposition rates measured by Leonard et al. (2006) increase with typical water speeds at the measurement points, following approximately a linear dependence in the speed range reported (0 to 1 cm/s). The linear fitting of this dependence gives the parameters numbered 15 and 17 in Table C.1. Moreover, the critical velocity for sediment resuspension was assumed to be zero, which is in accordance with other resuspension processes different from erosion, such as gas production in the sediment layer and thermal convective movement in the water column. Finally, after model testing, it was determined that the minimum value for X_{SED} necessary to assure

numerical stability (parameter No. 18) was 16,725 gdw/m^2, which is equivalent to a 5-cm-thick sediment layer.

C.3.4 Biotransformation (Table C.1, No. 19–23)

According to the EPI suite software (EPA, 2008), phenol is the only microconstituent from the six included in the literature review that is reported as biodegradable in all the literature sources. Please note that EPI suite software was developed with compounds not necessarily representative of microconstituent properties and that therefore these estimations might be off. In addition, the biotransformation rates depend on local conditions and the reported values cover a wide range. Therefore, we evaluated the most conservative case for biotransformation, as shown in Table C.1. The biodecay rate is considered to be zero for all the species, except for phenol, where the maximum half-life reported (120 h) is used. The dependence of the phenol biodecay rate on concentration and temperature was unknown and therefore not considered.

C.3.5 Photolysis (Table C.1, No. 25–26)

The photolysis decay rate at the surface was also assumed conservatively and set to the lowest value from the range reported in the literature review. The light attenuation in water column is used in the template to translate the decay rate at the surface to the whole water column. The minimum value for the attenuation coefficient is measured in pure water, and it is around 0.15 m^{-1} (Gallegos and Kenworthy, 1996). The conservative value presented in Table C.1 (2 m^{-1}) was reported by McPherson and Miller (1987) for Charlotte Harbor, FL.

C.3.6 Evaporation (Table C.1, No. 24, 27–31)

The microconstituent ECO Lab template computes the evaporation rate of the dissolved species by using Henry's constant, which was obtained from EPI suite software (EPA, 2008) at 25 ^oC. A negligible background concentration in air was assumed. None of the compounds are assumed acids or bases; thus, no dissociation effects in the evaporation rate are considered in the model. The effect of the wind velocity on the evaporation rate is included in the model. For wind velocity, which is a forcing variable in the template, a constant value of 1.5 m/s (a typical value for the area) was assumed.

C.3.7 Hydrolysis (Table C.1, No. 32–35)

Methyl parathion is the only microconstituent in the literature review that is reported degradable by hydrolysis. This contaminant is not among the three simulated in the water quality model; therefore, degradation by hydrolysis is not included in this study. The decay rate shown in Table C.1 was estimated conservatively from the range reported in the literature review. The dependence of this rate on the phenol is not well known and therefore not considered by the tabulated parameters.

C.4 AD TRANSPORT MODEL

The ECO Lab template computes all the water quality processes described in the previous section in the surface water (MIKE 11) network. The transport vehicle for the movement of contaminants in MIKE 11 is the AD module. The MIKE 11 AD can exchange solute transport with the AD module in MIKE SHE, which in turn can exchange solute transport in all its modules: overland flow, evapotranspiration (plant uptake), the unsaturated zone, and the SZ. The contaminant transport pathway of interest in the Plantation model begins at the WWTP point source discharge at the Holloway canal throughout the connecting canals and ultimately into the wellfields. Thus, the solute transport interaction between the canals in MIKE 11 and in the SZ in MIKE SHE is the most important. The overland flow AD is also included in the model because it is a requirement in MIKE SHE if MIKE 11 AD is linked. Transport through the unsaturated zone or plant uptake was not considered a significant pathway for the purposes of this study and can considerably increase model running time; thus, it has been excluded from the model.

