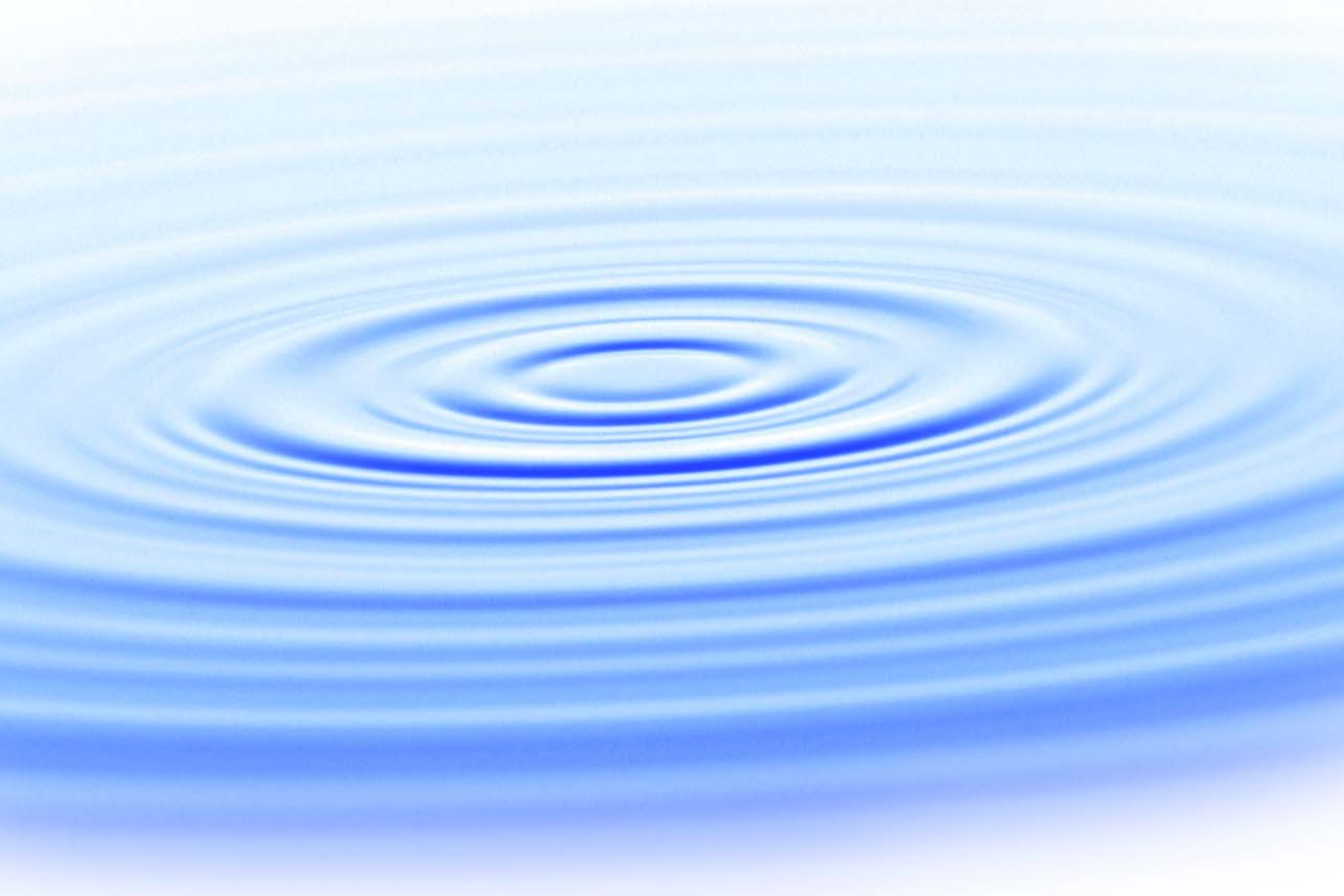
Role of Retention Time in the Environmental Buffer of Indirect Potable Reuse Projects

An Investigation on Managed Aquifer Recharge



WateReuse Research Foundation

Role of Retention Time in the Environmental Buffer of Indirect Potable Reuse Projects

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 for various uses 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, reduction of energy requirements, concentrate 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 providing a reliable, safe product for its intended use.

The Foundation's funding partners include the supporters of the California Direct Potable Reuse Initiative, Water Services Association of Australia, Pentair Foundation, and the U.S. Bureau of Reclamation. Funding is also provided by the Foundation's subscribers, water and wastewater agencies, and other interested organizations.

Role of Retention Time in the Environmental Buffer of Indirect Potable Reuse Projects

An Investigation on Managed Aquifer Recharge

Jörg E. Drewes
Julia Regnery
Eric Dickenson
Colorado School of Mines

Charles P. Gerba
Shane A. Snyder
The University of Arizona

Thomas Missimer
King Abdullah University of Science and Technology

Cosponsors

Bureau of Reclamation
California State Water Resources Control Board
Water Replenishment District of Southern California

WateReuse Research Foundation
Alexandria, VA

Disclaimer

This report was sponsored by the WateReuse Research Foundation and cosponsored by the Bureau of Reclamation, the State Water Resources Control Board (CA), and the Water Replenishment District of Southern California. The Foundation, its board members, and the project cosponsors assume no responsibility for the content of this publication or for the opinions or statements of facts expressed in the report. The mention of trade names of commercial products does not represent or imply the approval or endorsement of the WateReuse Research Foundation, its board members, or the cosponsors. This report is published solely for informational purposes.

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: WRRF-10-05
WateReuse Research Foundation Product Number: 10-05-1

ISBN: 978-1-941242-21-6

Contents

List of Figures viii
List of Tables xii
Abbreviations and Acronyms xiv
Foreword xvii
Acknowledgments xviii
Executive Summary xix

Chapter 1. Introduction 1
1.1 Background 1
1.2 Project Objectives 3
1.3 Related Research 3
1.3.1 Attenuation of Pathogens by MAR 3
1.3.2 Attenuation of Nitrogen by MAR 5
1.3.3 Attenuation of Organic Matter by MAR 5
1.3.4 Attenuation of Trace Organic Chemicals by MAR 6
1.3.5 Attenuation of Glucocorticoid Disruption by MAR 8
1.4 Project Approach 8

Chapter 2. Materials and Methods 11
2.1 Field Sampling Sites 11
2.1.1 Prairie Waters Project, Aurora Water 11
2.1.2 San Gabriel Spreading Grounds Test Basin 13
2.1.3 Sweetwater Recharge Facility, Tucson Water 17
2.2 Analytical Methods for Bulk Parameter and CEC Analyses 18
2.2.1 Physicochemical Parameters 18
2.2.2 Bulk Parameters 19
2.2.3 Chemicals of Emerging Concern 20
2.3 Virus Detection by qPCR 21
2.3.1 Selection of Studied Viruses 27
2.4 Analytical Methods for Glucocorticoids 28
2.4.1 SPE and LC-MS/MS 28
2.4.2 Glucocorticoid Receptor Bioassay 29
2.5 Experimental Methods 30
2.5.1 CEC and Bulk Organic Removal in Soil Columns 30
2.5.2 Temperature-Controlled CEC and Bulk Organic Removal in Soil Columns at KAUST 36
2.5.3 Glucocorticoid Removal in Soil Columns at CSM 36

2.5.4 Pathogen Removal in Soil Columns at CSM 37
2.5.5 First-Order Removal Calculation of CEC 37
2.5.6 Sorption Potential of Different Soil Types for CECs (K_d) 38

Chapter 3. Fate of Bulk Dissolved Organic Carbon, Nitrogen, CECs, and Pathogens in the Environmental Buffer Under Controlled Conditions 41
3.1 Bulk Dissolved Organic Carbon and Nitrogen Attenuation During Simulated MAR 41
3.1.1 Impact of Feed Water Composition 41
3.1.2 Influence of Temperature on Removal Efficiency 45
3.2 Attenuation of Viruses During Simulated MAR 46
3.2.1 Fate of Murine Norovirus and Bacteriophage MS-2 During Infiltration Through Soil Columns 47
3.3 CEC Attenuation During Simulated MAR 52
3.3.1 The Role of Key Environmental Conditions: Redox Conditions, BDOC, and Residence Time 52
3.3.2 Temperature Dependency of CEC Attenuation 57
3.4 Attenuation of Glucocorticoids During Simulated MAR 60
3.4.1 Bioassay Validation 60
3.4.2 Glucocorticoid Activity Change During MAR 62
3.4.3 Glucocorticoid Removal in Soil Column Systems 65
3.5 Sorption Potential of Different Soil Types 65
3.5.1 Soil Characterization 65
3.5.2 Sorption of CECs to Clay Materials 65
3.5.3 Breakthrough Curves and K_d Values 68
3.6 First-Order Removal Rates for Bulk Organic Carbon and CECs 70

Chapter 4. Field Studies to Evaluate the Fate of Enteric Pathogen Survival in the Environmental Buffer 73
4.1 Enteric Pathogen Survival in the Environmental Buffer 73
4.2 Occurrence and Fate of Viruses During Full-Scale MAR 74
4.2.1 Field Monitoring Efforts 74
4.2.2 Significant Findings and Relevance 78

Chapter 5. Field Studies to Evaluate the Fate of Bulk Organic Carbon, Nitrogen and CECs in the Environmental Buffer 79
5.1 Fate of TOC, CECs, and GR Activity During Full-Scale MAR 79
5.1.1 Case Study: San Gabriel Spreading Grounds 79
5.1.2 Case Study: Prairie Water Project, Aurora Water 86
5.1.3 Case Study: Sweetwater Recharge Facility, Tucson Water 93
5.2 CEC Removal Kinetics—Comparison of Laboratory and Field Results 98
5.2.1 San Gabriel Spreading Grounds 98

5.2.2 Prairie Waters Project, Aurora Water 101
5.2.3 Sweetwater Recharge Facility, Tucson Water 101

Chapter 6. Modeling Framework to Assess MAR Performance 103
6.1 STUMOD-MAR: A Tool for Predicting Fate and Transport of Microbial and Chemical Contaminants in MAR 103
6.1.1 Unsaturated Zone Hydraulics and Contaminant Transport 104
6.1.2 Saturated Zone Hydraulics and Contaminant Transport 106
6.1.3 Model Parameters for Nitrogen, DOC, CECs, and Pathogens 109
6.1.4 Model Calibration and Validation 115
6.1.5 Summary and Conclusion 121
6.2 Remarks on Model Use 121
6.2.1 Input and Output 121
6.2.2 Saturated Zone Model 122

Chapter 7. Conclusions and Recommendations 123
7.1 Role of Retention Time, Redox Conditions, and Primary Substrate 123
7.1.1 Relationships Between Pathogen Attenuation and Retention Time 123
7.1.2 Relationships Between Trace Organic Chemical Attenuation and Retention Time 125
7.2 Lessons Learned 126
7.3 Implementations 127

References 129

Appendix 139

Figures

2.1 Aerial map of the RBF well field along South Platte River at Brighton and map of the adjacent aquifer recharge and recovery site including well locations 12
2.2 Pathogen sampling of recovery well PW10 with NanoCeram filter 13
2.3 Map of the San Gabriel Spreading Grounds, Montebello Forebay, Los Angeles County, including well locations 16
2.4 Schematic map of the test basin at the San Gabriel Spreading Grounds including well locations 16
2.5 Montebello Forebay test basin during wetting operation for microbial community activation (November 5, 2012) 17
2.6 Aerial map of the Sweetwater Recharge Facility, Tucson, and sampled well locations 18
2.7 Average 12 month concentrations of human enteric viruses and pepper mild mottle virus in treated wastewater discharge of Roger Road (A) and Ina Road (B) sewage treatment plant in Tucson (genomes/L) 27
2.8 Seasonal variation of rotavirus and pepper mild mottle virus in the influent and treated effluent of two wastewater treatment plants in Tucson (genomes/L) 28
2.9 Soil column systems at CSM (left) and KAUST (right) 31
2.10 Schematic column configuration for PC and C1 column systems (left) and C2 column system (right) 32
2.11 Breakthrough curves for the conservative tracer potassium bromide at the large-scale column C4 at a flow rate of 1 mL/min 35

3.1 3D fluorescence excitation–emission matrices for secondary treated effluent purged with N_2 (A), 70:30 (v/v) oxic NF permeate–secondary treated effluent blend (B), NF permeate (C), and tap water (D) 43
3.2 SEC-DOC and SEC-UV chromatograms for soil column influent samples. Peaks represent (1) biopolymers, (2) humic-like substances, (3) polymer building blocks, (4) acids and low molecular weight humic substances, and (5) low molecular weight neutrals 44
3.3 DOC removal (in %) for different soil column systems and residence times 44
3.4 Biodegradable dissolved organic carbon delivered to the column at each temperature set-point 46
3.5 MS-2 removal by soil column during first 5 days (x axis is plaque-forming units per mL) after the start of spiking 50
3.6 MS-2 removal in soil column, Days 11 through 15 after the start of spiking 51
3.7 MS-2 removal by soil column, Days 1 through 23 after start of MS-2 spiking 52
3.8 Percentage removal of easily degradable compounds at varying redox and BDOC conditions after 3 days retention time 53
3.9 Percentage removal of moderately degradable compounds at low (0.17 mg/L) BDOC and high (4.16 mg/L) BDOC after 9 and 14 days retention time 54
3.10 Percentage removal of moderately degradable compounds at varying redox and BDOC conditions after 3 days retention time 55

3.11 Attenuation of compounds primidone (recalcitrant, n=4), DEET (intermediate, n=5), and gemfibrozil (intermediate, n=5) with different biodegradability under saturated anoxic flow conditions during extended subsurface travel time of 42 days (coupled soil column system C1-PC).....56
3.12 Percentage removal of CECs after 7 days of retention time in soil column C4 receiving NF permeate as influent (0.26 mg/L DOC influent).....57
3.13 Mean trimethoprim attenuation at temperature set-points 30° C (n=9), 20° C (n=9), 10° C (n=10), and 8° C (n=10).....59
3.14 Naproxen attenuation at temperature set-points 30° C (n=9), 20° C (n=9), 10° C (n=10), and 8° C (n=10).....59
3.15 Positive control response curve for the GR bioassay. Error bars represent ± standard deviation in all test response (n=3).....60
3.16 GR assay response for spiking standard set.....61
3.17 GR activities in WWTP influent and secondary treated effluent.....61
3.18 GR activities in soil columns (July 16, 2013, sampling).....62
3.19 GR activities in soil columns (July 1, 2013, sampling).....63
3.20 GR activity comparison in C2.....64
3.21 Sorption (in %) of different CECs to bentonite (Sigma-Aldrich), field clay, and sandy field soil (both from MAR site) using spiked RBF water (spiking level 2000 ng/L).....67
3.22 Breakthrough curve of gemfibrozil determined in an abiotic soil column at KAUST.....68
3.23 First-order removal rates for bulk organic carbon in soil column systems receiving different feed water quality.....70
3.24 Fit of first-order kinetic to data sets of atenolol (A–C), gemfibrozil (D–F), and primidone (G–I) for three different redox conditions (oxic, suboxic, anoxic; N≥5 for each experimental data set.....71

5.1 Comparison of sulfate and chloride concentrations in the test basin and groundwater monitoring wells during sampling campaigns #1 (December 2012) and #2 (April 2013).....80
5.2 Stiff diagrams displaying chemical matrix of the test basin influent sample and subsurface sampling location WP-Z on December 10, 2012.....80
5.3 Stiff diagrams displaying chemical matrix of the test basin influent samples during sampling campaigns #1 and #2.....81
5.4 DOC removal in the subsurface during SAT operation using tertiary treated effluent (n≥4) at the Montebello Forebay Spreading Facility Test Basin.....82
5.5 Average removal percentage of selected easy, intermediate, and recalcitrant biodegradable indicator compounds during SAT using tertiary treated effluent (n=17) based on subsurface travel times of 0.45 day (WP-Z, n=10), 3.5 days (PR-9, n=5), and 30.8 days (PR-13, n=5).....85
5.6 DOC concentrations in mg/L measured in the South Platte River, RBF production wells 10, 10A, and 12, and in ARR monitoring wells MW-25A and 28A.....87

5.7 Dissolved manganese (Mn^{2+}) in mg/L as measured in the South Platte River, RBF production wells 10, 10A, and 12, and in ARR monitoring wells MW-25A and 28A 87
5.8 Ratio of chloride to sulfate used to demonstrate that the water inside the ARR is similar to the influent in comparison with the background 88
5.9 Average CEC concentrations determined in South Platte River water (n=4), RBF water (n=5; wells 10, 10A, 12), and ARR filtered water (n=12; wells 18A, 28A, 20, 22, 27) during fall 2012 90
5.10 Normalized CEC tracer (carbamazepine, primidone) concentrations (n=4) along Transect II (e.g., infiltration basin and wells 25A, 28A, 22) at the ARR field site 91
5.11 Normalized CEC tracer (carbamazepine, primidone) concentrations (n=4) along Transect I (e.g., infiltration basin and wells 27A, 1, 2) at the ARR field site 91
5.12 Average removal percentage of selected easy, intermediate, and recalcitrant biodegradable indicator compounds during surface spreading via ARR applying RBF (n=4) based on subsurface travel times of 2 days (MW-25A, n=4), 5 days (MW-28A, n=4), and 14 days (RW-2, n=3) 92
5.13 Comparison of sulfate and chloride concentrations in the surface-spreading basin RB-1, piezometer MW-5, and groundwater monitoring well WR-69B during the sampling campaign in February/March 2013 94
5.14 Stiff diagrams displaying chemical matrix of the infiltration basin influent (morning and afternoon sample) as well as piezometer MW-5 and monitoring well WR-69B 94
5.15 Average removal percentage of selected easy, intermediate, and recalcitrant biodegradable indicator compounds during soil–aquifer treatment applying secondary treated reclaimed water (n=3) based on subsurface travel times of 5 days (MW-5, n=1) and 14 days (WR-069B, n=1) 96
5.16 GR activity in basin influent and groundwater samples at the Sweetwater Recharge Facility 97
5.17 Averaged concentration of both Montebello Forebay test basin sampling campaigns (n≥5) at different travel times for A) carbamazepine, B) atenolol, C) gemfibrozil, D) dilantin, E) trimethoprim, F) DEET 99–100
5.18 CEC removal efficiency of a full-scale RBF facility (blue bars) receiving high BDOC concentrations compared to an ARR (red bars) receiving low BDOC concentrations for an estimated travel time of 5 days 101

6.1 Flow chart of procedures in STUMOD-MAR 105
6.2 Model configuration for saturated zone module with assumptions about a mixing layer and source plane concentration 108
6.3 Graphical user interface for parameter inputs 114
6.4 Output for DOC concentration (mg/L) vs. retention time (calibration period) 116
6.5 STUMOD-MAR simulated DOC concentration (mg/L) vs. measured DOC concentrations (calibration period) 116
6.6 Output for DOC concentration (mg/L) vs. retention time (validation period) 117
6.7 STUMOD-MAR simulated vs. measured DOC concentration (mg/L; validation period) 117

6.8 Example output for the decrease in concentration (ng/L) of the selected CEC (gemfibrozil) vs. retention time 118
6.9 STUMOD-MAR simulated vs. measured concentration (ng/L) for the selected CEC (gemfibrozil) 118
6.10 Example output for pathogen removal (adenovirus) over retention time 119

Tables

1.1 Health- and Performance-Based Indicators and Performance Surrogates for MAR Practices 7

2.1 Sampled Wells at the San Gabriel Spreading Grounds During the December 2012 Field Campaign 15
2.2 Limit of Quantification for LC/MS-MS Method Determined in Ultrapure Water (Signal to Noise Ratio of >10) 21
2.3 qPCR Primers and Probes used in the Present Study 23
2.4 Average Mass Recoveries (in ng) and Standard Deviations of Different Glucocorticoids in Spiked Wastewater Effluent Samples 29
2.5 Soil Column Configurations at CSM and KAUST and Operational Parameters 33

3.1 Bulk Organic Parameters of Feed Water Applied to Soil Columns and Change in Redox Surrogates NO_{3-} and Mn^{2+} After Travel Through the Columns 42
3.2 Removal of Naturally Occurring Viruses in the Wastewater by qPCR (genomes/L) 48
3.3 Murine Norovirus Removal by Soil Column During 5 Days After a 24 Hour Pulse Spike (genomes/L) 49
3.4 Summary of CEC Removal 58
3.5 GR Activities Summary for the Second Batch of Samples (July 16, 2013) 63
3.6 GR Activities Summary for the First Batch of Samples (July 1, 2013) 64
3.7 Soil Properties Including Cation Exchange Capacity, Fraction of Organic Carbon (f_{OC}), Organic Matter, Soil pH, Bulk Density, Porosity, and Soil Classification 66
3.8 Characteristics of Field Soil, Field Clay, and Bentonite Used in Sorption Batch Experiments 67
3.9 Sorption Distribution Coefficients of Targeted Indicator Compounds for Different Soil Properties (Preliminary Results) 69
3.10 First-Order Removal Rates and DT_{50} Values for Selected CECs Under Different Redox Conditions Based on Laboratory-Scale Soil Column Experiments 72

4.1 Survival of Microorganisms in Groundwater Versus Temperature 73
4.2 Biphasic Inactivation of Viruses in Groundwater (log/day) 74
4.3 Occurrence of Viruses in Secondary Treated Wastewater, River Water, and RBF Wells (Including the Combined Collector for All Operational Wells) by qPCR at the Prairie Waters Project North Campus in Brighton 75
4.4 Occurrence of Viruses in Wastewater and Wells by qPCR at the California and Arizona Sites 76
4.5 Log Removals of Viruses by Recharge at Three MAR Sites 77

5.1 CEC Removal Efficiency (in %) of Well 10A at the RBF Well Field Between 2009 and 2012 89
5.2 GR Activities Summary for the Sweetwater Recharge Facility Samples 97

6.1 STUMOD-MAR Hydraulic Parameters 110
6.2 STUMOD-MAR Default Hydraulic Parameter Values 111
6.3 Parameters Used in Microbial and Chemical Contaminant Transport Models.....112
6.4 Default CEC Parameters Used in STUMOD-MAR 113
6.5 Calculated Coefficient of Determination for Selected CECs.....119
6.6 Default Pathogen Parameters Used in STUMOD-MAR 120

Abbreviations and Acronyms

ADE	advection–dispersion equation
ARR	artificial recharge and recovery
AWT	advanced water treatment
BDOC	biodegradable dissolved organic carbon
CEC	chemical of emerging concern
CPE	cytopathogenic effects
CSM	Colorado School of Mines
DEET	N,N-Diethyl-meta-toluamide
DEX	dexamethasone
DOC	dissolved organic carbon
DPR	direct potable reuse
DT_{50}	dissipation of 50% of the initial concentration
EC_{10}	effective concentration for 10%
EEM	excitation–emission matrix
EQ	equivalent concentration
ESI	electrospray ionization
GR	glucocorticoid receptor
GUI	graphical user interface
HLR	hydraulic loading rate
HRT	hydraulic retention time
IPR	indirect potable reuse
KAUST	King Abdullah University of Science and Technology
K_b	biodegradation rate coefficient
K_d	sorption distribution coefficient
LACSD	Los Angeles County Sanitation Districts
LC-MS/MS	liquid chromatography–mass spectrometry/ mass spectrometry
LOD	limit of detection
LOQ	limit of quantification
MAR	managed aquifer recharge
MeOH	methanol
MNV	murine norovirus
MTBE	methyl tertiary-butyl ether
NF	nanofiltration
NSAID	nonsteroidal anti-inflammatory drug
PCR	polymerase chain reaction
PMMoV	pepper mild mottle virus
qPCR	quantitative polymerase chain reaction
RBF	riverbank filtration

R^2	coefficient of determination
R_f	retardation factor
RT-PCR	reverse transcription polymerase chain reaction
SEC	size exclusion chromatography
SPE	solid-phase extraction
STUMOD	Soil Treatment Unit Model
SUVA	specific ultraviolet absorbance
SWRCB	California State Water Resources Control Board
SWRF	Sweetwater Recharge Facility
TCEP	tris(2-carboxyethyl)phosphine
TCPP	tris(1-chloro-2-propyl)phosphate
TDCP	tris[2-chloro-1-(chloromethyl)ethyl]phosphate
TOC	total organic carbon
UofA	The University of Arizona
USGS	United States Geological Survey
UV	ultraviolet
WRD	Water Replenishment District of Southern California
WRRF	WateReuse Research Foundation
WWTP	wastewater treatment plant

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 sustainable sources of high quality water, protect public health, and improve the environment.

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

- Defining and addressing emerging contaminants, including chemicals and pathogens
- Determining effective and efficient treatment technologies to create "fit for purpose" water
- Understanding public perceptions and increasing acceptance of water reuse
- Enhancing management practices related to direct and indirect potable reuse
- Managing concentrate resulting from desalination and potable reuse operations
- Demonstrating the feasibility and safety of direct potable reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project to 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.

This project investigated the *role* of the environmental buffer in indirect potable reuse projects with respect to quantifiable efficiencies regarding attenuation of chemicals of emerging concern (CECs) and pathogens. Retention time in the subsurface and predominant redox conditions were identified as key performance parameters. Regarding CECs, retention times of less than 30 days usually resulted in efficient removal. Pathogens, in particular viruses, exhibited a log-linear removal relationship.