MIKE SHE considers adsorption and decomposition processes in SZ layers and in the overland layer. However, it does not include the transport of suspended particles in the overland flow module and the corresponding adsorbed microconstituents. The SZ module considers groundwater abstractions from wells and drainage to the MIKE 11 canals as sinks, where the concentration is equal to the actual solute concentration in the SZ grids.

In order to solve the AD equation, the model requires initial and boundary conditions and dispersion coefficients. The values used for the MIKE SHE and MIKE 11 AD transport model parameters are described below.

C.4.1 Initial conditions

The background concentrations of the different microconstituents in the model area likely are very low. Thus, the model is assumed to have zero concentration of microconstituents at the beginning of the simulation, which is a conservative assumption. The initial mass for the overland flow component is set uniformly at 0 g/m^2. And the initial concentration is set at 0 g/m^3 in both the groundwater layers in MIKE SHE and at the canal network in MIKE 11.

C.4.2 Boundary conditions

For the canal network, all the boundary conditions for the dissolved and adsorbed microconstituents are assumed to have zero concentration, which means no external mass input. The only source of the microconstituents in the model is in the discharge coming out from the WWTP. The concentrations specified at the WWTP are shown in Table C.2. Those values are based on selected results from this project. The concentration of suspended particles is assumed to be 1 mg/L at all the open boundaries of the canal network. This value corresponds to the equilibrium concentration when water speed is around 0.4 cm/s (0.013 ft/s).

The concentrations of the dissolved microconstituent in overland and groundwater boundaries were set to zero. In the Plantation model, the concentration in the rainfall is also assumed to be zero and no plant uptake is considered. Pumping wells and drainage features extract mass from the SZ component at the existing groundwater concentration.

C.4.3 Dispersion coefficient

The dispersion coefficient for the overland flow layer in MIKE SHE is assumed to be isotropic. A value of 5 m^2/s is used in the model, which is a typical value according to the MIKE 11 user manual (DHI, 2008b). In MIKE SHE the dispersion coefficient is considered proportional to the velocity in the groundwater layers. The longitudinal and transversal dispersivity coefficients are set equal to 5 m and 0.5 m, respectively, which are typical ranges reported by Langevin (2001). For the canal network in MIKE 11, the dispersivity coefficient and the maximum dispersion coefficient are assumed to be 5 m and 5 m^2/s, respectively.

C.4.4 Adsorption processes

MIKE SHE considers the adsorption processes in SZ layers. In this model, a bulk density of 2000 kg/m^3, a porosity of 0.2, and an organic fraction of 0.05 are assumed for all five groundwater layers. The organic-carbon partitioning coefficients from Table C.1 are also used for groundwater adsorption. These values were converted to the MIKE SHE input units ($l/kg = 10^{-6}$ m^3/g).

C.4.5 Decay processes

The decay processes in MIKE SHE are represented by using a simpler approach than ECO Lab. In the overland layer, a total decay rate for each microconstituent is estimated from the sum of the biotransformation, photolysis, hydrolysis, and evaporation rates estimated under certain conditions, which are shown in Table C.2. Conservative values (0) were used for estimating the biodecay rates of the CT and all microconstituents except phenol. Decay in the SZ layers is assumed to occur only by hydrolysis. However, none of the microconstituents included in the model degrades by hydrolysis; thus, they do not undergo decay in the groundwater. The decay rates in Table C.2 are converted to half-life ($t_{1/2}$), which is the parameter input in MIKE SHE.

Table C.2. Input Parameters for AD Transport Model[a]