Douglas Owen
Chair
WateReuse Research Foundation

Melissa Meeker
Executive Director
WateReuse Research Foundation

Acknowledgments

This project was funded by the WateReuse Research Foundation in cooperation with the U.S. Bureau of Reclamation, California State Water Resources Control Board, and the Water Replenishment District of Southern California.

This study would not have been possible without the insights, efforts, and dedication of many individuals and organizations. These include the members of the research team and Project Advisory Committee members (as identified); the WateReuse Research Foundation's project managers, Jimena Pinzon and Julie Minton; many key individuals at the participating utilities and related organizations; and the outstanding staff, especially Dr. Dean Heil and Dr. Jennifer Teerlink of the Advanced Water Technology Center at the Colorado School of Mines, Bingfeng Dong at the University of Arizona, and Dr. Christiane Hoppe-Jones at King Abdullah University of Science and Technology.

The research team thanks the WateReuse Research Foundation for funding this research as well as the following organizations for their in-kind contributions: Aurora Water, County Sanitation Districts of Los Angeles County, Orange County Water District, Tucson Water, Water Replenishment District of Southern California, and Southern Nevada Water Authority.

Principal Investigators
Jörg E. Drewes, Ph.D., *Colorado School of Mines*
Charles P. Gerba, Ph.D., *The University of Arizona*
Shane A. Snyder, Ph.D., *The University of Arizona*
Thomas Missimer, Ph.D., *King Abdullah University of Science and Technology*
Julia Regnery, Ph.D., *Colorado School of Mines*
Eric Dickenson, Ph.D., *Colorado School of Mines*

Project Team
Mengistu Geza, Ph.D., *Colorado School of Mines*
Alexandre D. Wing, *Colorado School of Mines*
Mazahirali Alidina, *King Abdullah University of Science and Technology*
Walter Betancourt, Ph.D., *The University of Arizona*
Masaaki Kitajima, Ph.D., *The University of Arizona*
Ai Jia, Ph.D., *The University of Arizona*

Participating Agencies
Aurora Water, Colorado
County Sanitation Districts of Los Angeles County, California
Tucson Water, Arizona
Water Replenishment District of Southern California

Project Advisory Committee
David Balgobin, *California State Water Resources Control Board*
Stuart Khan, Ph.D., *The University of New South Wales*
Ronald P. LeBlanc, *U.S. Bureau of Reclamation*
Margaret H. Nellor, P.E., *Nellor Environmental Associates, Inc.*
Jeff Stone, *Water Resources Consultant*
Andrew Salveson, *Carollo Engineers*

Executive Summary

Project Background

Indirect potable reuse (IPR) schemes commonly employ a sequence of treatment processes after conventional biological wastewater treatment constituting multiple barriers of protection against potential contaminants and exposure to consumers. One important element within a multiple barrier concept can be the environmental buffer, which is defined as a surface water body or aquifer. IPR through managed aquifer recharge (MAR) can occur through recharge of unconfined or confined aquifers; by surface–groundwater infiltration (surface spreading) or subsurface application (direct injection or use of vadose zone wells), respectively, into an aquifer that serves as a source for drinking. MAR is achieved through soil–aquifer treatment (SAT) or riverbank filtration (RBF).

Within the context of MAR, retention time in an environmental buffer can serve two purposes: (1) provide time to respond to potential system failures or upsets; and (2) allow an additional opportunity for attenuation of microbial and chemical contaminants in situ. It has been generally assumed that the retention time in a MAR system is positively correlated with the level of treatment or contaminant attenuation achieved; performance standards for environmental buffers were never defined. Currently, the use and application of environmental buffers for IPR in the United States is based on regulatory guidance and current practice rather than specific knowledge-based science. In order to address these issues, the main goal of this research project was to develop and validate relationships between the removal and inactivation of pathogens and attenuation of chemical contaminants as a function of retention time, system characteristics, and operating conditions.

Project Objectives

The objectives of this project were to (1) develop correlations for the removal and inactivation of pathogens and attenuation of chemical contaminants as a function of retention time, system characteristics, and operating conditions to provide better guidance for design and operation of MAR systems; (2) develop predictive models to assess the attenuation of microbial and chemical contaminants in MAR facilities operated under various conditions; and (3) validate these relationships during field monitoring efforts at MAR facilities and through an assessment of historic water quality monitoring data from full-scale MAR installations representing various conditions.

This research was performed by a team of faculty, scientists, and graduate students from the Colorado School of Mines, the University of Arizona, and King Abdullah University of Science and Technology. The study was supported by researchers at the Water Replenishment District of Southern California, County Sanitation Districts of Los Angeles County, Aurora Water, and Tucson Water. It was funded by the WateReuse Research Foundation, U.S. Bureau of Reclamation, California State Water Resources Control Board, and the Water Replenishment District of Southern California.

Study Findings and Recommendations

A comprehensive literature review on the survival of viruses in groundwater revealed that adenoviruses, coliphages ΦX-174 and PRD-1, are among the longest surviving viruses in groundwater. Coliphages are similar in size and shape to many pathogenic human enteric viruses and commonly used as indicators for fecal pollution and potential indicators of enteric viruses. Inactivation rates of coliform bacteria and *Cryptosporidium parvum* during MAR, however, appeared to be much higher than virus inactivation rates; therefore, this study focused on the fate of viruses during MAR. Controlled laboratory studies simulating MAR conditions confirmed that pathogen inactivation does not fit linear filtration models. Inactivation rates are often not constant and may slow down with distance. Laboratory and field data suggest that linear-log functions best describe pathogen removal. These findings confirm those reported by Pang (2009) that removal rates are specific to the physical and chemical properties of the microbes, subsurface media, solution chemistry, transport scale, type of contaminated source (e.g., wastewater vs. surface water), and duration of contamination (years of operation). Where proper soil conditions are met, an inactivation of at least 2 log can be expected within a travel time of 5 to 10 days.

Trace organic chemicals detected in water are often generally referred to as chemicals of emerging concern (CECs) because the risk to human health and the environment associated with their presence, frequency of occurrence, or source may not be known. Regarding CECs for potable reuse applications, two mechanisms have been identified as important for attenuation during subsurface transport in MAR systems: sorption and biotransformation. Whereas the sorptive capacity of soil is well known for hydrophobic CECs, findings of this study suggest that more hydrophilic, water soluble CECs can be partially attenuated by sorption depending on soil properties (e.g., soil organic matter, clay content).

In laboratory-scale batch sorption experiments, the target compounds evaluated in this study, atenolol, caffeine, and trimethoprim, exhibited complete or nearly complete removal to below detection (>99%) in the presence of pure bentonite clay. The field soil taken from the initial layer of an infiltration basin was able to sorb 70% of atenolol, 91% of caffeine, and 70% of trimethoprim during this batch experiment. Concentrations of tris(2-carboxyethyl)phosphine (TCEP) and tris(1-chloro-2-propyl)phosphate (TCPP) did not decrease in the presence of field soil, whereas the concentration of the more hydrophobic tris[2-chloro-1-(chloromethyl)ethyl]phosphate (TDCP) was reduced by 57%. TDCP concentration was reduced by 71% on average by the field clay, which also removed 37 and 56% of TCEP and TCPP, respectively. These results suggest that clay, rather than organic carbon, is the dominant sorbent for these CECs in subsurface systems.

Biotransformation is another key mechanism for CEC attenuation in MAR systems. A determining factor for the biotransformation of trace organic chemicals in these systems is the redox condition prevailing in the subsurface. As electron acceptors are depleted during metabolism of dissolved organic carbon (DOC) while reclaimed water is infiltrating, the redox state of the system transitions from an oxic setting towards suboxic to an anoxic redox state. The depletion of DOC and subsequent shift in redox conditions both have direct impacts on the performance of the microbial community and therefore attenuation of CECs.

Findings from controlled laboratory studies confirmed by field monitoring campaigns revealed that reducing travel time in SAT to values of less than 30 days does not seem to result in a compromised water quality regarding chemical contaminants. During this study, a subsurface travel time of about 8 days in the aquifer was sufficient to remove the biodegradable portion of the DOC. If denitrification of remaining nitrate concentrations during SAT is desired, slightly longer travel times (10 to 30 days) might be needed where anoxic conditions can prevail. It is noteworthy that DOC removal was not affected by changes in temperature, indicating that the microorganisms responsible for DOC degradation were not sensitive to temperature changes within the studied range (8–30° C).

Field monitoring results revealed that feed water variations in concentration for biodegradable CECs were buffered during SAT and did not seem to affect the observed performance considering travel times of approximately 30 days. Although microbial diversity may converge with depth, the redox state of the system will differ depending on the amount and makeup of carbon present in the initial feed. Both of these factors affected the degree of biotransformation, in particular for moderately degradable CECs. In general, biotransformation of CECs under carbon-starving and specific redox conditions was compound specific. Moderately degradable compounds, with the exception of sulfamethoxazole, were removed significantly better under carbon-starving conditions than under high BDOC (>2 mg/L) conditions. Under oxic, carbon-starving conditions in controlled column experiments, complete removal was demonstrated for diclofenac, gemfibrozil, and naproxen within a retention time of 3 days. These results confirm that carbon-starving conditions characterized by low BDOC (~0.15–0.25 mg/L) improve removal efficiency of CECs. Carbon-starving conditions could also be established by aboveground treatment prior to MAR. Partial treatment by nanofiltration (NF) or reverse osmosis can reduce DOC concentrations, creating carbon-starving conditions after blending with a conventionally treated (tertiary effluent) reclaimed water. These DOC conditions are likely more favorable for CEC attenuation than using a tertiary effluent.

Overall, with the exception of a couple of compounds, lower temperatures did not significantly decrease CEC attenuation. Two of the compounds studied, trimethoprim and oxybenzone, were better removed as the operating temperature of the columns was reduced. This was unexpected because temperatures below 30° C have been shown to decrease bacterial respiration and growth rate.

Utilizing biotransformation rate constants for select CECs derived for predominant redox conditions (oxic, suboxic, anoxic) in controlled laboratory-scale studies allowed an accurate prediction of CEC removal under field conditions during short travel times in SAT (<30 days). Findings of this study confirmed the high reliability and efficiency of MAR and in particular SAT in removing BOC and trace organic chemicals as well as pathogens.

Future Research Needs

A number of research questions were raised during the completion of this study that should be investigated further to better understand the role of sorption/desorption processes for CECs and pathogens under dynamic recharge conditions and where different feed water types (e.g., reclaimed water, stormwater) are applied. In addition, modeling approaches for pathogen attenuation under various MAR conditions could be further improved. An important finding of this study revealed the role of carbon-starving conditions for CEC attenuation in the subsurface. Further research is needed to investigate how different engineering solutions could be implemented to utilize this concept under full-scale MAR conditions. This might

include the use of reclaimed water that has undergone partial advanced treatment in order to lower DOC concentrations prior to recharge (through NF treatment) or the use of recharge basins in sequence to quickly remove DOC during short retention times, followed by a second recharge event establishing carbon-starving conditions for CEC removal.

Chapter 1

Introduction

1.1. Background

With dwindling water supplies in the United States and many regions worldwide, potable reuse is becoming an increasingly important component of water resource management. Indirect potable reuse (IPR) is referred to as the purposeful addition of highly treated wastewater (e.g., reclaimed or recycled water) via an environmental buffer to a drinking water supply (Drewes and Khan, 2010). IPR schemes employ a sequence of treatment processes after conventional wastewater treatment, constituting multiple barriers of protection against potential contaminants and exposure to consumers. One important element within a multiple barrier concept is the environmental buffer, which is defined as a water body or aquifer, perceived by the public as natural, which serves to sever the connection between the water and its history.

In IPR schemes, the environmental buffer may also fulfill some or all of the following functions: (1) provide an opportunity to blend or dilute the reclaimed water ("blending"); (2) increase the amount of time between the treatment of reclaimed water and its introduction into the water supply ("retention" or "time to react"); and (3) decrease the concentration of microbial and chemical contaminants through various attenuation processes ("attenuation") involving physical, chemical, and microbiological transformations (Drewes and Khan, 2010). Regarding the latter, the environmental buffer may encompass aspects of treatment barriers suitable to control the concentrations of microbiological and chemical contaminants.

IPR through managed aquifer recharge (MAR) can occur through recharge of unconfined or confined aquifers via surface–groundwater infiltration (surface spreading) or subsurface application (direct injection or use of vadose zone wells) into an aquifer that serves as a source for drinking, respectively. Surface–groundwater infiltration is achieved through soil–aquifer treatment (SAT) or riverbank filtration (RBF). Within the context of MAR, retention time can serve two purposes: (1) provide time to respond to potential system failures or upsets and (2) allow additional opportunity for attenuation of contaminants in situ. It has been generally assumed that the retention time in a MAR system is positively correlated with the level of treatment or contaminant attenuation achieved.

Previous research has demonstrated that the relationship between retention time and attenuation varies depending on the type of contaminant, the MAR system characteristics, and the different MAR treatment strategies (Gerba et al., 1991; Rauch and Drewes, 2004; Drewes et al., 2006; Hoppe-Jones et al., 2010; Maeng et al., 2010). Site-specific differences among environmental buffers might explain why buffers will not always exhibit similar performance with respect to contaminant attenuation. Finally, for potable reuse projects practicing groundwater recharge, blending or dilution of reclaimed water with water not deemed to be of wastewater origin can occur prior to recharge or in the environmental buffer (e.g., the aquifer) itself.

Although three functions of an environmental buffer (blending, retention, and attenuation) have potentially important implications for public health, performance standards for buffers

were never defined. There is no universal standard for retention time in environmental buffers for potable reuse systems, and the retention provided by current projects in the United States varies from a few weeks to more than 6 months. Currently, the use and application of environmental buffers for IPR are based on regulatory guidance and current practice rather than specific knowledge-based science. Sufficient science does not currently exist to definitively articulate which retention time is in fact appropriately protective of public health in terms of providing an efficient barrier to chemical and microbiological contaminants. Rather, it is the perception that the water has passed through a natural system, such as groundwater aquifers, that increases public acceptance of the subsequent use of the water in potable supplies.

Very recently, a number of activities have been initiated related to the potential for direct reuse in the United States (NWRI, 2010). In contrast to IPR, direct potable reuse (DPR) is defined as the immediate addition of reclaimed water to a drinking water distribution system or the raw water supply directly upstream of a drinking water treatment facility. One of the key perceived challenges facing DPR is if and how the value of an environmental buffer could potentially be achieved by aboveground engineered treatment strategies in potable reuse systems.

In order to address these issues, the main goal of this research project was to develop and validate correlations with the removal and inactivation of pathogens and attenuation of chemical contaminants as a function of retention time, system characteristics, and operating conditions. These data will provide better guidance for design and operation of MAR systems.

The development of a practical understanding of the relationship between MAR system retention time and contaminant attenuation is essential to engineering MAR systems that will achieve the level of treatment necessary to meet the desired product water standards. A better understanding of these issues will increase the confidence in the role and effectiveness of an environmental buffer and provide scientific data that can be used to guide the regulatory process. Retention time represents a key factor for the physical sizing and location of a MAR project. For example, if water quality standards and objectives can be met with shorter retention times, more configurations and locations to utilize environmental buffers will be feasible and consequentially will increase the potential for potable reuse.

Conversely, it may require specific project management approaches to obtain retention times or limits to where projects can be sited if requirements can only be achieved with longer retention times. The relationships between attenuation and retention time developed during this study will allow determination of critical design parameters and predictions of performance within predefined operational conditions and suggest performance limitations of MAR systems. In addition, guidance will be provided to utilities and regulators regarding how to determine retention time and removal efficacy for microbial and chemical contaminants in subsurface systems. Findings of this study may also enable researchers and project designers to propose above-ground treatment strategies to replace the functions of an environmental buffer in future DPR systems.

1.2. Project Objectives

The primary objectives of this project were threefold:

1. Develop relationships between the removal and inactivation of pathogens and attenuation of chemical contaminants and retention time, system characteristics, and operating conditions to provide better guidance for design and operation of MAR systems.

2. Develop predictive models to assess the attenuation of microbial and chemical contaminants in MAR facilities operated under various conditions.

3. Validate these relationships during field monitoring efforts at MAR facilities and through an assessment of historic water quality monitoring data from full-scale MAR installations representing various conditions.

1.3. Related Research

1.3.1. Attenuation of Pathogens by MAR

More than 200 enteric pathogens can be expected to occur in untreated domestic wastewater. They occur in larger numbers than other groups of pathogens, have a lower infectious dose, and are more resistant to removal by conventional activated sludge wastewater treatment, including disinfection (Maier et al., 2009). Usually they can be reduced by approximately 99% by activated sludge treatment (Maier et al., 2009). Advanced treatment processes, such as filtration and extended disinfection, are required to reduce their numbers below detection. Thus, depending upon treatment, some viruses may be expected to occur in wastewater used for MAR. Viruses also survive longer than other enteric pathogens in aquatic environments and have the greatest potential for subsurface transport, although enteric bacteria and protozoa are also associated with groundwater disease outbreaks (Maier et al., 2009). Pathogen removal by MAR occurs primarily by filtration/adsorption and die-off within the soil matrix (Gerba et al., 1991). Numerous laboratory and field studies have been conducted on the transport of pathogens and surrogates through soil in wastewater and groundwater. Pang (2009) recently extensively reviewed the existing literature on the topic and concluded:

- Microbial removal determined from laboratory soil column studies can be one to three orders of magnitude greater than that determined by field studies regardless of water type and pertaining to both seeded and naturally occurring enteric organisms. This is because virus removal rate decreases with travel distance from the source.
- Removal does not fit linear filtration models. Removal rates are not always constant and may slow with distance. Field data suggest that linear-log functions best describe pathogen removal.
- Microbial populations associated with reclaimed water may be removed to a lesser degree than those associated with uncontaminated water because of a number of factors including the heterogeneity of the microbial population (size, surface charge, and survival time), pathogen association with particulates, and presence and type of organic matter (blocks adsorption sites).
- Vertical and horizontal removal rates differ.

- Organisms cultivated in the laboratory have lower removal rates than those naturally occurring in wastewater effluents because they only represent one strain of a particular organism (e.g., uniform size, surface charge).

Pang (2009) concluded that removal rates are specific to the physical and chemical properties of the microbes, subsurface media, solution chemistry, transport scale, type of contaminate source (e.g., wastewater vs. surface water), and duration of contamination (years of operation). He recommended that for predictive purposes it is best to match all experimental and environmental conditions, especially flow rate, when estimating removal rates at a specific site.

MAR systems have certain operational factors that may also influence the removal of pathogens and should be taken into consideration when assessing removal. These include:

- Impact of rainfall or recharge of stormwater. Rainfall can mobilize previously retained microorganisms, allowing greater transport (Lance et al., 1976).
- Impact of water quality changes. Alternate uses of wastewater and surface water with different water chemistries may impact transport of pathogens (Lance et al., 1976).
- Operational conditions resulting in change of infiltration rates (Taylor et al., 2004)
- Well pumping regimes resulting in changes in the amount and flow rate at which water is extracted while also influencing groundwater velocities (Taylor et al., 2004)
- Length of the unsaturated zone. Greater removal of some organisms occurs in the unsaturated zone (Chu et al., 2003).

Because organisms retained in the soil matrix may later be released (Lance et al., 1976), predicting die-off of the pathogen is necessary. All enteric organisms will eventually die off in the environment. Although numerous factors are involved, temperature is the most predictive (Gerba et al., 1991). Hepatitis A virus, adenoviruses, and parvoviruses appear to be the most thermally stable waterborne pathogens, although bacteria may persist for long periods of time if environmental conditions are favorable (Gerba, 2007). Die-off of organisms is not always linear, especially at low concentrations, and this must be taken into consideration in any attempts to estimate die-off rates (Gerba et al., 1991).

1.3.1.1. Impact of Molecular Methods for Pathogen Detection

Molecular methods, such as the polymerase chain reaction (PCR), have allowed for the detection of almost any enteric pathogen in wastewater. In recent years, they have been extensively applied to the detection of enteric viruses in wastewater and groundwater. Because infectivity assays cannot detect all the pathogens present (e.g., cell culture methods for viruses are only 1 to 10% efficient), greater numbers of viruses are detected by PCR (Mahalanabis et al., 2010).

In addition, although useful for detection of the presence of viruses, PCR techniques cannot determine infectivity. Thus, both infectious and noninfectious viruses may be detected. For example, proper disinfection removes viral infectivity in cell culture but not necessarily by PCR; however, the detection of the virus's nucleic acid suggests that an infectious virus could also be present. PCR is a more conservative measure of virus presence: absence of virus detection by PCR indicates that viruses are not present. For this reason, it is important to consider how long enteric viruses (and potentially other enteric pathogens) will be detected

after the virus is no longer capable of causing infection. It is possible that DNA of some viruses may be detected longer than RNA because of greater resistance to degradation. This should be considered in any attempts to predict pathogen removal by MAR.

1.3.1.2. Emerging Pathogens of Concern

One of the issues with estimating pathogen removal by MAR is that new enteric pathogens of concern continue to emerge (e.g., bocavirus, picobiranviruses, parvoviruses, enterovirus types 78-101, microsporidia; Maier et al., 2009). In addition, the application of molecular methods has revealed a large number of viruses that infect humans in domestic wastewater (e.g., polyomaviruses, torque teno virus; Ahmed et al., 2010; Vaidya et al., 2002). Although water may not be a primary route of transmission, viruses will be detectable in reclaimed water by molecular methods, and concerns regarding their presence will need to be addressed.

1.3.2. Attenuation of Nitrogen by MAR

Nitrogen species that are relevant to human health are nitrite and nitrate. Surface spreading or RBF facilities usually achieve additional nitrification of remaining ammonia in the initial phase of infiltration (Fox et al., 2001). Depending on the availability of organic carbon and predominant redox conditions in the subsurface, denitrification usually results in total nitrogen concentrations of less than 5 mg N/L (Hoppe-Jones et al., 2010; Laws et al., 2011) after SAT and RBF.

1.3.3. Attenuation of Organic Matter by MAR

The removal of organic matter during MAR is highly efficient and largely independent of the level of treatment provided above ground. Biodegradable organic carbon that is not attenuated during wastewater treatment represents an electron donor for microorganisms in the subsurface and is readily removed during groundwater recharge (Drewes and Fox, 2000; Rauch-Williams and Drewes, 2006). Monitoring efforts revealed that consistent removal of TOC between 70 and 90 percent can be achieved at full-scale SAT facilities that have been in operation for several decades (Quanrud et al., 2003; Amy and Drewes, 2007; Laws et al., 2011).

The removal of easily biodegradable organic carbon in the infiltration zone usually results in depletion of oxygen and the creation of anoxic conditions. Although this transition is advantageous to achieve denitrification, it might also lead to the solubilization of reduced manganese, iron, and arsenic from native aquifer materials. Relationships between attenuation of DOC and retention time have been proposed in the past, suggesting that DOC removal follows a first-order decay (Drewes and Jekel, 1998; Drewes and Fox, 2000).

1.3.4. Attenuation of Trace Organic Chemicals by MAR

Reclaimed water can contain thousands of chemicals originating from consumer products (e.g., household chemicals, personal care products, pharmaceutical residues), human waste (e.g., natural hormones), industrial and commercial discharge (e.g., solvents, heavy metals), or generated during water treatment (e.g., transformation products). Previous studies performed by the team and others have characterized the transformation and removal of select trace organic chemicals during MAR for travel times ranging from approximately 1 day to 8 years (Drewes et al., 2003; Montgomery-Brown et al., 2003; Grünheid et al., 2005; Amy and Drewes, 2007; Massmann et al., 2008; Laws et al., 2011).

Although it is difficult to determine which trace organic chemicals should be monitored to assess the efficacy of MAR systems, a conservative approach has evolved that combines the use of bulk parameters (i.e., surrogates) and a select number of indicator chemicals (Drewes et al., 2008; Dickenson et al., 2009, 2011). These studies demonstrated that changes in bulk parameters correlated with changes of indicator chemicals in the subsurface or during advanced treatment leading to direct injection (Drewes et al., 2011). Performance indicators and surrogate parameters are defined as follows:

- An indicator compound is an individual chemical occurring at a quantifiable level that represents certain physicochemical and biodegradable characteristics of a family of trace organic constituents that are relevant to fate and transport during treatment.
- A surrogate parameter is a quantifiable change of a bulk parameter that can measure the performance of individual unit processes (often in real time) or operations in removing trace organic compounds.

In 2013, the California State Water Resources Control Board (SWRCB) endorsed this concept following the recommendations of a Science Advisory Committee to ensure proper performance of MAR operations regarding the removal of trace organic chemicals (Anderson et al., 2010; Drewes et al., 2013). The SWRCB suggested a combination of appropriate surrogate parameters and health- and performance-based indicator chemicals for monitoring of SAT and direct injection projects (Table 1.1).

Selecting multiple indicators representing a broad range of properties and amenability to biotransformation will allow study of how changes in retention time affect the degree of removal achieved during MAR. Multiple indicators with various properties will also account for compounds currently not identified (unknowns) and new compounds synthesized and entering the environment in the future (e.g., new pharmaceuticals) provided they fall within the range of properties covered. This concept of using health- and performance-based indicators has been adopted for this study and augmented with additional compounds to derive relationships between attenuation and retention time for a wider range of representative compounds.

Table 1.1. Health- and Performance-Based Indicators and Performance Surrogates for MAR Practices

Reuse Practice	Health-Based Indicator	MRL (ng/L)	Performance-Based Indicator	Expected Removal[8]	MRL (ng/L)	Surrogate	Method	Expected Removal[8]
SAT	17β-estradiol[1]	1	Δgemfibrozil[5]	>90%	10	Δammonia	SM	>90%
	triclosan[2]	50	ΔDEET[6]	>90%	10	Δnitrate	SM	>30%
	caffeine[3]	50	Δcaffeine[3]	>90%	50	ΔDOC	SM	>30%
	NDMA[4]	2	Δiopromide[5]	>90%	50	ΔUVA	SM	>30%
			Δsucralose[7]	<25%	100			
Direct Injection	17β-estradiol[1]	1	ΔDEET	>90%	10	Δconductivity	SM	>90%
	triclosan[2]	50	Δsucralose	>90%	100	ΔDOC	SM	>90%
	caffeine[3]	50	ΔNDMA	25–50%	2			
	NDMA[4]	2	Δcaffeine	>90%	50			

Notes: Adopted from State of California (2013); 1=steroid hormones; 2=antimicrobial; 3=stimulant; 4=disinfection byproduct; 5=pharmaceutical residue; 6=personal care product; 7=food additive; 8=travel time in subsurface 2 weeks and no dilution, see details in Drewes et al. (2008); DEET=N,N-Diethyl-meta-toluamide; DOC=dissolved organic carbon; MRL=method reporting limit; NDMA=N-Nitrosodimethylamine; SAT=soil–aquifer treatment; SM=standard methods; UVA=ultraviolet absorbance.

1.3.5. Attenuation of Glucocorticoid Disruption by MAR

Reclaimed water contains a large number of unknown compounds, so the use of bioassays targeting certain endpoints can assist in the assessment of treatment performance and safe finished water qualities. Glucocorticoids are a group of steroid hormones that regulate an array of physiological processes crucial for development, metabolism, electrolyte balance, cell proliferation, and differentiation (Odermatt et al., 2006; Bovee et al., 2011). Glucocorticoid dysfunction has been associated with a range of conditions including cardiovascular, inflammatory, and immune diseases, osteoporosis, type 2 diabetes, and obesity (Odermatt et al., 2006). The importance of glucocorticoids for adipogenesis is also receiving increasing interest (Sargis et al., 2010).

Recent studies have demonstrated the potential ecotoxicological effects of glucocorticoid compounds on fish, including inhibited locomotion and aggressive behavior of rainbow trout (Kugathas and Sumpter, 2011). Natural and synthetic glucocorticoids have been widely applied as therapeutic pharmaceuticals as well as veterinary medicines often used to restore muscle strength or promote growth.

Despite the potential for environmental occurrence, glucocorticoid disruption has received far less interest than estrogens and androgens. Over the past 2 years, significant glucocorticoid activity has been consistently detected in secondary wastewater effluents from Tucson, AZ. A highly sensitive live cell assay based on subcellular relocalization of green fluorescent protein–tagged glucocorticoid receptors (GR) was used to screen water samples for glucocorticoid activity (Stavreva et al., 2012). This bioassay is based on the fact that, in the absence of a corresponding hormone, GR resides in the cytoplasm in a large multiprotein complex. Upon hormone binding, GR dissociates from this complex and transfers to the cell nucleus, where it interacts with GR regulatory elements to trigger hormone-specific transcription regulation (Stavreva et al., 2012).

1.4. Project Approach

The main approach of this study was to develop relationships between retention time and attenuation of microbial and chemical contaminants. The study utilized standardized methods as well as unique approaches using state-of-the-art analytical instrumentation, which were well established at laboratories of the Colorado School of Mines (CSM) and the University of Arizona (UofA). In addition, project partners at King Abdullah University of Science and Technology (KAUST) conducted supplemental laboratory-scale investigations to elucidate the impact of temperature and soil properties on attenuation. The study also built upon previously developed laboratory-scale systems simulating various MAR conditions. Study findings were validated at full-scale MAR facilities operated by participating utilities that provide a rich historic water quality database and have been comprehensively studied by members of the research team in the past.

The technical approach to this project was broken into four tasks, as follows:

1. Literature review
2. Laboratory studies
3. Field validation studies
4. Modeling framework

The literature review will soon be published in a peer-reviewed journal publication (Regnery et al., in review). The results of laboratory and field studies regarding attenuation of trace organic chemicals and pathogens are presented in this report, including a modeling framework. This modeling framework can assist stakeholders in assessing removal efficiencies of MAR facilities as a function of key operational conditions. The report concludes with recommendations and suggestions for future research.

Chapter 2

Materials and Methods

2.1. Field Sampling Sites

2.1.1. Prairie Waters Project, Aurora Water

In 2010, the city of Aurora, CO, launched the Prairie Waters Project to supplement its drinking water supply after experiencing extreme drought conditions in 2002 and 2003. A MAR system consisting of RBF galleries and an artificial recharge and recovery (ARR) system as part of an advanced water treatment (AWT) train was constructed downstream of Denver along the South Platte River in Brighton. The full-scale site was constructed in 2008 and launched in 2009 (Aurora Water, 2012). The site was designed with a capacity of approximately 200 m^3/s abstracted through 17 vertical RBF wells located along the riverbank (Figure 2.1). The screening intervals of the RBF wells are characterized by a depth of 30 to 50 ft below ground surface and are placed 300 ft off the river on average.

At the point of abstraction, the water quality of the South Platte River is highly influenced by wastewater effluent during low flow conditions and snowmelt during spring run-off. Annual mean flow through the river is 14 m^3/s. At low flow, the average flow is as low as 5 m^3/s with up to 90% wastewater effluent contribution; at high flow, the average flow reaches up to 120 m^3/s and is composed largely of snowmelt (Hoppe-Jones et al., 2010). The soil composition at the site is characterized by alluvial sand with some gravel and silt. The organic carbon content was determined to be approximately 0.05% (Hoppe-Jones et al., 2010). At current river flow, approximately 26 m^3/s is extracted through the riverbed each day.

Travel times during RBF treatment are on average 7 to 10 days before the combined RBF filtrate is fed via pipes into an array of surface spreading basins at the adjacent ARR facility. Infiltration rates in the basins range between 0.2 m/d (loams) and 0.5 m/d (sandy loams). A continuous slurry wall along the entire perimeter of the ARR facility extending from the surface to the bedrock is used to isolate the recharged water from the surrounding native groundwater system. A total of 26 recovery wells and 20 monitoring wells are placed throughout the ARR site. The site is designed to provide an additional retention time of approximately 20 days of subsurface travel for the recharged water before the recovered groundwater is conveyed to the AWT plant.

A field-scale sampling campaign was performed between September and November 2012 to evaluate full-scale MAR performance. For the targeted sampling program, the north cell of the southwest basin and the east cell of the central basin as well as appropriate downgradient monitoring and production wells were utilized to assess (1) flow paths and travel times in the subsurface, (2) blending ratios of individual wells with native groundwater still present at the site, and (3) water quality changes during ARR for several key parameters. An electric submerged pump was used to abstract samples from existing monitoring wells at the ARR site. Samples from RBF wells and combined collectors were taken from sampling taps. Prior to sampling, all wells were purged until a steady conductivity measurement was recorded

(>20 min purging). One surface water sample collected from South Platte River (adjacent to the well field) in July 2013 was analyzed for glucocorticoids.

The sampling campaign for pathogen inactivation was carried out between October 2012 and May 2013. During that time period, on a weekly basis, 2 L samples from the discharge of the Denver Metropolitan Water Reclamation Plant (secondary treated effluent) and the South Platte River across from well PW10 (see well location #1, Figure 2.1) at the Aurora ARR site were collected on a weekly basis and analyzed for pathogens. Residual chlorine in the wastewater samples was neutralized by addition of sodium thiosulfate when the samples were taken (5 mL of a 10% solution). In addition, groundwater samples were collected with sample volume sizes ranging from 5 to 400 L. Larger volume samples were processed on site using NanoCeram filters by connection of a spigot at the wellhead to a filter housing and flow meter in series (Figure 2.2).

Samples of 500 L and 1000 L were processed once for the RBF combined collector. Flow measurements at the recovery well have been conducted using a graduated cylinder (4 L) to confirm the processed volume through the filter. After sampling, filters are stored in a cooler inside a wetted bag to prevent dry-out and shipped to the UofA laboratory for further analysis. After each sampling event, the filter housing was soaked in a bucket with 1⁄4 cup of bleach per gallon for 15 min and then rinsed with 2 L of sterile water containing 10 g/L sodium thiosulfate for disinfection.

Figure 2.1. Aerial map of the RBF well field along South Platte River at Brighton and map of the adjacent aquifer recharge and recovery site including well locations.

Figure 2.2. Pathogen sampling of recovery Well PW10 with NanoCeram filter.

2.1.2. San Gabriel Spreading Grounds Test Basin

The United States Geological Survey (USGS)/Water Replenishment District of Southern California (WRD) test basin at the Montebello Forebay was constructed in the early 90s at the north end of the San Gabriel River Coastal Spreading Grounds, located between Whittier and Washington Boulevards in Pico Rivera, Los Angeles County, CA (Figure 2.3). Tertiary treated reclaimed water is delivered from the water reclamation facilities to the spreading grounds through an 8-foot diameter culvert. The tertiary treatment consists of dual-media filtration followed by chlorination and dechlorination. A small percentage of the total flow can be diverted to the 2023 m^2 large test basin through a 6-inch pipeline using a submersible pump. A constant head is maintained in the test basin by controlling the pump using a water-level control switch. The test basin is fully equipped with a multilevel sampler and monitoring wells (Figure 2.4). The infiltration rate for reclaimed water at the test basin was determined to be in the range of 0.6 to 0.9 m per day (Schroeder, 2003). A more detailed description of the site can be found in Schroeder (2003) and Anders et al. (2004).

Researchers from CSM conducted the first field sampling campaign at the test basin from December 10 to 12, 2012, and the second campaign from April 24 to 26, 2013. Though both sampling campaigns were scheduled to be outside the rainy season to avoid dilution of recycled water with stormwater during recharge operation, an unexpected storm system moved into the area a few days prior to sampling campaign #1. The total amount of rain (measured at Whittier, CA) during this storm event between November 30 and December 3, 2012, was less than 33 L/m^2. No stormwater was diverted into the San Gabriel Spreading Grounds desilting basin after this storm event according to observations of a WRD representative on December 5, 2012.

For both sampling campaigns, the spreading grounds were kept dry for 4 to 5 weeks prior to the infiltration test in order to minimize the influence of stormwater or other recycled water. Weather conditions during both sampling campaigns were dry and sunny with average daily air temperatures of about 16° C (campaign #1) and 19° C (campaign #2). The characteristics of all sampled wells within this study are summarized in Table 2.1. Well locations at the test basin and the San Gabriel Spreading Grounds are shown in Figures 2.3 and 2.4.

On the basis of travel times obtained in previous studies (Laws et al., 2011), the sampling of targeted groundwater monitoring wells at the test basin had been scheduled to track the initial plume of infiltrated reclaimed water throughout the aquifer (synoptic grab sampling). The underlying sandy aquifer was bisected by a clay lens a few feet thick, approximately 9.5 m below the basin (Anders et al., 2004). Wells MLS-9, MLS-10, MLS-14, WP-Z, PR-9, and PR-11 are located in the upper aquifer underneath the test basin, and Wells PR-8 and PR-10 are located in the lower aquifer (Laws et al., 2011). Wells MLS-9, MLS-10*, MLS-14*, MLS-20*, WP- Z*, PR-9, PR-11, PR-14, and the test basin* were sampled for bulk parameters and CECs (* indicates multiple samplings during each campaign). Wells WP-Z, PR-9, PR-14, and PR-15 were sampled for pathogens once in December 2012. One test basin influent sample during campaign #2 was analyzed for glucocorticoids by high performance liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS).

In total, the test basin influent (tertiary treated effluent provided by Los Angeles County Sanitation Districts (LACSD) was sampled nine times in total on eight different days to account for fluctuations of CEC and TOC concentrations in the receiving reclaimed water during both sampling campaigns. As CEC concentrations are known to exhibit a high variability in wastewater received on weekends and Mondays, sampling on Mondays and Tuesdays was avoided during the second sampling campaign. Unfortunately, sampling of well WP-Y failed because of a clogged well screen.

Readings of field parameters (e.g., temperature, conductivity, pH, dissolved oxygen, oxidization reduction potential, water level) for all sampled wells and the test basin were collected during the sampling events. During both campaigns, WRD staff conducted additional sampling of four monitoring wells (PR-8, PR-10, PR-13, PR-19) that provide travel times up to 40 days. Prior to both sampling campaigns, the filling of the test basin with reclaimed water to activate and maintain the indigenous microbial community was scheduled as shown for the April campaign (Figure 2.5):

- Between January 22 and March 19, 2013: Running water to the test basin once a week for approximately 0.5 to 1 h (routine operation)
- March 19, 2013: Running water to the test basin for approximately 8 h for wetting
- March 26, 2013: Running water to the test basin for approximately 8 h for wetting
- April 2, 2013: Filling of the test basin for 7 days at 300 gpm, filling level approximately 1 foot of standing water. Drying of the test basin started April 9, 2013.
- April 17, 2013: Filling of the test basin for CSM sampling at 300 gpm, running a constant head on the basin.
- May 1, 2013: Stop running water to the test basin, drying of the test basin started.

Table 2.1. Sampled Wells at the San Gabriel Spreading Grounds During the December 2012 Field Campaign

Well Name	Screen (ft)	Total Depth (ft)	RPE (ft)	Study Travel Times (days)[1]			
				2008	2009	2011	Average
PR-2 (AKA MLS 3-20)	N/A	3-20[a]	N/A	N/A	MLS8: 0.41 MLS14: 0.75 MLS20: 1.79	N/A	MLS8: 0.41 MLS14: 0.75 MLS20: 1.79
PR-8	54–59[b]	58.4[b]	172.42	62.1	60*	35.3	48.7
PR-9	30–35[b]	35[b]	172.44	3.4	2.1	3.5	3.0
PR-10	55–60	59.47	173.33	62.1	60*	43.6	52.9
PR-11	31–36	35.4	173.3	10.7	2.9	3.5	5.7
PR-13	30–40	40.5	173.24	N/A	N/A	30.4	30.4
WP-Y	19–21[b]	22.3[b]	171.17	N/A	0.6	N/A	0.6
WP-Z	18–20[b]	21.2[b]	172.49	N/A	0.5	0.4	0.45
PR-19	30–40	40.5	173.14	N/A	N/A	N/A	8.3^
PR-14	60–70	70.5	171.731	N/A	N/A	128.5	128.5
PR-15	30–40	40.5	171.817	N/A	N/A	49.5	49.5

Notes:
[a] = referenced from below the research-basin floor
[b] = from top of casing, which is approx 10 feet above bottom of test basin on catwalk. Total depths measured on 9/15/06.
[1] = Study travel times are based on measured peak temperature arrivals at the corresponding wells.
* = Values estimated based on rate of travel
^ = Travel time estimate provided by WRD (well constructed in 2012).

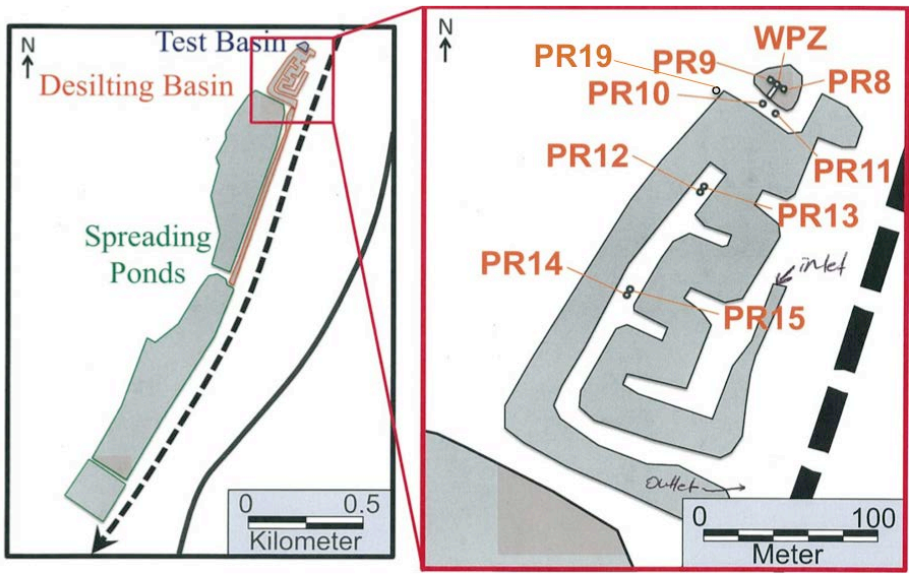


Figure 2.3. Map of the San Gabriel Spreading Grounds, Montebello Forebay, Los Angeles County, including well locations.

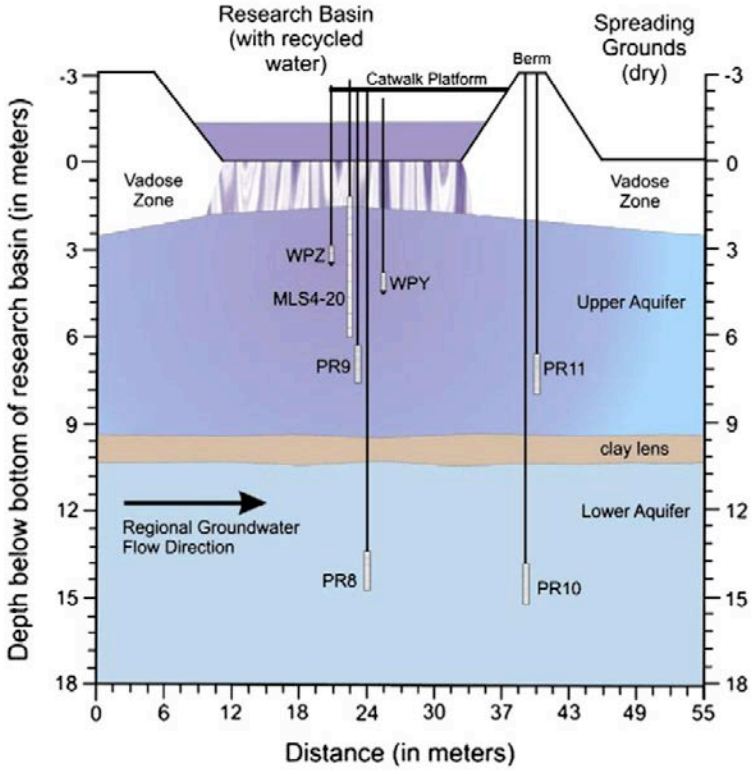


Figure 2.4. Schematic map of the test basin at the San Gabriel Spreading Grounds including well locations.

Source: Adapted from Laws et al. (2011).

As discussed with WRD staff, the test basin was expected to receive tertiary treated effluent from the same source (LACSD water reclamation plant) for all recharge events prior to and

during both sampling campaigns. Table 2.1 denotes the subsurface travel time CSM researchers have considered for the synoptic sampling. Travel time estimates for additional monitoring wells installed in April 2012 by WRD were not available (except Well PR-19). WRD provided the travel time estimate for the shallow Well PR-19 based on water temperature measurements; however, there is a wide range of travel times reported for some of the wells (e.g., data provided by WRD, Anders et al., 2004), which sapped the synoptic sampling strategy, as discussed later.

Figure 2.5. Montebello Forebay test basin during wetting operation for microbial community activation (November 5, 2012).

2.1.3. Sweetwater Recharge Facility, Tucson Water

Water reuse is a critical part of regional water supply planning for the city of Tucson, AZ. Approximately 60,000 L per day of reclaimed water is infiltrated, stored (6–12 months), recovered, and subsequently reused for landscape irrigation at the Sweetwater Recharge Facility (SWRF). SWRF is located in Tucson along the east and west banks of the Santa Cruz River. The facility receives chlorinated, non-nitrified, secondary effluent from Pima County's 41 mgd Roger Road Wastewater Treatment Plant (WWTP). At the time of the study, this plant employed non-nitrifying trickling filters as secondary treatment. The SWRF consists of eight infiltration basins that have been in operation since 1989. The basin soils have been classified as sandy loam with a porosity of 0.39 (Quanrud et al., 1996). The basins are underlain with a coarse sand and sandy gravel and are infiltrated on wet–dry cycles varying from 2 to 7 days depending upon the season. Additional details of the operation of the site can be found in Wilson et al. (1995).

For this study, operation of only research basin RB-1 (13,355 m^2 in size) was investigated (Figure 2.6). Average cycle infiltration rates in recharge basin RB-1 are approximately 1 foot per day (0.3 m/day). The SWRF site is characterized by a moderate 37 m deep vadose zone. Unfortunately, Well WR-199A, which sits directly adjacent to the basin, was clogged and not operational during the sampling campaign. Samples were collected from spreading basin RB-1, a piezometer (MW-5, 1.5 m below ground surface), and the next closest monitoring well, located nearby at the northeast corner of the basin (WR-069B, well screen 29–41 m below ground surface). Well WR-069B is partially affected by native groundwater.

Figure 2.6. Aerial map of the Sweetwater Recharge Facility, Tucson, and sampled well locations.
Source: Google Maps (2013).

Synoptic grab sampling at the site was conducted between February 21 and March 8, 2013, for the analysis of bulk organic carbon, CECs, pathogens, and GR activity. Travel times to the piezometer (MW-5) and the groundwater monitoring well (WR-069B) were estimated from previous studies (Fox et al., 2001) at approximately 5 days and 2 weeks, respectively. To account for source water quality variability, the influent of the basin was sampled three times a day. An additional field blank sample was included in GR activity analysis. Samples for bulk organic carbon and CEC analysis were preserved and immediately shipped to CSM. CEC samples were analyzed in triplicate to avoid misinterpretation caused by outliers.

2.2. Analytical Methods for Bulk Parameter and CEC Analyses

2.2.1. Physicochemical Parameters

2.2.1.1. pH and Conductivity

Conductivity, pH, and temperature were measured using an OAKTON waterproof pH/CON 300 m (OAKTON Instruments, Vernon Hill, IL; Standard Method 2510, APHA, 2012).

2.2.1.2. Redox Potential and Dissolved Oxygen

Dissolved oxygen was determined using a YSI model 55 m (YSI Incorporated, Yellow Springs, OH). The oxidization reduction potential was measured in mV by an Ion 6+ electrode (Oakton Instruments, Vernon Hills, IL) calibrated with Ag/AgCl (4M KCl) reference solution at room temperature (YSI 3682 Zobell Solution, YSI Incorporated; APHA, 2012). Oxidization reduction potential readings are reported as standard reduction potential (E_0).

2.2.2. Bulk Parameters

2.2.2.1 Inorganic Anions

Inorganic anions were determined using a Dionex IS 90 Ion Chromatography system according to Standard Method 4110 B. The anions that were examined are fluoride, bromide, chloride, nitrate, phosphate, and sulfate. Ammonia was measured according to the Hach Nessler Method 8038 adapted from Standard Methods 4500-NH_3 B and C (APHA, 2012). Metals were determined by using a Perkin-Elmer Elan 6100 inductively coupled plasma mass spectrometry system (Standard Method 3125 B; APHA, 2012). This method measured a suite of metals, including Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Si, Sn, Sr, Ti, U, V, and Zn.

2.2.2.2. Bulk Organic Carbon

All samples for organic chemical analyses were preserved to minimize biotransformation and stored at 5° C pending analysis.

At CSM, the total organic carbon (TOC)/DOC was quantified using a Sievers 5310 TOC analyzer with autosampler (Ionics Instruments, Boulder, CO) according to Standard Method 5310 B (APHA, 2012). The samples were placed in 17 mL sample vials and acidified with phosphoric acid. Measurements of TOC are based on calibration with potassium hydrogen phthalate standards. DOC was measured by the same procedure used for TOC, except the sample was prefiltered (0.45 μm pore size).

Biodegradable dissolved organic carbon (BDOC) is an operationally defined parameter and was determined as differential measurements of DOC measured in the reclaimed water prior to and after SAT. The BDOC value corresponds to the difference between the initial DOC and the final concentration reached in a defined period.

Ultraviolet absorbance (UVA) was analyzed using a Beckman UV/VIS spectrophotometer with a 1 cm quartz cell (Standard Method 5910 B; APHA, 2012). Samples were measured at wavelengths of 200 to 400 nm. The specific ultraviolet absorbance (SUVA) is defined as the ratio between UVA (254 nm) and DOC.

Size exclusion chromatography (SEC) was carried out using paired ultraviolet (UV; 254 nm) and DOC detection, with an injection volume of 2 mL, an acid addition rate of 2 μL/min, and an oxidizer addition rate of 0.7 μL/min. SEC measures the molecular weight distribution of heterogeneous natural organic matter in aqueous samples using an LC-600 liquid chromatograph (Shimadzu, Kyoto, Japan) coupled with a SPD-10 A VP UV-VIS detector (Shimadzu, Kyoto, Japan) at 254 nm (Rauch and Drewes, 2005; Drewes et al., 2006; Drewes et al., 2011).