Description	Unit	Values for:						
		CT	SM	TS	IB	4NP	MP	PH
Concentration in water coming from WWTP	ng/L	100	76	5	2.7	25	25	100
Biodecay rate	1/day	0	0	0	0	0	0	0.14
Photolysis rate at surface	1/day	0	2.52	0.07	0.00	1.11	0.09	0.01
Hydrolysis rate	1/day	0	0	0	0	0	0.00779	0
Evaporation lost rate (at 1-m/s wind speed, 1-m water depth)	1/day	0	0.00	0.06	0.21	0.22	0.20	0.27
Total decay rate OL (all four processes)	1/day	0	2.52	0.13	0.21	1.33	0.29	0.42
	1/h	0	0.105	0.005	0.008	0.055	0.012	0.017
Half-life ($t_{1/2}$) in OL (all four processes)	10^{-3} yr	10^9	0.753	14.6	9.14	1.43	6.56	4.55
Total decay rate GW (only hydrolysis)	1/day	0	0	0	0	0	0.00779	0
Half-life ($t_{1/2}$) in GW	yrs	10^6	10^6	10^6	10^6	10^6	0.244	10^6

[a] OL, overland layer; GW, groundwater, SM, sulfamethoxazole; TS, trciclosan; IB, ibuprofen, 4NP, 4-nonylphenol; MP, methyl parathion; PH, phenol.

C.5 SIMULATION DESCRIPTION

C.5.1 Hydrodynamic model

The Plantation submodel, extracted from the Broward County model, includes only the surface water and groundwater features that would have a direct hydraulic connection to the Holloway canal. For this initial phase of the project, the spatial resolution remains the same as the Broward model (500-ft cell size). In later phases of the project, the model can be refined to represent the area more accurately if necessary.

The model area was determined considering the surface water basin divides and the groundwater capture areas. The primary surface water basins included in the model are the C-12 and the eastern North New River basins. The eastern North New River basin is defined by the areas east of the C-42 canal, which include the OPWCD and the area east of the G-54 gates. The western subbasins (Plantation Acres ID subbasin and the areas west of it) were considered to be hydraulically disconnected and were excluded. The entire C-12 basin is included in the model area, but the secondary canals north of the C-12 canal were not included. Flows into and out of the C-12 canal from these secondary canals were taken from the Broward County model results and are represented as boundary conditions.

The hydrodynamic model is run for a 4-year period (January 1, 1999, to December 31, 2002); which corresponds to the Broward County model calibration (January 1, 1999, to December 31, 2000) and verification (January 1, 2001, to December 31, 2002) periods. This period includes one wet year, including a hurricane event (1999), one dry year (2000), and two average years (2001 through 2002). The river network and the surface topography are shown in Figures C.6 and C.7, respectively.

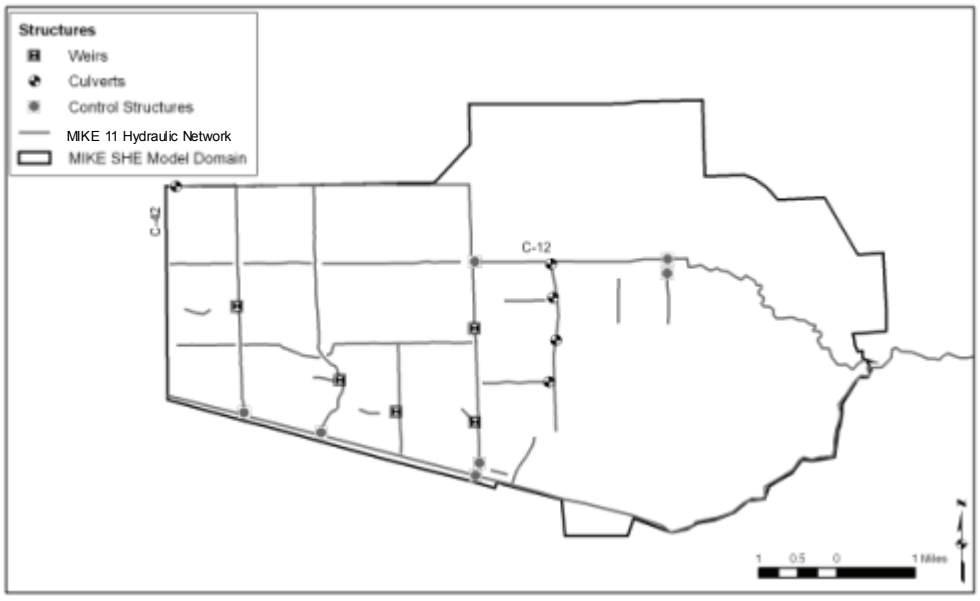


Figure C.6. River network and structures in the Plantation model.