Three-dimensional fluorescence excitation–emission matrix (EEM) spectra were generated using a Fluoromax 4 spectrofluorometer with a xenon lamp (Horiba Jobin Yvon) across an excitation spectrum of 240 to 450 nm and an emission spectrum of 290 to 580 nm (Cory and McKnight, 2005).

At KAUST, samples were filtered using a 0.45 μm glass microfiber filter and analyzed for DOC using a Fusion Total Organic Carbon Analyzer (Teledyne Tekmar; Mason, OH) and UV absorbance (254 nm) using a UV-2550 Spectrophotometer (Shimadzu, Japan).

2.2.3. Chemicals of Emerging Concern

At CSM, CEC analysis by LC-MS/MS was performed using an isotope dilution method modified from Vanderford and Snyder (2006) as reported in Teerlink et al. (2012). Prior to analysis by LC-MS/MS, samples were extracted by Waters Oasis HLB cartridges (500 mg adsorbate) using an automated solid-phase extraction (SPE) unit (AutoTrace 280, Thermo Scientific, USA). Isotope standards (100 ppb in methanol) were obtained for all target analytes and spiked into the water samples (100–200 mL) prior to SPE. Cartridges were conditioned with 5 mL methyl tertiary-butyl ether (MTBE), 5 mL methanol, and 5 mL of ultrapure water. The water sample was passed through each cartridge with a flow of 4 mL/min. The cartridges were then dried under a nitrogen stream for 1 h, and analytes were eluted from the cartridges with 5 mL methanol followed by 5 mL of 10% methanol in MTBE. The eluent was dried down under a gentle nitrogen stream and resolved in 1 mL methanol. The final sample was prepared in a ratio of 10:90 methanol–water (v/v) for LC-MS/MS analysis.

LC-MS/MS analysis was performed using an Agilent 1200 HPLC and a CTC Analytics HTS PAL autosampler equipped with a 1 mL sample loop for chromatography, coupled with an Applied Biosystems (USA) 3200 QTRAP MS/MS system. Compounds were separated using a 150 mmxx4.6 mm Luna C18 column with 5 μm particle size. A binary gradient with a flow rate of 800 μL/min was used for both electrospray ionization (ESI) positive and ESI negative methods. ESI positive eluents consist of 4 mM ammonia formate and 0.1% formic acid solution in water (A) and methanol (B) with the following gradient: 10% B for 0.5 min, 50% B at 0.51 min, linear increase to 95% B at 8 min, 95% B for 6 min. A 4 min equilibration step at 10% B is applied for a total run time of 18 min.

The ESI negative eluent is a 2 mM ammonium acetate solution in water (A) and methanol (B). The ESI negative gradient is as follows: 10% B for 0.5 min, 40% B at 0.51 min, linear increase to 95% B at 8 min, 95% B for 3 min. A 5 min equilibration step at 10% B is used for a total run time of 16 min. A summary of target compound specific mass spectrometry tuning parameters for positive and negative ionization mode is provided in Teerlink et al. (2012). The limits of quantification (LOQ) for all analyzed CECs are summarized in Table 2.2. The LOQ was calculated as three times the limit of detection (LOD). In general, the signal-to-noise ratio must exceed 10 to meet quantification criteria. Furthermore, blanks were run on the instrument on a regular basis. Recoveries are provided in Table A.1 in the Appendix.

At KAUST, CEC concentrations were quantified using LC-MS/MS with isotope dilution subsequent to SPE using a method detailed in Alidina et al. (2014). Briefly, 50 mL of each water sample was spiked with 100 μL of isotope internal standard and extracted using a 500 mg HLB cartridge (Waters, MA) using an automated Dionex AutoTrace 280 SPE workstation (Sunnyvale, CA). The extract was brought to a final volume of 1 mL using methanol for the subsequent LC-MS/MS analysis using an Agilent Technology 1260 Infinity Liquid Chromatography unit with tandem MS spectroscopy (AB Sciex 5500 Q-Trap). Details of mobile phases utilized in ESI positive and negative modes together with detailed LC-MS/MS parameters (product ions, retention time, declustering potential, collision energy, and collision cell exit potential) are provided in Alidina et al. (2014).

Table 2.2. Limit of Quantification for LC-MS/MS Method Determined in Ultrapure Water (Signal to Noise Ratio of >10)

Compounds (ESI^+)	LOQ KAUST* (ng/L)	LOQ CSM (ng/L)	Compounds (ESI^-)	LOQ KAUST* (ng/L)	LOQ CSM (ng/L)
Acetaminophen	NA	10	acesulfame	30	100
Amitriptyline	10	25	bisphenol A	20	50
Atenolol	10	10	diclofenac	10	10
Atrazine	6	5	gemfibrozil	6	10
Benzophenone	300	250	ibuprofen	10	100
Caffeine	60	10	ketoprofen	NA	50
Carbamazepine	6	25	methylparaben	30	10
DEET	30	25	naproxen	6	10
Diazepam	NA	5	propylparaben	20	5
Dilantin	20	25	sucralose	20	500
Diphenhydramine	20	25	triclocarban	30	10
Fluoexetine	10	5	triclosan	250	NA
Iopromide	NA	50			
Meprobamate	NA	10			
Oxybenzone	30	100			
Primidone	3	25			
Sulfamethoxazole	6	5			
TCEP	NA	10			
TCPP	NA	25			
TDCP	NA	50			
Trimethoprim	10	10			

Notes: *=details explained in Alidina et al. (2014); DEET=N,N-Diethyl-meta-toluamide; NA=compound not analyzed at respective laboratory; TCEP=tris(2-carboxyethyl)phosphine; TCPP= tris(1-chloro-2-propyl)phosphate; TDCP=tris[2-chloro-1-(chloromethyl)ethyl]phosphate.

2.3. Virus Detection by qPCR

One of the objectives of this study was to gather data on the removal of viruses at three full-scale MAR operations to be used for model validation. Samples were tested by quantitative polymerase chain reaction (qPCR) for selected viruses, and if viruses were detected the samples were assayed on cell culture to determine if infectious viruses were present. Volume sample sizes ranged from 2 L for wastewater to 5 to 400 L for groundwater samples. Wastewater and groundwater samples up to 10 L were processed using the method of Haramoto et al. (2004), as it has been used in numerous studies for the detection of viruses by qPCR in water and wastewater (Ikner et al., 2011). It also has a low affinity for detection of free nucleic acids (Haramoto et al., 2007). The efficiency for detecting free RNA is less than 3.4% versus 50% for intact viruses from sewage with this method. For larger volumes of

groundwater, NanoCeram filters were used, as they have been found to result in the concentration of fewer substances that interfere with virus detection by PCR (Ikner et al., 2011). In some cases, two different methods for the elution of viruses from the NanoCeram filters were performed to compare results. One method involved the use of beef extract followed by organic flocculation, and the other involved sodium polyphosphate followed by ultrafiltration (Ikner et al., 2011).

Direct PCR was used for the detection of reoviruses; the primers are listed in Table 2.3. Primers have not yet been published for the detection of reoviruses, which was not part of the original testing plan. When cytopathogenic (CPE) effects were observed in one sample from the recharge site in Colorado, the CPE resembled that of reovirus. PCR was conducted to identify the virus present in the sample.

Details of methods for preparation of samples for detection by qPCR are described in Kitajima et al. (2013). Briefly, viral nucleic acid was extracted from the viral concentrates, and the viral genomes were determined by qPCR. Nested reverse transcription polymerase chain reaction (RT-PCR) for reovirus was performed as described in Leary et al. (2002). The qPCR primers and probes used in the present study are shown in Table 2.3.

Table 2.3. qPCR Primers and Probes Used in the Present Study

Target	Primer/Probe	Name	Sequence (5'→3')[a, b]	Reference
GI NoV	qPCR primer	COG1F	CGYTGGATGC GNTTYCATGA	Kageyama et al. (2003)
		COG1R	CTTAGACGCCA TCATCATTYAC	
	qPCR probe	RING1(a)TP	FAM-AGATYGCGAT CYCCTGTCCA-BHQ1	
		RING1(b)TP	FAM-AGATCGCGGT CTCCTGTCCA-BHQ1	
GII NoV	qPCR primer	COG2F	CARGARBCNA TGTTYAGRTG GATGAG	Kageyama et al. (2003)
		COG2R	TCGACGCCAT CTTCATTCACA	
	qPCR probe	RING2-TP	FAM-TGGGAGGGCG ATCGCAATCT-BHQ1	
GIV NoV	qPCR primer	COG4F	TTTGAGTCYAT GTAYAAGTGG ATGC	Trujillo et al. (2006)
	qPCR probe	RING4-TP	FAM-TGGGAGGGGG ATCGCGATCT-BHQ1	

(continued)

Target	Primer/Probe	Name	Sequence (5'→3')[a, b]	Reference
SaV	qPCR primer	SaV124F	GAYCASGCTCT CGCYACCTAC	Oka et al. (2006)
		SaV1F	TTGGCCCTCGC CACCTAC	
		SaV5F	TTTGAACAAG CTGTGGCATG CTAC	
		SaV1245R	CCCTCCATYTC AAACACTA	
	qPCR probe	SaV124TP	FAM-CCRCCTATRAA CCA-MGB-NFQ	
		SaV5TP	FAM–TGCCACCAAT GTACCA-MGB-NFQ	
EV	qPCR primer	EV1F	CCCTGAATGC GGCTAAT	Gregory et al. (2006)
		EV1R	TGTCACCATA AGCAGCCA	
	qPCR probe	EV probe	FAM-ACGGACACCC AAAGTAGTCG GTTC-BHQ1	
AiV	qPCR primer	AiV-AB-F	GTCTCCACHG ACACYAAYTG GAC	Kitajima et al. (2013)
		AiV-AB-R	GTTGTACATRG CAGCCCAGG	
	qPCR probe	AiV-AB-TP	FAM-TTYTCCTTYGT GCGTGC-MGB-NFQ	

(continued)

Target	Primer/Probe	Name	Sequence (5'→3')[a, b]	Reference
AdV	qPCR primer	AQ2	GCCCCAGTGG TCTTACATGCA CATC	Heim et al. (2003)
		AQ1	GCCACGGTGG GGTTTCTAAAC TT	
	qPCR probe	AP	FAM-TGCACCAGAC CCGGGCTCAG GTACTCCGA-BHQ1	
ARV	qPCR primer	JVKF	CAGTGGTTGA TGCTCAAGAT GGA	Jothikumar et al. (2009)
		JVKR	TCATTGTAATC ATATTGAATA CCCA	
	qPCR probe	JVKP	FAM-ACAACTGCAG CTTCAAAAGA AGWGT-BHQ1	
PMMoV	qPCR primer	PMMV-FP1rev	GAGTGGTTTG ACCTTAACGTT TGA	this study
		PMMV-RP1	TTGTCGGTTGC AATGCAAGT	Zhang et al. (2006)
	qPCR probe	PMMV-Probe1	FAM-CCTACCGAAG CAAATG-BHQ1	
MNV	qPCR primer	MNV-S	CCGCAGGAAC GCTCAGCAG	Kitajima et al. (2010)
		MNV-AS	GGYTGAATGG GGACGGCCTG	
	qPCR probe	MNV-TP	FAM-ATGAGTGATG GCGCA-MGB-NFQ	

(continued)

Target	Primer/Probe	Name	Sequence (5'→3')a, b	Reference
Reovirus	1st PCR	L1.rv5	GCATCCATTGT AAATGACGAG TCTG	Leary et al. (2002)
	1st PCR	L1.rv6	CTTGAGATTA GCTCTAGCATC TTCTG	
	2nd PCR	L1.rv7	GCTAGGCCGA TATCGGGAAT GCAG	
	2nd PCR	L1.rv8	GTCTCACTATT CACCTTACCA GCAG	

Notes: [a]=mixed base in degenerate primer and probe is as follows: Y stands for C or T; N stands for any; R stands for A or G; B stands for not A; W stands for A or T; S stands for C or G; K stands for G or T; H stands for not G; [b]=FAM, 6-carboxyfluorescein; TAMRA=6-carboxytetramethylrhodamine; MGB=minor groove binder; NFQ=non-fluorescent quencher.

2.3.1. Selection of Studied Viruses

Currently, there are more than 200 human pathogenic viruses known to occur in wastewater, with several new ones being added every year (Maier et al., 2009). The occurrence and concentration of enteric viruses in treated wastewater is dependent on numerous factors. including disease incidence within the community, season, per capita water use, and type of treatment. To better assess which enteric viruses occur in the greatest numbers over the year, team members at UofA collected data on occurrence of several enteric viruses at two WWTPs in Tucson, AZ.

During these campaigns, data on the occurrence of pepper mild mottle virus (PMMoV) were also collected because it had been suggested as an indicator of sewage pollution and it is the virus detected in the highest concentration in untreated and treated sewage (Rosario et al., 2009). The data in Figure 2.7 illustrate the highest average concentrations of the viruses studied. Based on these findings, PMMoV was the most abundant virus, followed by aichiviruses, adenoviruses, and enteroviruses. The results show that human adenovirus and PMMoV vary the least over the course of the year. Most enteric viruses demonstrated a 1 to 2 log removal during the activated sludge treatment, except PMMoV, which experienced little removal (data not shown).

Virus occurrence will also vary seasonally with the incidence of the viruses in the community. Thus, rotaviruses occur most commonly in the fall and winter, and enteroviruses are most common in the summer and early fall (Maier et al., 2009). As shown in Figure 2.8, PMMoV exhibited little seasonal variation in concentration throughout the year compared to rotavirus. Less variation was also observed for adenoviruses and aichiviruses.

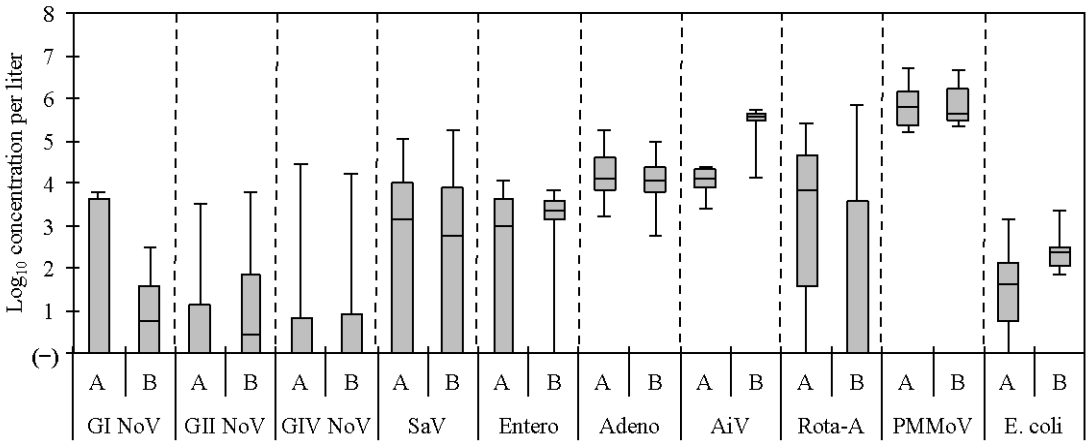


Figure 2.7. Average 12 months concentrations of human enteric viruses and pepper mild mottle virus in treated wastewater discharge of Roger Road (A) and Ina Road (B) sewage treatment plant in Tucson (genomes/L).

Notes: Detection was by qPCR; GINoV=norovirus genotype G1; GIINoV=norovirus genotype G2; GIVNoV=norovirus genotype 4; SaV=sapovirus; Entero=enteroviruses; Adeno=adenoviruses; AiV=aichiviruses; Rota-A=rotaviruses; PMMoV=pepper mild mottle virus.

Source: Masaaki et al. (2013).

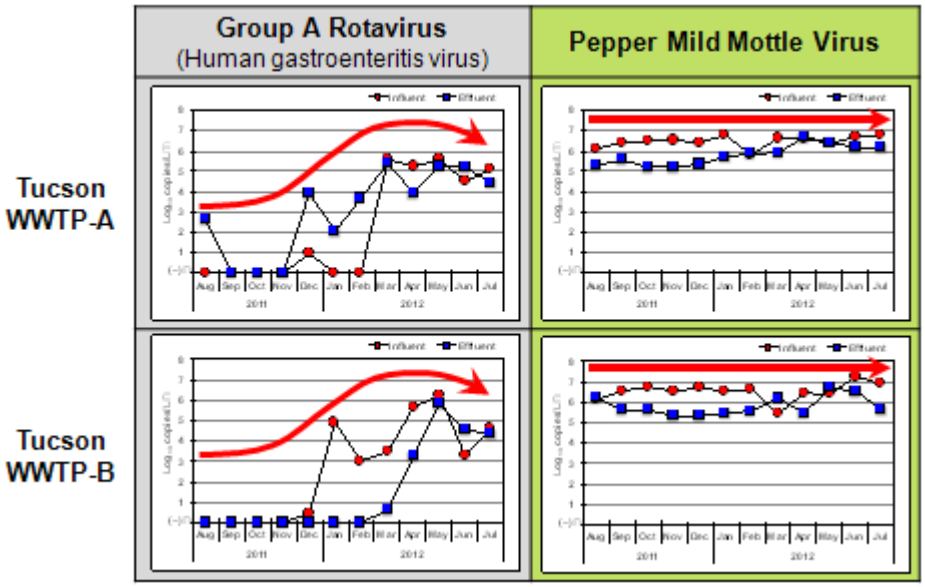


Figure 2.8. Seasonal variation of rotavirus and pepper mild mottle virus in the influent and treated effluent of two wastewater treatment plants in Tucson (genomes/L).

Source: Masaaki et al. (2013)

On the basis of high concentration and year-round abundance in treated wastewater effluents, the following viruses were chosen for this study:

- Enteroviruses
- Adenoviruses
- Aichiviruses
- PMMoV

2.4. Analytical Methods for Glucocorticoids

2.4.1. SPE and LC-MS/MS

At KAUST, glucocorticoid concentrations (corticosterone, cortisone, fludrocortisone, hydrocortisone [cortisol], methylprednisolone, prednisolone, prednisone) were quantified using LC-MS/MS with isotope dilution subsequent to SPE. SPE was carried out at CSM immediately after sampling (for soil column and field samples). The nitrogen-dried SPE cartridges were kept at 4° C before express shipment to the laboratory at KAUST for further analysis. From each water sample, 200 mL was spiked with 100 µL of isotope internal standard (corticosterone-d8, cortisone-d8, fludrocortisone-d5, hydrocortisone-d4 [cortisol], methylprednisolone-d2, prednisolone-d6) and extracted using a 500 mg HLB cartridge (Waters, MA) using an automated Dionex AutoTrace 280 SPE workstation (Sunnyvale, CA). No isotope internal standard was available for prednisone.

Table 2.4. Average Mass Recoveries (in ng) and Standard Deviations of Different Glucocorticoids in Spiked Wastewater Effluent Samples

Compound	Spiking Concentration		
	1 ng into 100 mL	10 ng into 100 mL	20 ng into 100 mL
Cortisol	0.9±0.3	9.6±1.2	21.3±2.0
Fludrocortisone	1.1±0.2	9.1±1.5	18.9±1.4
Cortisone	1.1±0.4	9.2±1.7	19.5±1.3
Corticosterone	0.85±0.05	9.6±0.5	19.9±0.6
Methylprednisolone	1.05±0.22	9.9±0.7	20.1±0.2
Prednisolone	0.92±0.22	9.3±1.1	19.6±1.9

SPE cartridges were conditioned as follows: 5 mL MTBE, 5 mL methanol (MeOH), and 5 mL ultrapure water. After loading with sample, cartridges were rinsed with 5 mL ultrapure water and dried under a nitrogen stream for longer than 60 min. For elution of target compounds, 5 mL of 9:1 (v/v) MTBE–MeOH and 5 mL of MeOH were used. The extract was brought to a final volume of 1 mL using methanol for the subsequent LC-MS/MS analysis using an Agilent Technology 1260 Infinity Liquid Chromatography unit with tandem MS spectroscopy (AB Sciex 5500 Q-Trap). LC-MS/MS parameters were adopted from a method published by Vanderford and Snyder (2006) and modified for the respective glucocorticoids. Detection limits for all compounds were in the range of 1 ng/L. Recoveries for all glucocorticoids (except prednisolone) in spiked wastewater effluent samples exceeded 85%. Average recoveries and standard deviations at different concentration levels are provided in Table 2.4.

2.4.2. Glucocorticoid Receptor Bioassay

A commercially available GR assay kit (#1391, GeneBLAzer® GR DA Assay, Life Tech, Victoria, Australia) was used to evaluate the GR activity, and dexamethasone (DEX) was used as the positive control. Samples (~500 mL) were extracted using Oasis HLB cartridges (500 mg, Waters. MA) by automated SPE (AutoTrace 280, Thermo Scientific, USA) at CS M. The cartridges were then shipped overnight to UofA. Upon arrival, the cartridges were eluted with 5 mL MTBE–MeOH (90:10 v/v) and 5 mL of MeOH. The eluted solvents were completely dried under a gentle flow of nitrogen and resuspended in dimethyl sulfoxide for the GR bioassay.

The GR bioassay utilized GeneBLAzer® (Life Technologies, New York) GR HEK 293T DA (division-arrested) cells. This cell line contains a stably integrated GR ligand-binding domain, the Gal4 DNA binding domain chimera. It also contains a beta-lactamase reporter gene under control of a UAS response element. In brief, the frozen DA cell aliquot was thawed quickly in a 37° C water bath, transferred to 10 mL of assay medium, and centrifuged at 200 x g for 5 min. The supernatant was discarded, and the cell pellet was reconstituted to a cell density of 4×10^5 to 5×10^5 cells/mL.

With a multichannel pipette, 90 µL of the cell suspension was added to each well of a black-wall, clear-bottom 96 well plate (Corning), and 90 µL of assay medium was added into the cell-free negative control wells. Then 10 µL of sample concentrate, which had already been serially diluted into 5% of assay medium was added into each well (0.5% solvent in the final well for all test samples). DEX was used as the positive control. Negative control and solvent control (triplicates) were always included in each plate for quality control.

Each sample was two-fold serially diluted, and the final concentration in the wells was 25, 12.5, 6.25, 3.13, and 1.56, whereas the DEX concentration ranged from $7.62xx10^{-11}$ to $5.0xx10^{-7}$ M. The plate was then incubated for 16 h in a humidified 37° C, 5% CO_2 incubator. At the end of the incubation, 20 µL of substrate mixture (provided in the kit) was added, and the plates were further incubated for 2 h in the dark at room temperature.

Fluorescence was then read with a plate reader (FlexStation 3, Molecular Devices LLC., Sunnyvale, CA) at emissions of 460 nm (blue) and 530 nm (green) after excitation at 409 nm. Background fluorescence (determined in the cell-free control wells) was subtracted from all readings, and a β-lactamase expression ratio calculated by dividing the net fluorescence at 460 nm by net fluorescence at 530 nm. Samples were deemed as positive when they exceeded the effective concentration for 10% (EC_{10}; determined from the DEX standard curve) and the equivalent concentrations (EQ) were calculated based on the standard curve.

In order to further investigate the attenuation of glucocorticoid activity during MAR, two one-dimensional soil column systems were established at CS M. Each column represented different geochemical subsurface conditions (e.g., oxic vs. anoxic) and feed water qualities (e.g., primary substrate composition), as well as different travel times, as described in Section 2.5.1.

2.5. Experimental Methods

2.5.1. CEC and Bulk Organic Removal in Soil Columns

2.5.1.1. Soil Column Systems at CSM

Different one-dimensional soil column systems filled with sandy aquifer material (grain size <2 mm, $f_{oc} \leq 0.1\%$) and equipped with intermediate sampling ports have been established over several years to simulate the prevailing conditions in MAR systems. According to the design and operation, water flow in these soil column systems is predominantly in a vertical direction (one-dimensional). Two new large-scale soil columns, C3 and C4 (each 4.5 m in length; see Figure 2.9), filled with a blend of 50:50 (v/v) technical sand and sandy soil (grain size <2 mm, $f_{oc} \leq 0.3\%$) from the MAR facility in Brighton, CO, were constructed in spring 2012. These columns were used to investigate both the attenuation of pathogens (as a function of adsorption/die-off) and trace organic chemicals.

Figure 2.9. Soil column systems at CSM (left) and KAUST (right).

Both columns were equipped with four intermediate soil and seven water sampling ports at different depths (Figure 2.9). For the pathogen study, specific stainless steel sampling ports were developed at CSM to avoid sorption effects and obtain water samples from the center of the column. One column received secondary treated effluent with a high BDOC content, and the other one received nanofiltration (NF) permeate representing low BDOC conditions. The intent was to keep the NF column close to sterile conditions (by continuous UV disinfection of the permeate feed water) to simulate direct injection of highly treated reclaimed water into a deep aquifer.

Soil column systems PC and C1 were composed of two 1 m Plexiglas columns (i.d. 15 cm) coupled in line; C2 consisted of a single 1.2 m column (Figures 2.9 and 2.10). Secondary treated wastewater effluent obtained from a local WWTP employing nitrification and partial denitrification served as soil column feed at a flow rate of 1 mL/min under saturated conditions. To adjust the DOC level in the feed water, different blends with NF permeate were applied. NF permeate was produced from tap water filtered through a 20 gpm NF membrane skid equipped with 21 Dow/Filmtec 4040 NF 270 elements.

To achieve carbon-starving conditions in the PC column system during one experiment, dechlorinated tap water was used. Except for column system C2, the column influent was regularly purged with nitrogen gas to keep DOC below 0.5 mg/L. Column feeds were housed in plastic carboys, with the exception of C4. The C4 feed was stored in a capped 100 L stainless steel drum equipped with a Sterilight SC1 UV lamp on a separate recirculation line. The NF permeate in this container recirculated through the lamp delivering a dose of 40 mJ/cm^2 for 1 h per day. Secondary treated effluent was obtained from the Denver Metro Reclamation Facility and stored at room temperature in plastic carboys. In the case of column system C4, 60 mg/L $CaCO_3$ and 60 mg/L $NaHCO_3$ were added to the feed to adjust the saturation index of the NF permeate to 0+/-0.5.

Experimental conditions of the soil column systems used in this study are summarized in Table 2.5. All CSM column systems except C4 were operated in top to bottom flow at room temperature (20° C). Because of operational difficulties, soil column C4 was operated in bottom to top flow. Column systems PC, C1, C2, and C4 were continuously spiked with a mix of 20 CECs at the medium ng/L level. Continuous CEC spiking on column system C2 was discontinued in spring 2013, and the column was switched over to glucocorticoid spiking at the 200 ng/L level in May 2013. Column system C3 did not receive CEC spiking and was used to determine virus removal and the attenuation of glucocorticoid activity during simulated MAR.

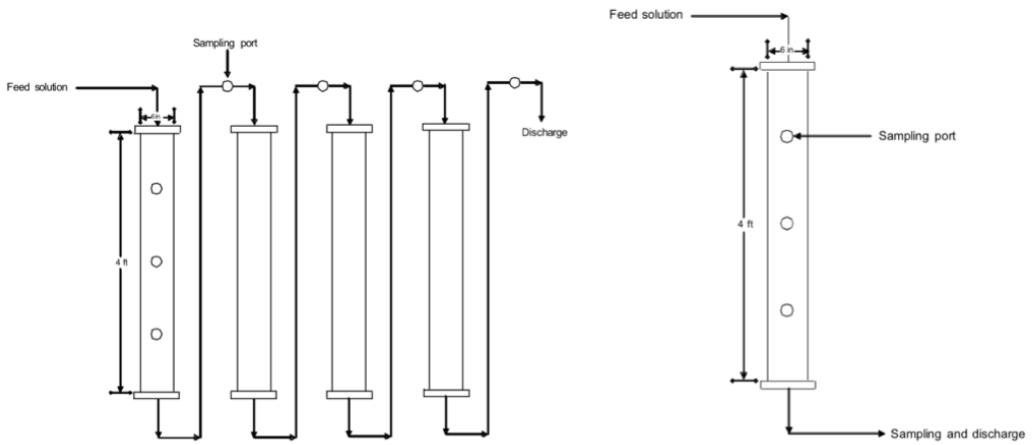


Figure 2.10. Schematic column configuration for PC and C1 column systems (left) and C2 column system (right).

Source: Adapted from Drewes et al. (2011).

Tabe 2.5. Soil Column Configurations at CSM and KAUST and Operational Parameters

Column System	Design	Media	Conditions	Feed Water	Flow Rate/ Direction	Residence Time
CSM						
PC	Four 1 m acrylic columns in series, 15 cm i.d.	Native alluvial material (sieved <2 mm, f_{oc}<0.1%)	Biodegradation under saturated suboxic flow conditions	Tap water, N_2 purged, low BDOC	1 mL/min top to bottom	17 days
C1	Four 1.2 m acrylic columns in series, 15 cm i.d.	Native alluvial material (sieved <2 mm, f_{oc} 0.1%)	Biodegradation under saturated anoxic flow conditions	Secondary treated effluent, N_2 purged, high BDOC	1 mL/min top to bottom	25 days
C1-PC	Eight 1.5 m acrylic columns in series, 15 cm i.d.	Native alluvial material (sieved <2 mm, f_{oc}≤0.1%)	Biodegradation under saturated anoxic flow conditions	50:50 blend secondary treated effluent–deionized water, N_2 purged, high BDOC	1 mL/min top to bottom	42 days
C2	One 1.2 m acrylic column, 15 cm i.d.	Native alluvial material (sieved <2 mm, f_{oc} 0.1%)	Biodegradation under unsaturated oxic flow conditions	(a) secondary treated effluent, high BDOC (b) 30:70 blend secondary treated effluent–NF permeate, low BDOC	1 mL/min top to bottom	7 days
C3	One 4.4 m PVC column, 15 cm i.d.	50:50 blend technical sand and sandy soil (sieved <2 mm, f_{OC} <0.3%)	Biodegradation under saturated anoxic flow conditions	a) secondary treated effluent, N_2 purged, high BDOC (b) 50:50 blend secondary effluent–NF permeate, N_2 purged, high BDOC	1 mL/min a) top to bottom b) bottom to top	16 days

Column System	Design	Media	Conditions	Feed Water	Flow Rate/ Direction	Residence Time
C4	One 4.4 m PVC column, 15 cm i.d.	50:50 blend technical sand and sandy soil (sieved <2 mm, f_{oc}<0.3%)	Sterile (UV) under saturated suboxic flow conditions	NF permeate, N_2 purged, low BDOC	1 mL/min bottom to top	20 days
Abiotic	One 1 m acrylic column, 15 cm i.d.	Native alluvial material (sieved <2 mm, f_{oc} 0.1%)	Abiotic under saturated suboxic flow conditions	Synthetic wastewater, n_2 purged, low bdoc	1 mL/min top to bottom	6 days
KAUST						
Abiotic	One 0.3 m glass column, 5 cm i.d.	Sandy wadi soil (sieved <2 mm, f_{oc} 0.1%)	Abiotic under saturated oxic flow conditions	Synthetic wastewater with peptone, yeast, and humic substances, low bdoc	2 mL/min bottom to top	3.3 h
30, 20, 10, 8˚C	Eight 0.3 m glass columns in series, 5 cm i.d.	Sandy wadi soil (sieved <2 mm, f_{oc} 0.1%)	Biodegradation under saturated suboxic flow conditions	Synthetic wastewater with peptone, yeast, and humic substances, low bdoc	1 mL/min bottom to top	2 days

Notes: BDOC=biodegradable dissolved oxygen concentration; CSM=Colorado School of Mines; i.d.=inner diameter; KAUST=King Abdullah University of Science and Technology; N_2=nitrogen; NF=nanofiltration; PVC=polyvinylchloride; UV=ultraviolet.

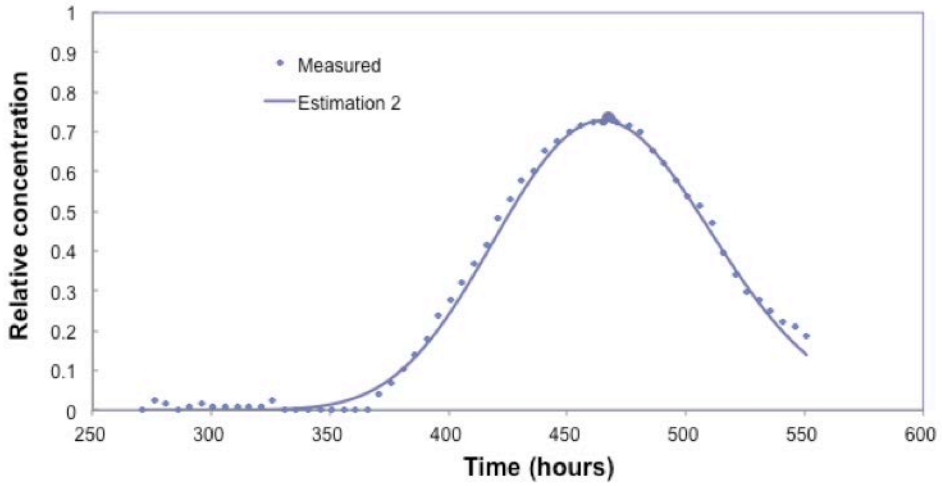


Figure 2.11. Breakthrough curves for the conservative tracer potassium bromide at the large-scale column C4 at a flow rate of 1 mL/min.

Note: Measured: conductivity probe; estimation: CXTFIT.

Hydraulic retention times (HRT) for each of the 1 m column systems were determined in previous experiments using potassium bromide as a conservative tracer (Rauch-Williams et al., 2010; Hoppe-Jones, 2012). For the two large-scale soil columns, C3 and C4, a conservative tracer test using potassium bromide was conducted to determine the hydraulic residence time in soil columns. The calculated breakthrough curves for the large-scale column C4 receiving NF permeate using CXTFIT is shown in Figure 2.11. Based on these data, hydrological parameters as well as retention times for all intermediate sampling ports have been determined.

CEC spiking solution was kept in the dark at 5° C and renewed every other day. These chemicals (e.g., pharmaceuticals, personal care products, flame retardants) exhibit different degrees of biodegradability during MAR and have been evaluated previously to be suitable indicator compounds to assess MAR performance (Drewes et al., 2008, 2011). For each CEC spiking experiment, five or six sampling campaigns were carried out from September 2011 to April 2013 using the soil column systems described in Table 2.4.

Resulting data were grouped into four bins based on key controlling factors and prevailing geochemical conditions in the soil columns to derive first-order rate constants for CEC removal as described in Section 2.4.5. In general, 100 mL water samples were collected for each soil column system at different depths plus influent during each spiking experiment and immediately preserved prior to SPE.

2.5.1.2. Soil Column Systems at KAUST

The column setup consisted of eight columns (GE Healthcare XK 50/30 glass columns, Sweden; length: 30 cm, internal diameter: 5 cm) connected in series (Figure 2.9). The columns were in operation for more than 15 months prior to commencement of this experiment and operated in saturated up-flow mode. Pretreated native soil collected upstream of a wastewater discharge from Wadi Wajj in Saudi Arabia and sieved to retain the fraction below 2 mm was used to fill the columns. The soil was washed with deionized (DI) water and

transferred into the columns totally submerged in water to minimize introduction of any air bubbles. The soil used in the columns had low organic matter content with f_{OC} of 0.10±0.01%. The hydraulic conductivity was determined to be 0.070±0.006 cm/s, and the porosity was 0.32±0.03.

Feed to the columns was a synthetic wastewater blend comprising peptone (BD BactoTM Peptone, Becton, Dickenson & Co.), yeast (BD BactoTM Yeast Extract, Becton, Dickenson & Co.), and humic substances (humic acid sodium salt, Sigma-Aldrich), delivered at a target level of 2.5±0.5 mg/L. The peptone and yeast provided 40% of the DOC to the columns, whereas the humic substances provided 60% of the DOC. The synthetic wastewater in each column also contained a mix of salts, as described in Alidina et al. (in review).

In addition to the primary substrate present in the feed, the columns also continuously received a mixture of CECs at environmentally relevant concentrations of 300±100 ng/L, several orders of magnitude lower than those in the primary substrate. The synthetic wastewater feed was prepared twice a week and stored at 4° C to prevent biodegradation during storage. Feed lines were cleaned regularly using sodium hypochlorite solution and ascorbic acid and subsequently rinsed with MilliQ water to minimize back growth of bacteria.

2.5.2. Temperature-Controlled CEC and Bulk Organic Removal in Soil Columns at KAUST

In order to study the impact of temperature on CEC removal, all the columns were placed inside a Thermo Scientific Forma Environmental Chamber (Model 3940; Marietta, OH) with an operating range of 0 to 60° C. The environmental chamber was fitted with a digital electronic controller allowing temperature transitions of 0.1° C. The columns were operated at four temperature set-points: 30, 20, 10, and 8° C, with a minimum duration of 9 weeks at each temperature set-point. The temperature set-point was defined as the temperature in the effluent collected after flow through the columns. Achieving this goal required some adjustment from the displayed temperature of the environmental chamber. Weekly temperature readings of the effluent ensured minimal deviation from the set-points.

Flow rate measurements were carried out at each temperature set-point to investigate whether lower temperatures affected the flow rate and would require some adjustment in the pump flow rates. No differences were noticed between flow rates at the different temperatures; therefore, no changes in pump flow rates were required. Influent and effluent samples (following travel through eight columns) were collected weekly for analysis over a period of 38 weeks.

2.5.3. Glucocorticoid Removal in Soil Columns at CSM

Two different soil column systems were used to investigate GR during simulated MAR (Table 2.5): C2 (1 mxx15 cm i.d.) was filled with sandy aquifer material, and C3 (4.5 mxx15 cm i.d.) was filled with technical sand and sandy field soil (50:50 v/v, grain size <2 mm). Both columns were equipped with intermediate sampling ports at different depths and had been established for more than 1 year to simulate the prevailing conditions in MAR systems. C2 was receiving a blend of NF permeate and secondary treated effluent (70:30 v/v) from top to bottom flow at 1 mL/min flow rate. C2 feeds were never purged with nitrogen, resulting in oxic conditions, while applying low BDOC levels. During this experiment, C3 was operated in reverse flow (saturated from bottom to top) at a flow rate of 1 mL/min, receiving a nitrogen-purged NF permeate and secondary treated effluent blend (50:50 v/v). Anoxic redox

conditions were established in C3. Travel times for C2 were 7 days (3 days for intermediate port #7 at depth 0.5 m) and 16 days for C3 (10 days for intermediate port #5 at depth 2.75 m).

Beginning in early June 2013, C2 was continuously spiked with a mix of seven glucocorticoids (corticosterone, cortisone, fludrocortisone, hydrocortisone [cortisol], methylprednisolone, prednisolone, and prednisone) at a nominal concentration of 200 ng/L. C3 was not spiked with the glucocorticoid mixture. For the bioassay analysis, two sampling campaigns were carried out in July 2013 (July 1 and 15) using both soil columns. Samples (each ~500 mL) were collected at the inflow, outflow, and intermediate sampling ports of C2 and C3. Prior to the spiking experiment, the GR activity of the influent and secondary effluent of the WWTP in Colorado was evaluated. For LC-MS/MS analysis, four sampling events (influent, effluent, one intermediate sampling port) were carried out in July and August 2013 using the glucocorticoid spiked column system C2. Sample volumes were in the range of 200 mL and were immediately extracted after sampling by automated SPE.

2.5.4. Pathogen Removal in Soil Columns at CSM

The pathogen spiking experiment at CSM, using bacteriophage MS-2 and murine norovirus (MNV) to assess pathogen removal kinetics and properties during MAR, was initiated on January 16, 2013, and lasted for 26 days. MNV was added to the large soil column C3 (travel distance 4.4 m) as a 1-day pulse at the start of the experiment (10^4/mL input), whereas MS2 was continuously added (10^7/mL input per day) over the entire run time of the experiment. C3 received secondary treated effluent at a flow rate of 1 mL/min in top to bottom flow (Table 2.4). MS-2 spiking solution was kept at 4° C in the dark and renewed every 24 h during the experiment.

The column system was equipped with seven sampling ports at the following depths: 10, 25, 55, 85, 175, 300, and 440 cm. Each sampling port plus column influent and effluent was sampled once a day over a period of 15 days. After Day 15, all sampling ports as well as column influent and effluent were sampled every second day until the end of spiking on Day 26. A drop of sera was added to each sample before freezing to preserve the MS-2 phage during freezing. Samples were immediately placed in a freezer after sampling and shipped overnight on dry ice to the UofA laboratory for analysis.

2.5.5. First-Order Removal Calculation of CEC

For the experimental bulk organic carbon and CEC data, an exponential first-order decay model (Eq. 2.1) was used to calculate the degradation rate constant λ:

$$C_{(t)} = C_0 e^{-\lambda t} \qquad \text{(Eq. 2.1)}$$

where $C_{(t)}$ is the concentration at time *t* (ng/L) and C_0 is the concentration at time 0 (ng/L). The logarithmically transformed average concentration of up to six sampling events per experiment for each individual sampling port was used to fit a linear regression. CEC concentration was plotted against soil column residence time. Concentrations below the compound LOD were set equal to half the LOD. Each soil column sampling port represents a different residence time. A linear relationship is given for the logarithmic form of Eq. 2.1 with:

$$\ln C_{(t)} = \ln C_0 - \lambda t \quad \text{(Eq. 2.2)}$$

Half-lives ($t_{1/2}$) are defined as the time at which concentration reaches half the initial concentration and were calculated by the equation:

$$t_{1/2} = \frac{\ln 2}{\lambda} \quad \text{(Eq. 2.3)}$$

In the soil column experiments, other attenuation processes leading to CEC dissipation besides degradation cannot always be ruled out. The term DT_{50} is used instead as it reflects the time for the dissipation of 50% of the initial concentration. Although the logarithmic transformation (Eq. 2.2) assigns a larger weight to smaller concentrations and might result in more conservative DT_{50} values (Beulke and Brown, 2001), this approach was chosen to allow for the determination of outliers in the data set. Removal rate constants were indicated as <0.001 if compounds showed no decrease in concentration over the duration of the experiment (also reflected by a poor R^2 value) or if λ turned negative (Burke et al., 2013). The first-order equation was considered acceptable for R^2 values above 0.63 (Beulke and Brown, 2001).

2.5.6. Sorption Potential of Different Soil Types for CECs (K_d)

The removal of CECs during soil infiltration is primarily due to both biological transformation and sorption to the solid phases present. Sorption may be particularly important for recalcitrant CECs. A sorption distribution coefficient (K_d) describes sorption of a specific chemical between water and soil phases of a system. The K_d value is a characteristic specific to the chemical in question and a specific soil and thus an important parameter for modeling contaminant transport at different field sites. A detailed description of the different soil types used in this experiment is provided in Section 3.5.1.

2.5.6.1. Soil Column Systems

Biologically inactive (abiotic) soil columns at KAUST (soil type F) and CSM (soil type G) were used to determine the retardation factors (R_f) through the soil for a set of indicator compounds listed in Section 3.5. The resulting breakthrough curves were used to evaluate the retardation coefficients for each compound by two modeling processes, CXTFIT and the method of moments (Oldham, 2008). Based on the obtained R_f values for the specific soil used, values for K_d were calculated for each compound according to the following equation. The relationship between R_f and K_d is:

$$R_f = 1 + \frac{K_d \cdot \rho_b}{\phi} \Rightarrow K_d = \frac{(R_f - 1) \cdot \phi}{\rho_b} \quad \text{(Eq. 2.4)}$$

where: R_f retardation factor

K_d distribution coefficient
ρ_b bulk density
ϕ porosity

$$\phi = 1 - \frac{\rho_b}{\rho_p} \qquad \text{(Eq. 2.5)}$$

where: ρ_p = particle density (assumption ρ_p = 2.65 g/cm^3)
ϕ = 0.45
ρ_b = 1.46 g/cm^3

2.5.6.2. Batch Experiments

Five soils (soil ID A–E) were selected to represent a wide range of physical and chemical properties typically observed at MAR facilities. A series of batch sorption experiments were conducted to develop isotherms for certain CECs. Soil characteristics (e.g., f_{OC}, organic matter [OM], cations, pH, bulk density) for the different soil types are provided in Section 3.5. The resultant data were fit with the Freundlich sorption model as described in Teerlink (2012), enabling comparisons of sorption affinity between the various compounds and soils.

An additional batch experiment was carried out to assess the sorption potential of clay for CECs during MAR operation. Clay lenses/pockets were frequently found at the MAR site in Colorado during excavation work in the infiltration basins. Therefore, tests were carried out with technical grade bentonite (100% montmorillonite clay, Sigma-Aldrich) as well as homogenized field soil (~6% clay) and field clay (23% clay) from the MAR site in Colorado. To avoid disturbance of the geochemical composition of the field soils, RBF water from the same field site was used for the experiments and spiked at a concentration of 2000 ng/L. A detailed description of the experiments as well as quality assurance and quality control can be found in Teerlink (2012) and Wing (2013).

In brief, all sorption experiments were conducted using 15 mL glass centrifuge tubes. The aqueous phase for sorption experiments was either a synthetic wastewater or RBF water obtained from the Prairie Waters Project RBF site in Brighton, both spiked with 1 g/L sodium azide to minimize microbial activity. Isotherms included five spike concentrations plus an unspiked control, targeted to span the range of CEC concentrations commonly observed in reclaimed water (0–50,000 ng/L). Sorption experiments included isotherms in triplicate for each of the five soils. A full isotherm, in triplicate, was conducted without any soil present to account for potential losses to the walls of the vials. Vials were protected from light to prevent losses due to photolytic transformations. Vials were placed on a shaker table for 24 h to achieve sorption equilibrium based on preliminary kinetic observations (Teerlink, 2012). After reaching equilibrium, sorption reactors were centrifuged for 20 min at 2000 rcf. Subsequently, 5 mL of the supernatant was transferred to a 100 mL glass bottle, diluted with DI water to a volume of 50 mL, and analyzed for target CECs using the isotope dilution method on LC-MS/MS. A subset (~20%) of soils was extracted and analyzed for target CECs to perform mass balance calculations to ensure that the aqueous loss was accounted for by CEC losses to solid phases.

Chapter 3

Fate of Bulk Dissolved Organic Carbon, Nitrogen, CECs, and Pathogens in the Environmental Buffer Under Controlled Conditions

3.1. Bulk Dissolved Organic Carbon and Nitrogen Attenuation During Simulated MAR

3.1.1. Impact of Feed Water Composition

Relevant organic water quality parameters in the feed water applied to the soil columns and the changes in nitrate and manganese after travel through the columns are summarized in Table 3.1. The DOC concentration in the secondary treated effluent applied to column systems C1, C2, and C3 was on average in the range of 7 to 8 mg/L, with UV_{254nm} absorbance values greater than 14 m^{-1} and a SUVA value between 1.8 and 2.4 L/mg/m. The secondary treated effluent that was not purged with nitrogen did not maintain its previously oxic condition during passage through soil column C2. Because of the reduction of nitrate and the release of dissolved manganese, the redox state turned into anoxic conditions (Table 3.1).

For secondary treated effluent, BDOC levels varied and were in the range of 2.4 to 4.2 mg/L. In general, the level of influent BDOC heavily influences the system's redox state. DOC is an electron donor, and as it is consumed by microbial activity it requires electron acceptors. As electron acceptors are depleted during metabolism of DOC, the redox state of the system moves from an oxic setting towards suboxic and anoxic redox states.

The 70:30 (v/v) NF permeate–secondary treated effluent blend reduced influent DOC to 2.46 mg/L with UV_{254nm} values equal to 5 m^{-1} and a SUVA value equal to 2 L/mg/m. This reduction in influent DOC was sufficient to maintain oxic conditions throughout the soil column, as nitrate was not reduced and there was no detectable change in dissolved manganese.

The N_2 purged tap water exhibited a DOC concentration of 1.17 mg/L on average, a UV_{254nm} absorbance value of 3.74 m^{-1}, and a SUVA value equal to 2.93 L/mg/m. This is the highest SUVA value of all the water blends, suggesting the organic carbon present in this feed is more aromatic in nature. This feed water, purged of dissolved oxygen and low in nitrate and ammonia, exhibited reduction of the small amount of nitrate present and resulted in a slight nitrate decrease of 0.13 mg/L, but no dissolved manganese was produced. The NF permeate contained 0.26 mg/L DOC with a UV_{254nm} value equal to 0.21 m^{-1} and a SUVA value equal to 0.79 L/mg/m. No measureable nitrate was detected in the influent or effluent, but a slight dissolution of manganese was measured (0.12 mg/L). The experimental conditions for the soil columns, including redox classification and retention time, are summarized in Table 2.5.

EEMs were generated for four different water types with different DOC levels (Figure 3.1). The relative intensity of the three major peaks shows a similar pattern among the undiluted

secondary treated effluent feed and the 70:30 (v/v) NF permeate–secondary treated effluent blend despite the different fluorescence intensities.

Table 3.1. Bulk Organic Parameters of Feed Water Applied to Soil Columns and Change in Redox Surrogates NO_3^- and Mn^{2+} After Travel Through the Columns

Column System	Feed Water	DOC (mg/L)	BDOC (mg/L)	UV_{254} (m^{-1})	SUVA (L/mg/m)	NO_3^- (mg/L)	Mn^{2+} (mg/L)
PC	Tap water	1.2±0.3	0.2±0.1	3.74	2.93	-0.13	BDL
C1	Secondary treated effluent	7.9±1.3	4.2±1.2	14.52	1.84	-8.75	0.98
C2	(a) secondary treated effluent	7.95±1.31	2.56±1.04	14.1	1.79	-5.4	0.92
	(b) 30:70 secondary treated effluent–NF permeate	3.3±0.43	1.53±0.19	4.99	2.03	1.01	BDL
C3	(a) secondary treated effluent	6.78±0.74	2.39±0.2	15.8	2.41	-0.72	0.11
	(b) 50:50 secondary treated effluent–NF permeate	4.88±0.58	2.01±0.44	7.7	1.58	-2.96	0.47
C4	NF permeate	0.26±0.31	BDL	0.21	0.79	BDL	0.12
C1-PC	50:50 secondary treated effluent–DI water	7.32±3.42	4.02±1.97	8.21	1.62	-8.18	0.82

Notes: BDL=below detection limit; BDOC=biodegradable dissolved organic carbon; DI=deionized; DOC=dissolved organic carbon; NF=nanofiltration; SUVA=specific ultraviolet absorbance; UV=ultraviolet.