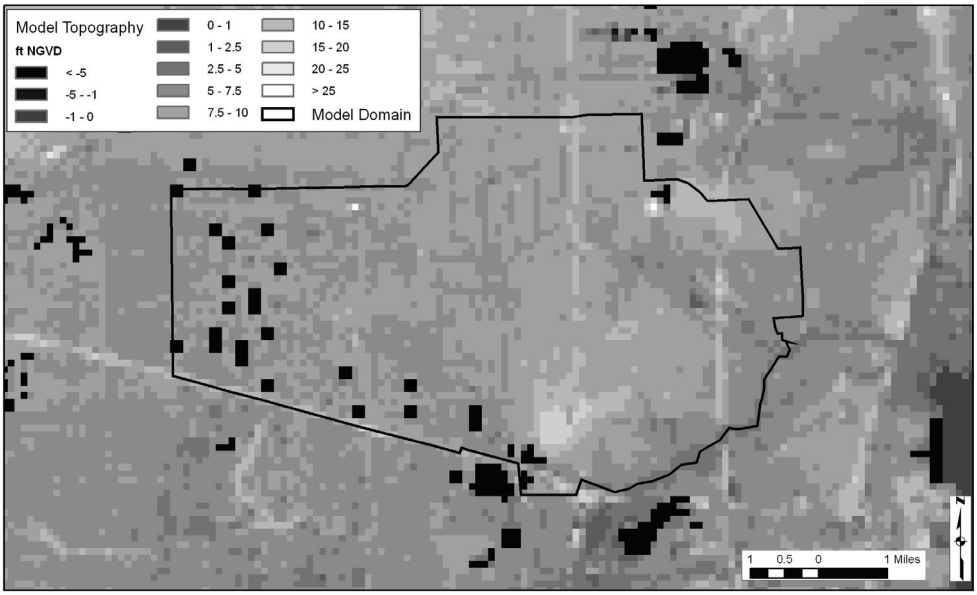


Figure C.7. Model topography (ft NGVD 29).

C.5.2 Water quality model

Preliminary water quality model runs for the 4-year period show that the concentration of the microconstituents in groundwater at the potable-water wellfield locations does not reach steady concentration levels when one is starting from a zero-concentration model. Thus, the water quality simulation period was extended to 20 years in order to see the maximum concentrations in groundwater at wellfield locations at the end of that period. The simulation period was extended by concatenating five times all the 4-year data from the hydrodynamic model. In other words, the hydrologic information for the period of 1999 through 2002 is repeated five times.

Separate water quality models were built for each of the three selected microconstituents: sulfamethoxazole, triclosan, and phenol and for the CT. The objective of the water quality model is to study the transport of microconstituents that exhibit different removal/retention mechanisms: adsorption, biotransformation, photolysis, and evaporation. Thus, the selection of the microconstituents for the model was mainly based on their possible degradation pathways. Also the concentrations detected during the chemical analysis at different stages of the WWTP were considered.

Triclosan and phenol have very high and very low adsorption coefficients in soil, respectively. Phenol is the only microconstituent, based on the literature review in this report, that biodegrades. It has the highest evaporation rate. Sulfamethoxazole is the microconstituent with highest photolysis decomposition rate. The effect of those processes (adsorption, biotransformation, photolysis, and evaporation) can be observed by comparing the results for the three microconstituents and the CT.

Advancing the Science of Water Reuse and Desalination

WATEREUSE RESEARCH

1199 North Fairfax Street, Suite 410
Alexandria, VA 22314 USA
(703) 548-0880
Fax (703) 548-5085
E-mail: Foundation@WateReuse.org
www.WateReuse.org/Foundation