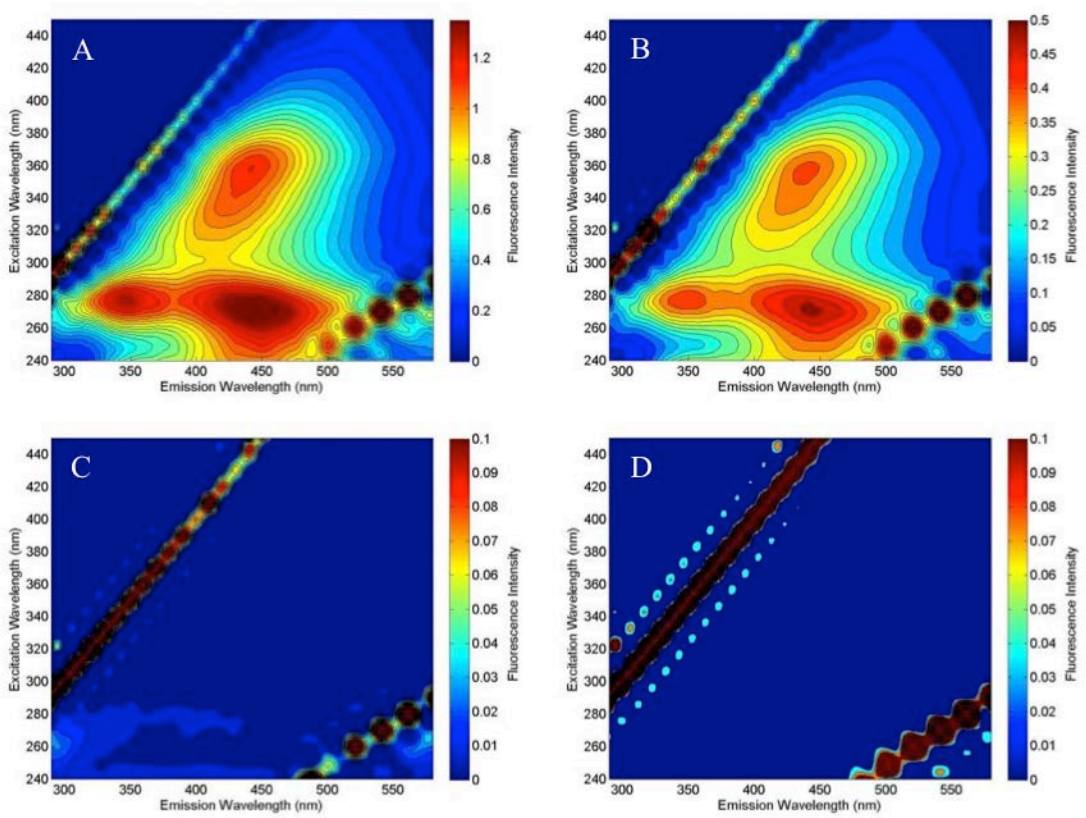


Figure 3.1. 3D fluorescence excitation–emission matrices for secondary treated effluent purged with N_2 (A), 70:30 (v/v) oxic NF permeate–secondary treated effluent blend (B), NF permeate (C), and tap water (D).

Note: Notice changing fluorescence intensity scale.

SEC-DOC and SEC-UV analysis of feed waters applied to the column systems (Figure 3.2) indicates that dilution of secondary treated effluent with NF permeate reduces the concentration of biopolymers and humic-like substances but maintains acids, low molecular weight humic substances, and neutrals. The UV and SEC-DOC chromatograms indicate that these low molecular weight fractions are retained to a larger degree than higher molecular weight substances, which are removed by membrane filtration. Tap water exhibited a similar pattern to the 70:30 (v/v) NF permeate–secondary treated effluent blend but at lower concentrations and with fewer biopolymers and further reduced humic-like substances. The percent removal in DOC for the different experimental soil column set-ups with variable retention times (Tables 2.5 and 3.1) are summarized in Figure 3.3.

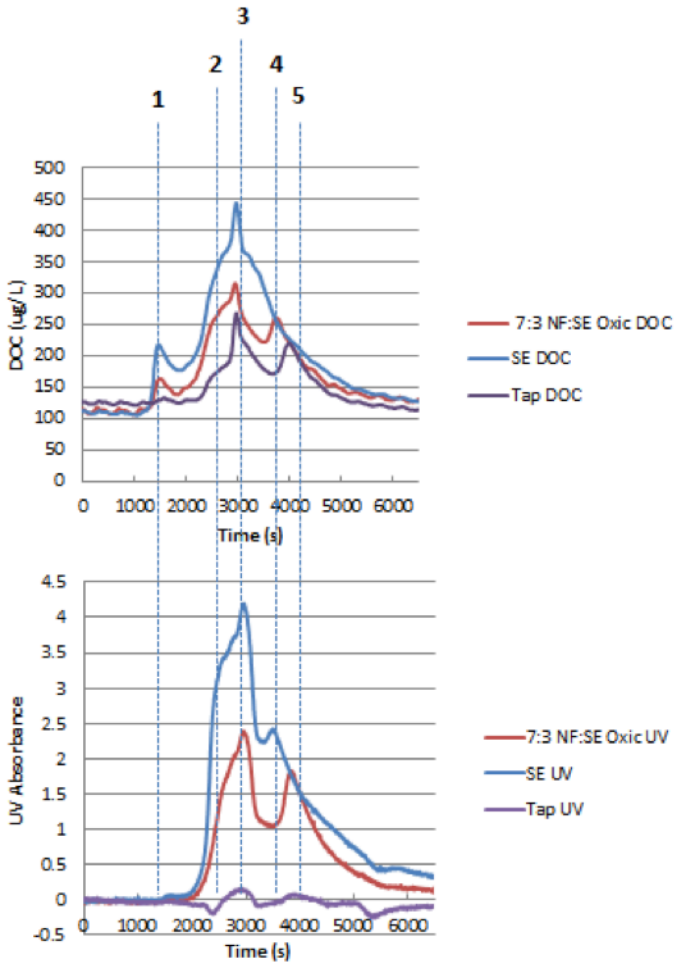


Figure 3.2. SEC-DOC and SEC-UV chromatograms for soil column influent samples. Peaks represent (1) biopolymers, (2) humic-like substances, (3) polymer building blocks, (4) acids and low molecular weight humic substances, and (5) low molecular weight neutrals.

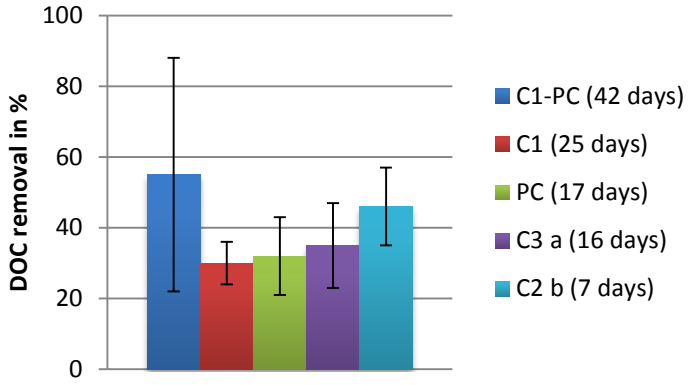


Figure 3.3. DOC removal (in %) for different soil column systems and residence times.

Note: Refer to Table 2.5 for soil column conditions (feed water quality, redox).

Li et al. (2012, 2013) reported that a reduced amount of BDOC and the corresponding shift towards more refractory primary substrates such as humic material resulted in a more diverse microbial community in microbially active soil systems. However, Li et al. (2013) also revealed that microbial diversity converges with depth, suggesting that after sufficient retention time BDOC is depleted, and both high and low BDOC receiving soil columns exhibit a similar degree of diversity. Therefore, if microbial diversity is the only controlling factor, after extended residence time both high and low BDOC receiving columns should perform similarly in terms of CEC attenuation. Thus, whereas diversity may converge with depth, the redox state of the system will differ depending on the amount and makeup of carbon present in the initial feed.

3.1.2. Influence of Temperature on Removal Efficiency

At all temperature set-points, the amount of DOC delivered to the column remained similar, ranging between 2.24±0.31 mg/L and 2.78±0.37 mg/L. Influent nitrate concentrations averaging 1 mg/L increased slightly to 1.4 mg/L in the effluent, suggesting that redox conditions remained oxic/suboxic and did not change to anoxic during column travel. Nitrate concentrations in the influent and effluent were unaffected by changes in temperature. Abel et al. (2012) found that nitrifying bacteria were slowed down at a temperature of ≤5° C but remained active and provided limited ammonia removal during simulated SAT. The amount of BDOC attenuated following passage through the eight columns is illustrated in Figure 3.4.

DOC removal was consistent and unaffected by changes in temperature, indicating that the microorganisms responsible for DOC degradation were not sensitive to temperature changes within the studied range. This finding is consistent with a study conducted by Massmann et al. (2006) that investigated the impact on variable temperatures on redox condition at an operational artificial recharge site. Despite significant changes in ambient temperature between 0 and 24° C, DOC attenuation between the recharge pond and two monitoring wells remained consistent (Massmann et al., 2006).

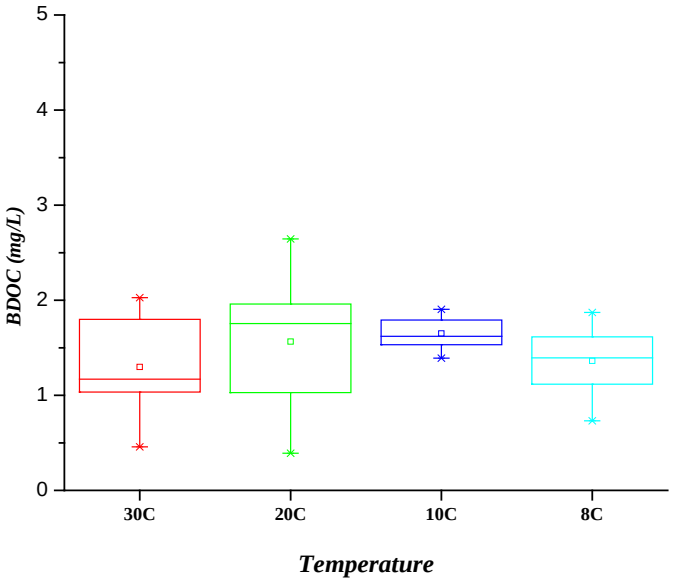


Figure 3.4. Biodegradable dissolved organic carbon delivered to the column at each temperature set-point.

3.2. Attenuation of Viruses During Simulated MAR

Prediction of enteric pathogen survival in any natural environment is difficult because of the wide variety of pathogen types and heterogeneous nature of microbial populations. Viruses are usually the longest surviving enteric pathogens in natural environments (Maier et al., 2009). Recent studies on the survival of enteric pathogens in groundwater at MAR operations in Australia have substantiated the importance of temperature and also native microflora on pathogen persistence (Sidhu and Toze, 2012).

To obtain a better understanding of removal of viruses tested in this study at full-scale recharge sites, samples were also collected during laboratory-scale coliphage transport studies and assayed for PMMoV and enteric viruses (Table 3.2). Soil column C3, 15 cm in diameter and 4.4 m long, was filled with soil from the Prairie Waters Project MAR site in Colorado. C3 had received secondary treated effluent from the Denver Metro Reclamation District WWTP before disinfection as feed since early summer 2012. This column was maintained under saturated flow conditions with the exception of equipment failure, which happened occasionally (clogged tubing, for example). Column C3 was partially drained in November 2012. Saturated flow conditions were re-established in the first week of December 2012. Spiking of the influent with MS-2 coliphage (see following section) began on January 16, 2013. On January 26, 2013, additional samples were collected from the column and assayed for naturally occurring viruses in the wastewater.

Only 1 mL samples could be collected for assays through the porous cup samplers at the various depths in column C3; however, a 1 L sample could be processed for the soil column effluent. Only PMMoV and aichiviruses could be detected in the effluent in the 1 mL volumes. Aichiviruses were removed by 0.63 log after 15 cm of travel and by greater than 2.35 log after 30 cm of travel. PMMoV was detected in the column effluent, indicating a removal of 4.9 log after travel through 4.4 m (13.2 ft). It required 90 cm to remove the virus by approximately 1 log, but little virus removal occurred between 90 and 180 cm. Reovirus was detected by direct PCR in one sample from the 430 cm sampling port and in the effluent. Direct PCR was used, so the number of genomes could not be determined.

3.2.1. Fate of Murine Norovirus and Bacteriophage MS-2 During Infiltration Through Soil Columns

The MNV was added for a 24 h pulse spike to the first batch of the MS-2 spiking solution. This solution was spiked in-line to the feed using Teflon tubing. A sampling tap on the feed line (after the spiking, but just before entering the column) was used to collect all influent samples. MNV (genomic units) was detected up to sampling port 2 at a depth of 30 cm over a sampling period of 5 days (Table 3.3). A removal of almost 5 log was achieved for MNV within 30 cm of soil passage; however, MNV was still detected in low numbers (E+02) in the influent sample on Day 5, 4 days after the MNV spiking stopped (Table 3.3). Most likely, the MNV was sorbing to the tubing during spiking and desorbing from the tubing when MS-2 spiking continued.

Table 3.2. Removal of Naturally Occurring Viruses in the Wastewater by qPCR (genomes/L)

Depth (cm)	Pepper Mild Mottle Virus	Aichivirus	Reovirus (Direct PCR)	Enterovirus Adenovirus
Influent	400,000	125,000	negative	negative
15	275,000	29,000	negative	negative
30	71,000	<550	negative	negative
60	21,000	<550	negative	negative
90	36,500	<550	negative	negative
180	24,000	<550	negative	negative
305	<550	<550	negative	negative
430	<550	<550	positive	negative
440	5*	<5*	positive	negative

Notes: Samples collected 6 weeks after flooding of the soil column with wastewater.*=1 L was sampled; all other depths, only 1 mL could be sampled. PCR=polymerase chain reaction; qPCR=quantitative polymerase chain reaction.

Table 3.3. Murine Norovirus Removal by Soil Column During 5 Days After a 24 Hour Pulse Spike (genomes/L)

Sample Port	Depth (cm)	Day 1 1/17/13	Day 2 1/18/13	Day 3 1/19/13	Day 4 1/20/13	Day 5 1/21/13
Influent	0	1.44E+06	6.89E+03	4.21E+03	6.53E+02	8.30E+02
Port 1	15	1.58E+02	3.82E+02	4.71E+01	3.29E+01	1.61E+02
Port 2	30	1.79E+01	1.89E+01	negative	1.35E+01	negative
Port 3	60	negative	negative	negative	negative	negative
Port 4	90	negative	negative	negative	negative	negative
Port 5	180	-	-	-	-	-
Port 6	305	-	-	-	-	-
Port 7	430	-	-	-	-	-
Effluent	440	-	-	-	-	-

Coliphage MS-2 has been used in numerous studies on the transport of viruses through soils. It generally demonstrates lower adsorption to soils than many enteric viruses and is often seen as a conservative model for enteric viruses. Conditions for soil column C3 are described in the previous section. Continuous spiking with coliphage MS-2 occurred for 22 days. Samples were collected through porous cup samplers at various depths and the final effluent from the column. A conservative tracer study using potassium bromide indicated 15.3 days for effluent to pass through the column (see Chapter 2). Figure 3.5 illustrates the MS-2 concentration at various depths in the soil column.

MS-2 was detected in the soil column at 430 cm depth after 5 days of spiking. It took the chemical tracer almost 15 days to be detected at this depth. The faster transport of the virus through porous media is due to its transport through larger pores than the solute tracer itself and the greater sensitivity of the detection method for viruses versus solute chemical tracers (Bales et al., 1989). Also, the solute can diffuse into smaller pore sizes, which the virus cannot. MS-2 was transported three times faster than the chemical tracer in this uniform soil. Viruses have been observed to travel 100 times faster than solute tracers in non-uniform substrata (Hinsby et al., 1996). Thus, chemical tracers cannot always be relied upon to reflect the transport or retention time for viruses during MAR.

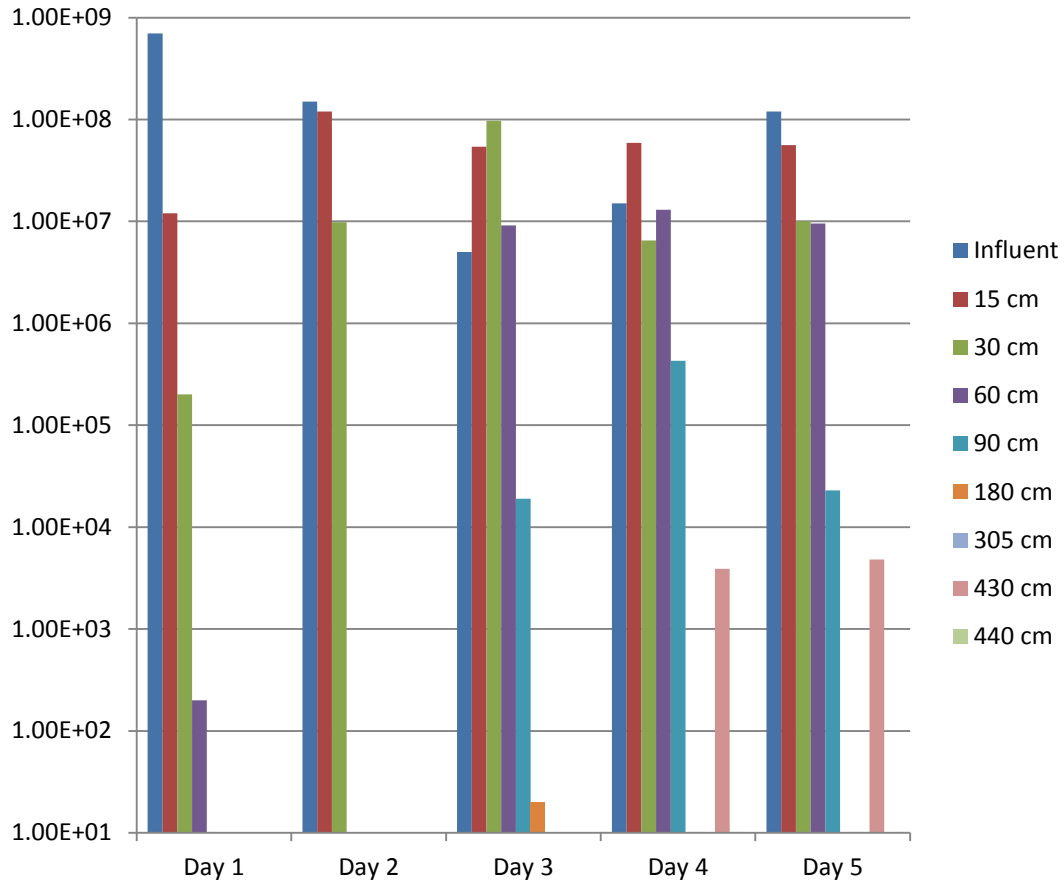


Figure 3.5. MS-2 removal by soil column during first 5 days (x-axis is plaque-forming units per mL) after the start of spiking.

Figure 3.6 illustrates the concentration of MS-2 from 11 to 15 days after addition to the influent. The virus was detected in the effluent from the column on Day 12, about 3 days ahead of the chemical tracer. The apparent faster movement of the virus is due to greater sensitivity of the assay method (one virus can be detected in 1 mL) and movement of the viruses with the faster moving water because it is restricted to the larger pores (chemical tracers can diffuse into smaller pores, slowing their movement). Similar phenomena have been observed in field studies (Maier et al., 2009). Furthermore, preferential flow might have occurred within the column.

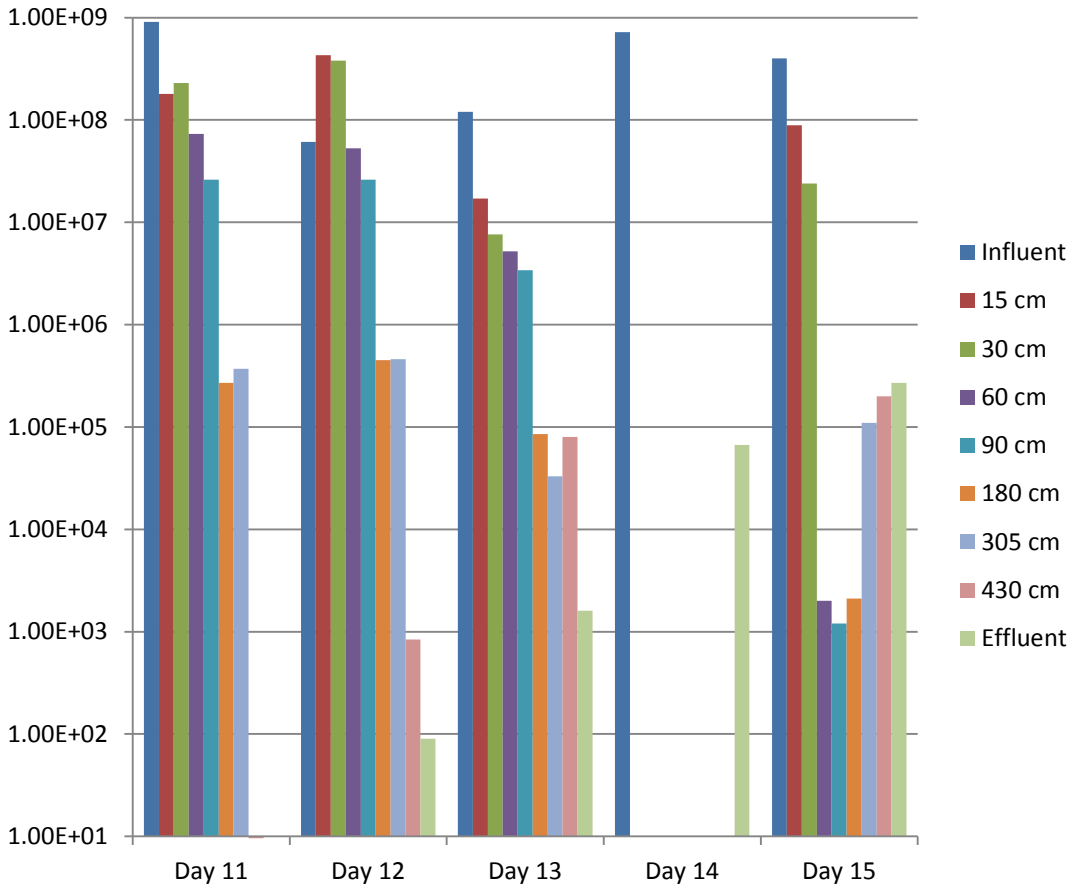


Figure 3.6. MS-2 removal in soil column, Days 11 through 15 after the start of spiking.

Figure 3.7 shows the concentration of the MS-2 coliphage throughout the entire experiment. Addition of MS-2 was terminated on Day 22. As can be seen in Figure 3.7, most of the virus removal occurred within the first 60 cm, with little additional removal through the next 380 cm of the column after 13 to 15 days. During the spiking study, the soil column removed 3 to 4 log of MS-2 after travel through 440 cm. Numerous other studies in the field and in laboratory soil columns have documented that most virus removal occurs near the soil surface; however, most studies used soil column lengths of 1 m or less and did not continuously flood or saturate the soil columns over the length of time in this study. The results appear to support the conclusions of Pang (2009) in his comprehensive literature review of field studies and soil cores. He suggested that virus removal decreases with travel distance and may be due to a number of factors, including genetic differences resulting in different charges on the surface of the virus, longer survival times, and ability to form aggregates.

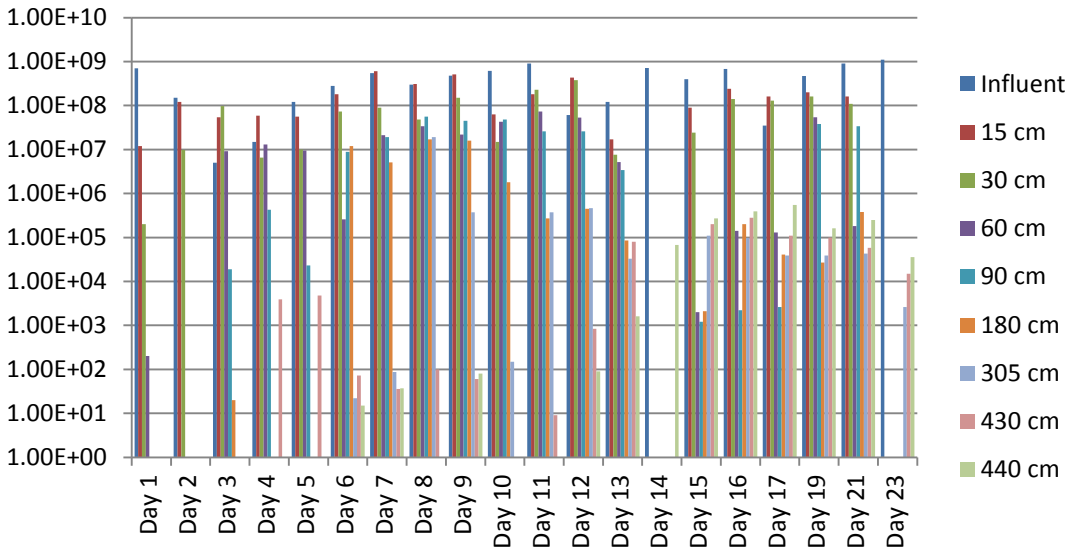


Figure 3.7. MS-2 removal by soil column, Days 1 through 23 after start of MS-2 spiking.

3.3. CEC Attenuation During Simulated MAR

3.3.1. The Role of Key Environmental Conditions: Redox Conditions, BDOC, and Residence Time

The removal of the easily biodegradable CECs, caffeine, trimethoprim, and atenolol, after 3 days of travel under three different conditions: (1) oxic, low BDOC (BDOC= 0.19 mg/L); (2) suboxic, low BDOC (BDOC=0.17 mg/L); and (3) anoxic, high BDOC (BDOC=4.17 mg/L) is presented in Figure 3.8. Actual BDOC levels are shown in ppm. Caffeine exhibited good removal (~70% or greater) under all redox and carbon conditions. Trimethoprim was removed significantly faster under high BDOC conditions, the only compound to perform best under this condition throughout the study. Atenolol was very sensitive to BDOC concentrations and less sensitive to redox conditions. Under low BDOC and suboxic conditions, atenolol was removed to greater than 95% in 3 days. The compound was removed less efficiently under oxic conditions (~85% removal) but was removed notably less under high BDOC/anoxic conditions (<60% removal).

The apparent indifference of caffeine removal to operational conditions suggests that this chemical could primarily be removed by sorption processes instead of immediate biotransformation (Figure 3.8). Sorption of caffeine to clays has been demonstrated previously in batch and soil column experiments (Sotelo et al., 2013). The results also suggest that atenolol and trimethoprim were affected by operational conditions, indicating that bioattenuation plays a major role in addition to sorption. Sorption could facilitate biotransformation by extending the residence time of these compounds relative to the HRT of the infiltrating water.

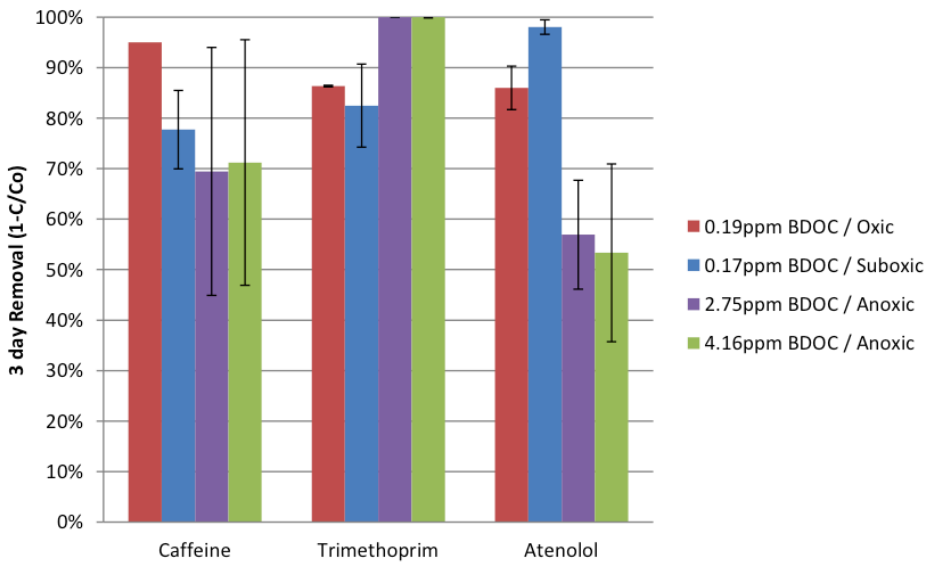


Figure 3.8. Percentage removal of easily degradable compounds at varying redox and BDOC conditions after 3 days retention time.

Moderately degradable compounds were studied under two carbon feed conditions: 0.17 mg/L BDOC and 4.16 mg/L BDOC (Figure 3.9). The retention times in this case were 9 days for the low carbon feed condition (PC) and 14 days for the higher carbon feed condition (C1). A common retention time was not available for comparison because of different sampling port locations in the two column systems. The effect of BDOC varied depending on the compound, but in general removal was most efficient (>70%) under low BDOC (<0.5 mg/L) conditions (Figure 3.9).

With the exception of sulfamethoxazole, the moderately degradable compounds were removed significantly better under carbon-starving conditions than under high BDOC (>2 mg/L) conditions. Diclofenac and gemfibrozil exhibited good removal of greater than 70% on average after 9 days of travel under carbon-starving conditions, but under carbon-rich conditions they exhibited little to no removal after 14 days of travel. Naproxen was completely removed within 9 days with carbon-starving conditions compared to an average removal of only 60% after 14 days with carbon-rich feed. Carbon-starving conditions improved N,N-Diethyl-meta-toluamide (DEET) removal by more than 40% on average, even with 5 fewer days of travel time. These results confirm that carbon-starving conditions characterized by low BDOC (~0.15–0.25 mg/L) improves removal efficiency of CECs.

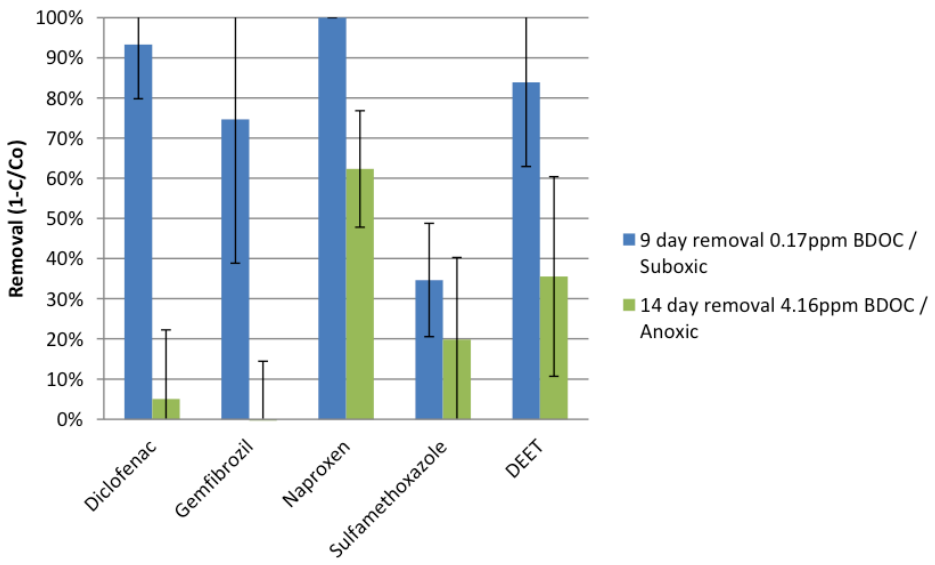


Figure 3.9. Percentage removal of moderately degradable compounds at low (0.17 mg/L) BDOC and high (4.16 mg/L) BDOC after 9 and 14 days retention time.

Columns operated under oxic conditions outperformed suboxic and anoxic columns for all of the moderately degradable compounds (Figure 3.10). Under oxic, carbon-starving conditions, and within a retention time of 3 days, complete removal was demonstrated for diclofenac, gemfibrozil, and naproxen. The optimal redox condition for diclofenac removal is disputed in the literature, as reported by Rauch-Williams et al. (2010). Several studies reported diclofenac was best removed under anoxic conditions (e.g., Rauch-Williams et al., 2010; Zwiener and Frimmel, 2003; Hua et al., 2003), whereas others report the compound was removed best under oxic conditions (Wiese et al., 2011). Sulfamethoxazole and DEET were removed greater than 80% on average under oxic conditions during this study (Figure 3.10).

The soil columns with suboxic and anoxic experimental conditions performed poorly in comparison to the oxic conditions within a residence time of 3 days, with less than 35% removal of moderately degradable compounds. Improved removal of sulfamethoxazole under oxic conditions confirms studies by Baumgarten et al. (2011) and Grünheid et al. (2005), although these studies report much slower removal at this spiking level (ng/L range), requiring at least 14 days for 60% removal (half-lives of only 1 day were reported at higher spike concentrations). At 3 days retention time, removal among the suboxic and anoxic columns was indistinguishable between each condition. A study investigating how different blending ratios of membrane permeate affect MAR efficiency showed similar performance under low BDOC/oxic conditions (Drewes, 2010; see Figure 3.10).

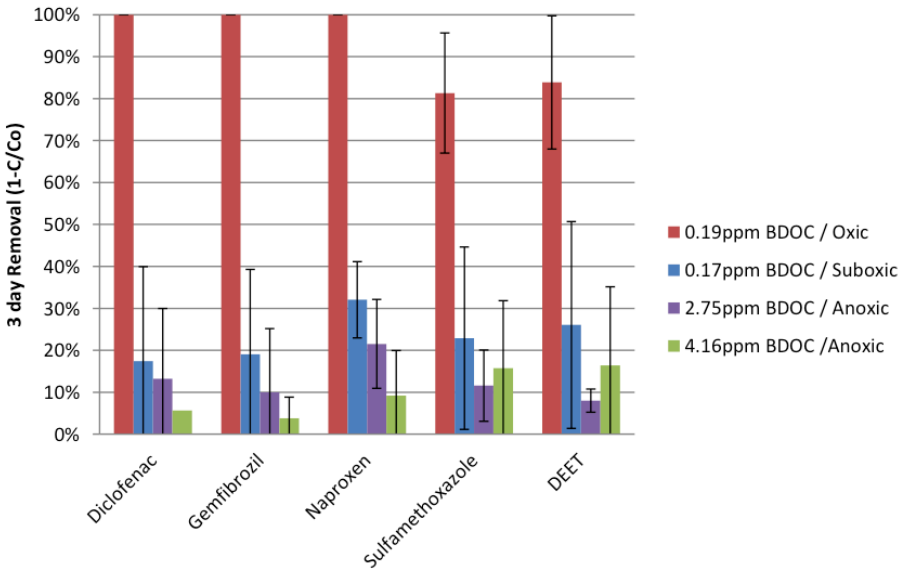


Figure 3.10. Percentage removal of moderately degradable compounds at varying redox and BDOC conditions after 3 days retention time.

No attenuation was observed for the recalcitrant anticonvulsants primidone and carbamazepine, the herbicide atrazine, and the artificial sweetener sucralose during simulated MAR in the laboratory-scale soil column study. Attenuation was less than 10% throughout all experimental soil column conditions (e.g., BDOC, redox, residence time). An extended residence time of 42 days (C1-PC) and 7.5 m of soil percolation under saturated anoxic flow did not enhance attenuation of these compounds, as shown for primidone in Figure 3.11.

Enhanced removal was demonstrated for the anticonvulsant dilantin (34%) and the artificial sweetener acesulfame (64%) as well as the flame retardants tris(2-carboxyethyl)phosphine (TCEP; 72%), tris(1-chloro-2-propyl)phosphate (TCPP; 65%), and tris[2-chloro-1-(chloromethyl)ethyl]phosphate (TDCP; 58%) under low BDOC/oxic conditions after 7 days residence time, although no removal occurred during suboxic (14 days residence time) or anoxic soil column conditions with up to 42 days retention time. It is interesting to note that removal of gemfibrozil and DEET improved significantly under anoxic redox conditions after 2 weeks of subsurface travel (Figure 3.11). By that time, the high amount of BDOC (>4.5 mg/L) present in the influent had been consumed by soil microorganisms, resulting in more carbon-starving conditions. Easily to moderately biodegradable compounds such as naproxen, atenolol, caffeine, trimethoprim, or ibuprofen were degraded fast in the coupled C1-PC soil column system.

The antidepressant fluoxetine as well as the antihistamine diphenhydramine were immediately attenuated after a few cm of soil infiltration in the columns, most likely through sorption processes. Frequently, both compounds were only detected in the spiked soil column influent samples. Fluoxetine is known to be not biodegradable in soil–water systems (Monteiro and Boxall, 2010).

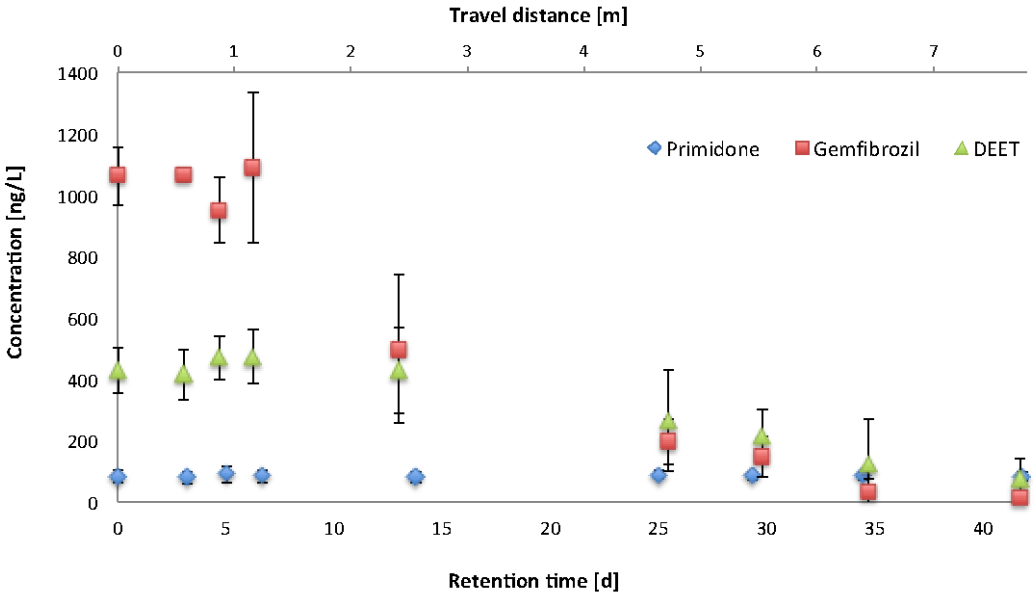


Figure 3.11. Attenuation of compounds primidone (recalcitrant, n=4), DEET (intermediate, n=5), and gemfibrozil (intermediate, n=5) with different biodegradability under saturated anoxic flow conditions during extended subsurface travel time of 42 days (coupled soil column system C1-PC).

Soil column system C4 was used to simulate an extremely carbon-limited condition that may be common in direct injection systems. The feed supplied to this 4.4 m long column consisted of NF permeate (0.26 mg/L DOC, suboxic conditions) sterilized by UV irradiation. The column set-up was as sterile as is reasonably possible. Although a completely sterile condition is unlikely, the only compounds well removed in this soil column have also been shown to strongly sorb to field soils and clays (Figure 3.12), which compose approximately 50% of the C4 column soil media. Thus, bioattenuation under these conditions is probably limited and ineffective for removing CECs.

The C4 column removed atenolol to below the detection limit after 7 days of residence time and removed caffeine by 77% in the same period (Figure 3.12). Sulfamethoxazole and iopromide on average were removed by 31 and 18%, respectively, whereas carbamazepine, TCEP, and TCPP showed no significant removal. Direct injection strategies into a potable aquifer employ water of similar quality to that supplied to this column, and therefore similar ineffectiveness of CEC bioattenuation could be assumed in these systems.

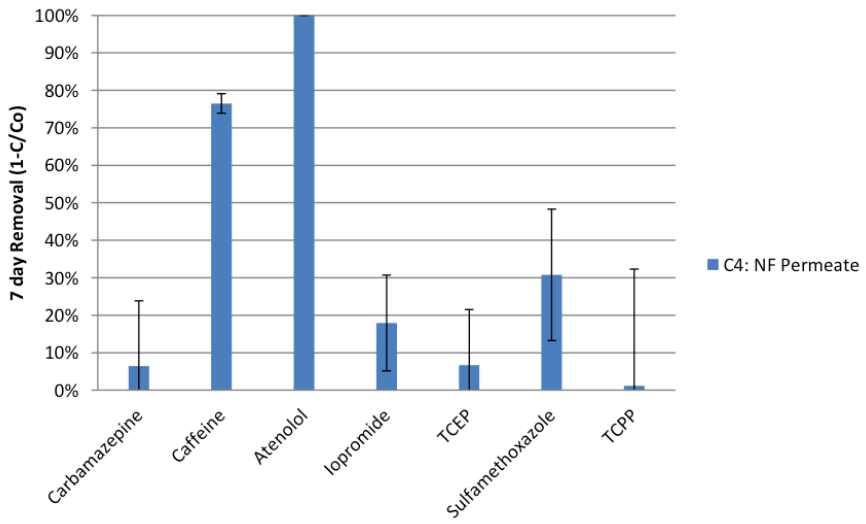


Figure 3.12. Percentage removal of CECs after 7 days of retention time in soil column C4 receiving NF permeate as influent (0.26 mg/L DOC influent).

3.3.2. Temperature Dependency of CEC Attenuation

A range of removal efficiencies was exhibited for the various CECs following passage through the soil columns. The temperature dependency of CEC attenuation varied by compound. Table 3.4 summarizes observed removals for the various compounds as well as their temperature dependency.

Eight compounds displayed good removal, exceeding 70%, regardless of the temperature. This experiment did not differentiate between removal by biodegradation and adsorption, and hence the results summarize the effect of temperature by both of these attenuation processes. Another group of eight compounds exhibited poor removal, less than 30%, at all tested temperature levels. Within this group were the anticonvulsants carbamazepine, dilantin, and primidone, which are known to be recalcitrant (Maeng et al., 2011; Drewes et al., 2003) as well as the artificial sweeteners acesulfame and sucralose, which have been used as tracers in WWTPs as a result of their persistence.

Attenuation of six of the compounds was noted to change with temperature (Table 3.4). Our previous studies indicated that, with the exception of oxybenzone, none of the other compounds exhibit sorptive losses, hence biodegradation can be assumed as the predominant removal mechanism. Two of these compounds, trimethoprim (Figure 3.13) and oxybenzone were better removed as the operating temperature of the columns was reduced. This is a significant finding because the opposite would have been expected given that both respiration and bacterial growth rates in the soil have been shown to decrease as temperatures decrease from 30 to 0° C (Pietikäinen et al., 2005). Further research is required to investigate whether other compounds also exhibit similar attenuation patterns and identify the microbial groups responsible for increased attenuation of such compounds.

Four of the nonsteroidal anti-inflammatory drugs (NSAIDs), diclofenac, gemfibrozil, ketoprofen, and naproxen, were better removed at higher temperatures. Gemfibrozil and naproxen exhibited a significant loss in attenuation as the temperature dropped from 20 to 10° C, as illustrated in Figure 3.14 for naproxen. Diclofenac and ketoprofen displayed reduced attenuation at 10 and 8° C compared to the higher temperatures, although the sudden drop noted in gemfibrozil and naproxen attenuation was not evident. This suggests that, despite all four compounds being NSAIDs, different microbial groups are responsible for their degradation. This is supported by the fact that ibuprofen, another NSAID, exhibited high removal (>90%) regardless of the temperature. The microbial community degrading gemfibrozil and naproxen seems significantly inhibited at some temperature between 10 and 20° C, whereas the microbial community degrading ibuprofen seems unaffected by temperature changes.

Overall, with the exception of a couple of compounds, lower temperatures did not significantly decrease CEC attenuation. This was counter to expectations that lower temperatures would decrease microbial activity and in turn reduce CEC attenuation. For the most part, it appears that the microbial communities are still active and uninhibited at temperatures as low as 8° C.

Table 3.4. Summary of CEC Removal

Amount of Removal	Temperature-Independent Removal		Temperature-Dependent Removal
Good Removal (70–100%)	amitriptyline atenolol bisphenol A diphenhydramine	fluoxetine ibuprofen propylparaben triclosan	
Moderate Removal (30–70%)			diclofenac gemfibrozil ketoprofen naproxen oxybenzone trimethoprim
Poor Removal (0–30%)	atrazine acesulfame carbamazepine DEET	dilantin primidone sucralose sulfamethoxazole	

Note: DEET=N,N-Diethyl-meta-toluamide.

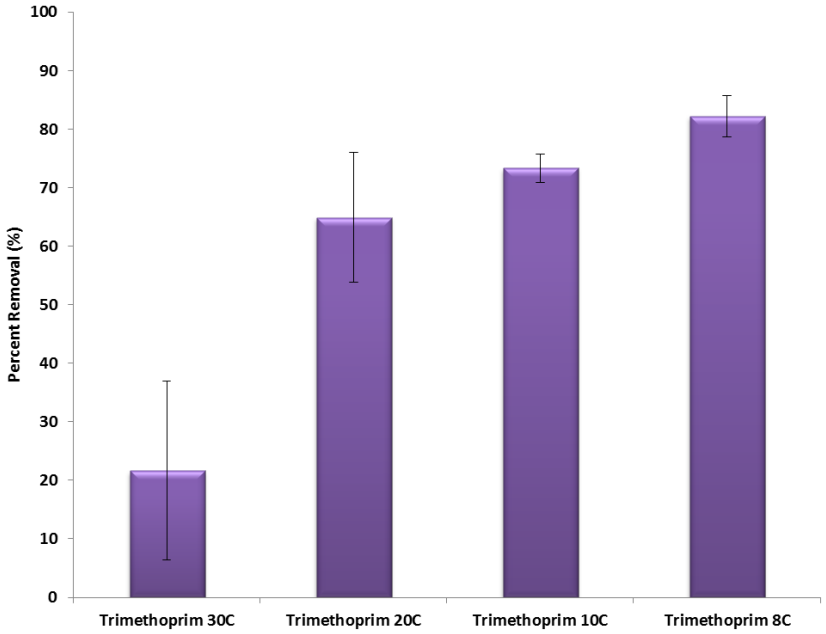


Figure 3.13. Mean trimethoprim attenuation at temperature set-points 30° C (n=9), 20° C (n=9), 10° C (n=10), and 8° C (n=10).

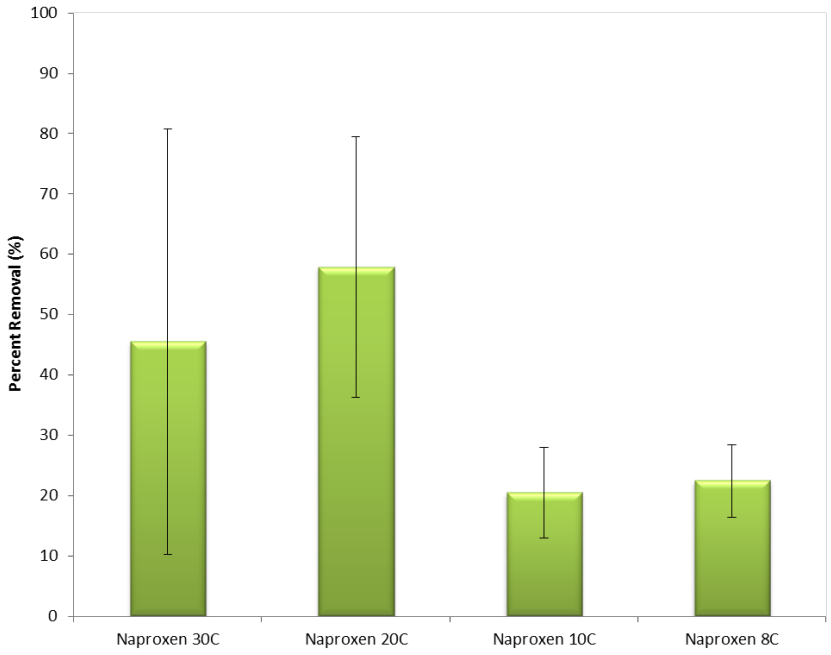


Figure 3.14. Naproxen attenuation at temperature set-points 30° C (n=9), 20° C (n=9), 10° C (n=10), and 8° C (n=10).

3.4. Attenuation of Glucocorticoids During Simulated MAR

3.4.1. Bioassay Validation

Each plate was run with the positive control standard curve in every assay, and the samples were assessed on two different days. Figure 3.15 shows the dose–response curve of positive control (DEX) on the two different experiment days. The response was expressed as % effect where the sample blue–green ratio was divided by the maximum ratio at the same experiment day (background subtracted first):

$$\%\text{effect} = \frac{\text{signal}_{\text{sample}} - \text{signal}_{\text{control}}}{\text{signal}_{\text{max}} - \text{signal}_{\text{control}}} \quad (3.1)$$

It was observed that the shapes of the positive control curves are comparable. The decrease in effect at higher DEX doses is largely the result of cytotoxicity. Although variations exist in the absolute value at the highest concentrations, the assay showed consistent sensitivity during different batches of experiments. The calculated EC_{10} for DEX is stable between 1.1 and 2.0 nM within all samples.

The spiking standard mixture was also tested and compared with the positive control (Figure 3.16). It can be observed that the total tested seven glucocorticoid agonists spiked into the soil column have similar total activity when compared with DEX at the ppb level.

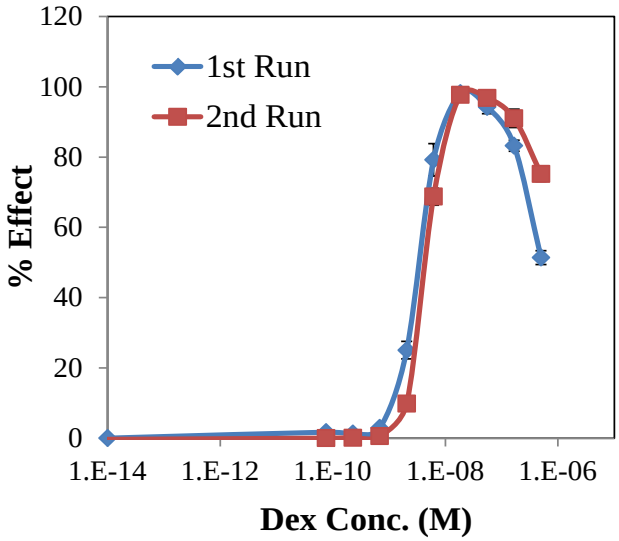


Figure 3.15. Positive control response curve for the GR bioassay. Error bars represent ± standard deviation in all test responses (n=3).

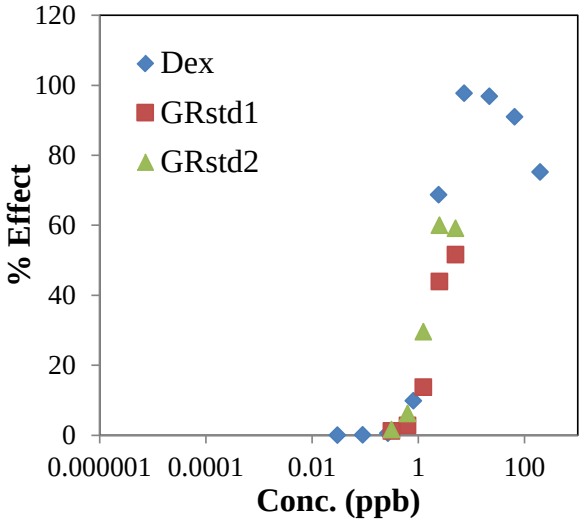


Figure 3.16. GR assay response for spiking standard set.

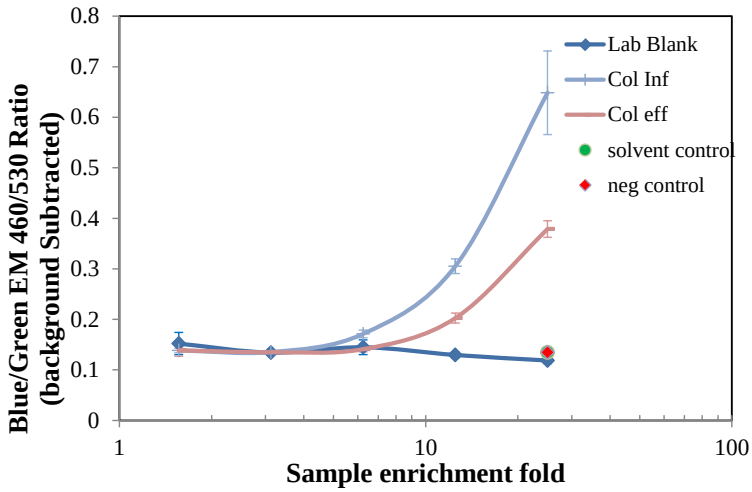


Figure 3.17. GR activities in WWTP influent and secondary treated effluent.

3.4.2. Glucocorticoid Activity Change During MAR

The primary GR screen on the wastewater influent and effluent from Colorado WWTP (Col Inf and Col Eff in Figure 3.17) showed that the activity existed in both of the samples at low concentrations (<25 fold). The EC_{10} for the influent and effluent were 11 and 21 (enrichment fold), with a DEX-EQ of 82 and 43 ng/L, respectively.

On the basis of the GR occurrence data in the secondary treated effluent, we set up the spiking level as 200 ng/L. The second batch of soil column samples was analyzed first, and the results are summarized in Figure 3.18. Both of the column inflows exhibited positive GR activity; however, there was no significant GR activity either in the intermediate port (3 days residence time) or the final outflow (>7 days residence time). The results suggest that the glucocorticoid active compounds evaluated can be efficiently attenuated by aquifer recharge in less than 3 days of residence time.

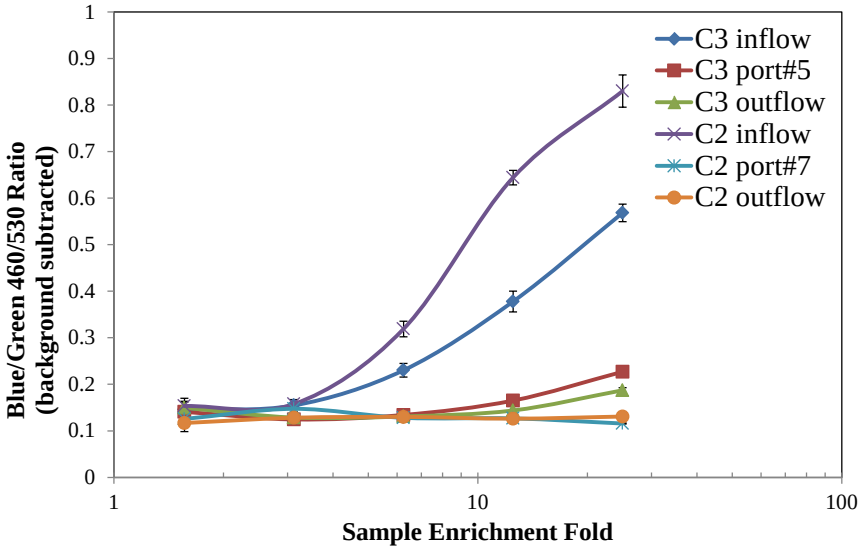


Figure 3.18. GR activities in soil columns (July 16, 2013, sampling).

Table 3.5. GR Activities Summary for the Second Batch of Samples (July 16, 2013)

Sample	EC_{10} (REF)	DEX-EQ (ng/L)
C3 inflow	12	36.0
C3 port #5	>25	ND
C3 outflow	>25	ND
C2 inflow	7.3	59.1
C2 port #7	>25	ND
C2 outflow	>25	ND

Note: ND=not detected under current enrichment fold.

The EC_{10} for C2 and C3 were 7.3 and 12 (enrichment fold), with a DEX-EQ of 59.1 and 36.0 ng/L, respectively (Table 3.5). The GR activity of C2 is higher than that of C3, which is expected because C2 contained the GR mixture spike.

To further evaluate and confirm these results, the first batch of samples was also analyzed for GR activity on a different day. The seven standard mixtures were added at the same concentration level as the spiked soil column samples for spiking validation (Figure 3.19). Higher glucocorticoid activity was detected in the inflow of the C2 column because of the spiking of the glucocorticoid standard set. GR activity was not detected in the samples taken from port #7 (3 days residence time) or the effluent of the column (7 days residence time). For the C3 column, the GR activity of the intermediate sampling port #5 (~8 days residence time) was even higher than that of the inflow, possibly caused by the transformation of some compounds of low or no glucocorticoid activity into compounds with higher GR activity under the anoxic conditions created in the C3 column. When we measured the outflow of this column (16 days residence time), however, the level of GR activity was almost nondetectable (Figure 3.19).

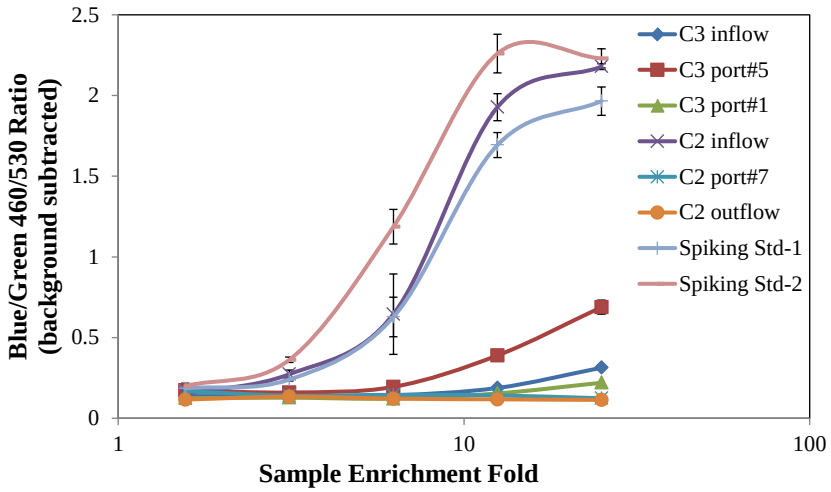


Figure 3.19. GR activities in soil columns (July 1, 2013, sampling).

The EC_{10} and DEX-EQ values for the first batch of samples are summarized in Table 3.6. The C2 inflow has quite similar DEX-EQ values to the spiking standard and reasonable agreement with the original spiking concentration (200 ng/L).

The trend of GR activity changes in C2 is the same during both sampling events (Figure 3.20). The results indicate that this column can effectively remove GR activity in less than 3 days residence time (<0.5 m subsurface travel distance).

Table 3.6. GR Activities Summary for the First Batch of Samples (July 1, 2013)

Sample	EC_{10} (REF)	DEX-EQ (ng/L)
C3 inflow	>25	ND
C3 port #5	10.5	74.8
C3 port #1	>25	ND
C2 inflow	5.2	150.9
C2 port #7	>25	ND
C2 outflow	>25	ND
Spiking Std-1	3.5	224.3
Spiking Std-2	5.2	150.9

Notes: DEX-EQ=dexamethasone equivalent concentrations; EC_{10} (REF)=sample enrichment fold where the activity is 10% of the maximum response in the same experiment day (% effect); ND=not detected under current enrichment fold.

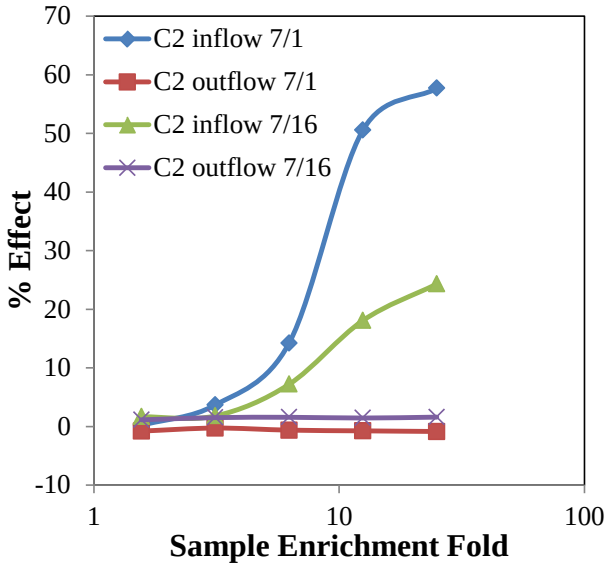


Figure 3.20. GR activity comparison in C2.

3.4.3. Glucocorticoid Removal in Soil Column Systems

The glucocorticoids corticosterone, fludrocortisone, cortisol, methylprednisolone, prednisolone, and prednisone were removed by 100 percent in samples collected from the intermediate sampling port of the low BDOC/oxic soil column C2 (3 days residence time, n2) and not detected in effluent samples of this column (7 days residence time, n=4). Cortisone was the only spiked compound (53–214 ng/L) detected in samples collected at the intermediate sampling port and the column outlet in low ng/L concentrations (≤2.5 ng/L). Average removal for cortisone was in the range of 92±3.2% (3 days) and 99±1.4% (7 days). These findings are in agreement with the bioassay results for removal of GR activity in C2 under low BDOC/oxic conditions.

3.5. Sorption Potential of Different Soil Types

The removal of CECs during soil infiltration is primarily due to both biological transformation and sorption to the solid phases present. Sorption may be particularly important for recalcitrant CECs. K_d describes sorption of a specific chemical between water and soil phases of a system. The K_d value is a characteristic specific to the chemical in question and a specific soil, and thus an important parameter for modeling contaminant transport at different field sites.

3.5.1. Soil Characterization

All soils used in the laboratory-scale experiments (e.g., soil column systems, batch tests) within this study were characterized. The abiotic control columns at CSM (soil ID F) and KAUST (soil ID G) that were used to determine R_f and K_d values are filled with the same sandy soil as the biotic soil columns (e.g., C1, C2) used to derive CEC removal rate constants. Soil characteristics for the two long soil columns, C3 and C4 (both filled with a 50:50 v/v blend of technical sand and field soil), are listed in Table 3.7. In addition, five soils with a wide range of physical and chemical properties (soil ID A–E), bentonite, field soil (soil ID FS), and field clay from the MAR facility in Colorado were chosen for the batch experiments to test sorption behavior of indicator CECs. The relevant soil characteristics are summarized in Table 3.7.

3.5.2. Sorption of CECs to Clay Materials

The soils used in this experiment covered a range of clay percentages (6–100%, Table 3.8). Field soil was taken from the initial layer (top 3 cm) of an infiltration basin at the field site in Colorado. Field clay consisted of ground and homogenized clay aggregates taken from the first 1 m depth of an active infiltration basin. The field soil and clay were previously loaded with CECs from RBF water for approximately 6 months. Manganese and iron were present in significant concentrations because of metal oxide deposition in the ARR infiltration basins from where the soil samples were retrieved. Manganese and iron content were not determined for bentonite.

Table 3.7. Soil Properties Including Cation Exchange Capacity, Fraction of Organic Carbon (f_{OC}), Organic Matter, Soil pH, Bulk Density, Porosity, and Soil Classification

Soil ID	f_{oc} (%)	OM (%)	Bulk Density (g/cm^3)	Porosity	pH	Cation EC (meq/100g)	Sand (%)	Silt (%)	Clay (%)	Class
Batch Tests										
A	0.1	0.1	1.53	n.a.	8.4	2.7	100	0	0	sand
B	1.1	1.9	1.15	n.a.	7.1	12.6	79	10	11	sandy loam
C	1.4	2.4	1.02	n.a.	7.4	17	63	16	21	sandy clay loam
D	5.4	9.3	0.87	n.a.	7.2	29.2	29	40	31	clay loam
E	0.8	1.3	1.11	n.a.	5.2	5.2	49	18	33	sandy clay loam
FS	0.3	n.a.	1.48	0.3	n.a.	n.a.	94	0	6	sand
Soil Columns										
F	0.066	0.1	1.81	0.36	7.5	n.a.	93	2	5	sand
G	0.1	0.1	1.46	0.45	7.4	n.a.	n.a.	n.a.	n.a.	n.a.*
C3/C4	0.1	0.1	1.8	0.34	7.7	7.2	95	4	1	sand

Notes: n.a.=data not available; *=Wadi sediments do not meet the current classification; EC=Electrical conductivity; OM=organic matter.

Source: Modified from Teerlink (2012) and Rauch-Williams et al. (2010).

Table 3.8. Characteristics of Field Soil, Field Clay, and Bentonite Used in Sorption Batch Experiments

Soil ID	f_{oc} (%)	Clay (%)	Mn (mg/kg)	Fe (mg/kg)
FS	0.3	6	32.67	1091.43
FC	<0.3	23	46.14	1986.46
BT	0	100	n.a.	n.a.

Notes: BT=bentonite; FC=field clay; Fe=iron; FS=field soil; Mn=manganese; n.a.=data not available.

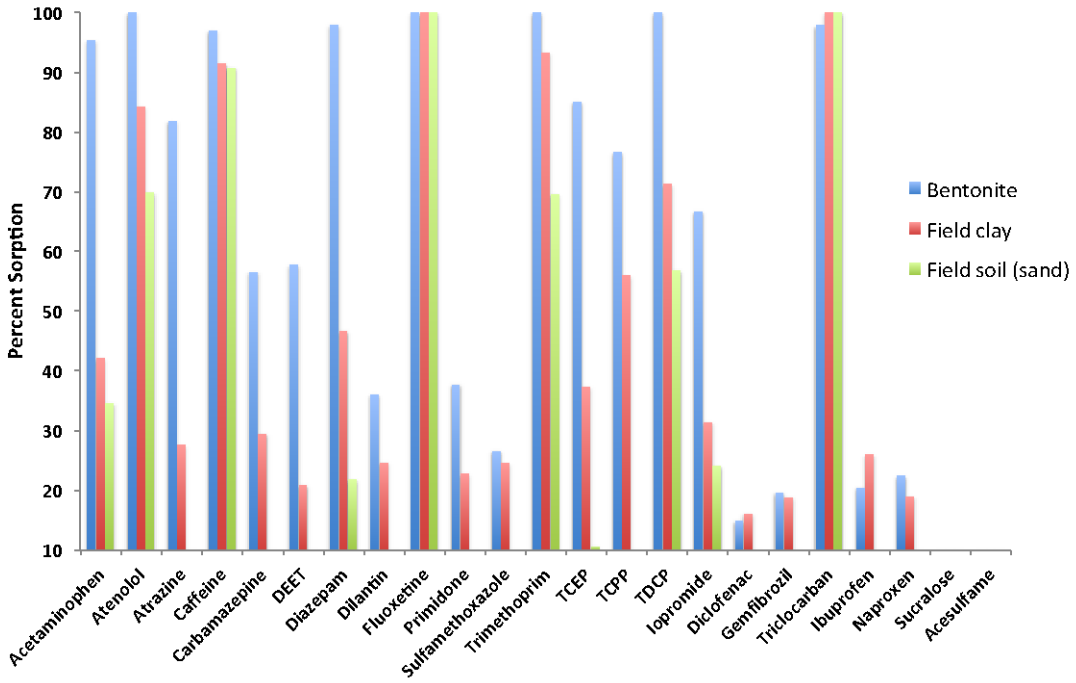


Figure 3.21. Sorption (in %) of different CECs to bentonite (Sigma-Aldrich), field clay, and sandy field soil (both from MAR site) using spiked RBF water (spiking level 2000 ng/L).

Note: A preservative was added to the soil–water mix to prevent biotransformation.

The compounds atenolol, caffeine, and trimethoprim showed strong sorption to all three soils tested, as illustrated in Figure 3.21. On average, all three compounds showed complete or nearly complete removal to below detection in the presence of bentonite clay. The field soil taken from the initial layer of an infiltration basin was able to sorb 70% of atenolol, 91% of caffeine, and 70% of trimethoprim. The field clay sorbed a greater percentage of atenolol and trimethoprim than the field soil and removed 84 and 93% of these two compounds, respectively. All samples were immediately preserved at the beginning of the batch sorption test to avoid biodegradation during the run time of the experiment. Sorption of diclofenac, gemfibrozil, naproxen, and sulfamethoxazole to bentonite clay was less than 30%. DEET was 58% removed by bentonite. The field soil provided little sorptive capacity for these compounds, as removal was within the standard deviation of 10%. The field clay removed 15 to 25% of all five compounds.

Sorption results for the chlorinated flame retardants TCEP, TCPP, and TDCP, along with the anticonvulsant drugs carbamazepine and primidone, are also shown in Figure 3.21. The chlorinated flame retardants sorbed strongly to bentonite, which removed greater than 75% on average; 57% of carbamazepine and 38% of primidone were removed in the presence of bentonite. Concentrations of TCEP and TCPP did not decrease in the presence of field soil, whereas the concentration of the more hydrophobic TDCP was reduced by 57%. TDCP concentration was reduced 71% on average by the field clay, and the anticonvulsant concentrations were reduced by less than 30%. The field clay removed 37 and 56% of TCEP and TCPP, respectively. For every compound in this experiment, bentonite clay sorbed the greatest percentage of the initial concentration, followed by the field clay, which has a higher clay percentage than the field soil. These results suggest that clay, rather than organic carbon, is the dominant sorbent for these experimental conditions.

3.5.3. Breakthrough Curves and K_d Values

Breakthrough curves of targeted indicator compounds as shown for gemfibrozil in Figure 3.22 are based on soil column experiments with abiotic column systems. Data for both sorption experiments (batch tests and soil columns) are presented in Table 3.9. As the table indicates, calculation of K_d was not successful for all of the analyzed compounds. Therefore,, the literature was reviewed to provide appropriate K_d values for all compounds and soil types used in the contaminant transport model (Chapter 6) where our own data were missing.

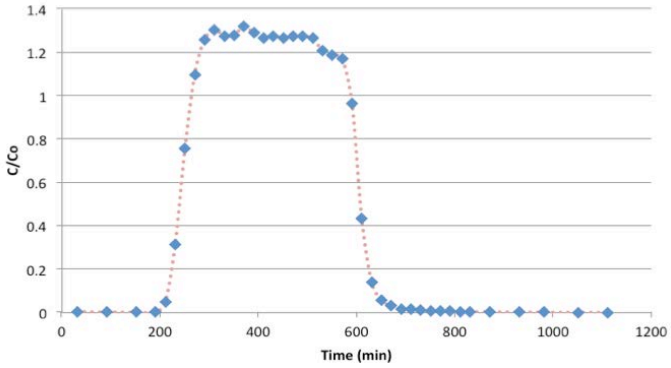


Figure 3.22. Breakthrough curve of gemfibrozil determined in an abiotic soil column at KAUST.

Table 3.9. Sorption Distribution Coefficients of Targeted Indicator Compounds for Different Soil Properties (Preliminary Results)

		Soil Batch Tests					Soil Column Tests	
	Log D_{OW}	Log K_d					K_d	
Compound	pH 7.4	A	B	C	D	E	F	G
Acesulfame	-2.88	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0
Acetaminophen	0.47	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0
Amitriptyline	2.65	1.85	2.15	3.07	2.75	1.43	n.a.	n.a.
Atenolol	-1.74	0.09	1.31	n.a.	1.55	n.a.	n.a.	n.a.
Atrazine	2.64	n.a.	-0.55	0.19	n.a.	0.01	n.a.	0.009
Bisphenol A	3.64	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.068
Caffeine	-0.63	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Carbamazepine	1.9	1.39	0.78	1.53	1.4	0.51	0.24	0.031
DEET	2.42	0	0	0	0	0	n.a.	0.006
Diclofenac	1.44	n.a.	n.a.	n.a.	n.a.	n.a.	0.01	0
Dilantin	1.81	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.025
Diphenhydramine	1.63	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Fluoxetine	1.41	n.a.	3.92	2.79	3.86	n.a.	n.a.	n.a.
Gemfibrozil	1.69	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.003
Hydrocodone	0.25	0.62	1.76	2.04	1.89	1.09	n.a.	n.a.
Ibuprofen	0.58	n.a.	n.a.	n.a.	n.a.	n.a.	0.03	0
Iopromide	-2.66	0	0	0	0	0	n.a.	0
Ketoprofen	-0.16	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0
Methylparaben	1.83	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.012
Naproxen	0.35	n.a.	n.a.	n.a.	n.a.	n.a.	0.08	0
Oxybenzone	3.77	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.382
Primidone	0.83	0	0	0	0	0	<0.001	0
Propylparaben	2.84	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.037
Sucralose	0.23	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0
Sulfamethoxazole	-0.54	0	0	0	0	n.a.	n.a.	0
TCEP	1.47	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.028
TCPP	2.59	-0.33	-0.02	n.a.	0.41	n.a.	n.a.	n.a.
Triclocarban	6.07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Triclosan	5.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.12
Trimethoprim	0.47	0.26	1.78	2.34	1.98	n.a.	n.a.	n.a.

Notes: DEET=N,N-Diethyl-meta-toluamide; D_{ow}= octanol/water distribution coefficient; K_d=sorption distribution coefficient; n.a.=not available;
TCEP=tris(2-carboxyethyl)phosphine; TCPP=tris(1-chloro-2-propyl)phosphate. See Table 3.7 for soil IDs (A–F).

3.6. First-Order Removal Rates for Bulk Organic Carbon and CECs

DOC profiles for different soil column systems are illustrated in Figure 3.23. The removal rate of bulk organic carbon is dependent on the composition of the bulk organic matter, that is, the amount of easily biodegradable carbon. The higher the initial DOC concentration and amount of BDOC, the faster the removal of this easily biodegradable carbon portion by microorganisms. In laboratory-scale soil column experiments, removal rate is approximately 0.01 d^{-1} for an initial BDOC concentration of less than 1 mg/L and approximately 0.08 d^{-1} for an initial BDOC concentration of greater than 1 mg/L.

In laboratory-scale soil column experiments, oxic conditions are difficult to maintain under high BDOC levels in the feed water. As described in Section 3.1.1, the secondary treated effluent that was not purged with nitrogen did not maintain its oxic condition throughout the 1.2 m long soil column, C2, and a sequence of oxic, suboxic, and anoxic redox zones evolved. This study will only focus on four experiments with steady redox conditions throughout the soil column system for the calculation of first-order removal kinetics for selected CECs. These conditions are referred to as the following four bins: anoxic (high BDOC), suboxic (low BDOC), oxic (low BDOC), and NF suboxic (low BDOC). The derived first-order removal rates and DT_{50} values under these four conditions are summarized in Table 3.10.

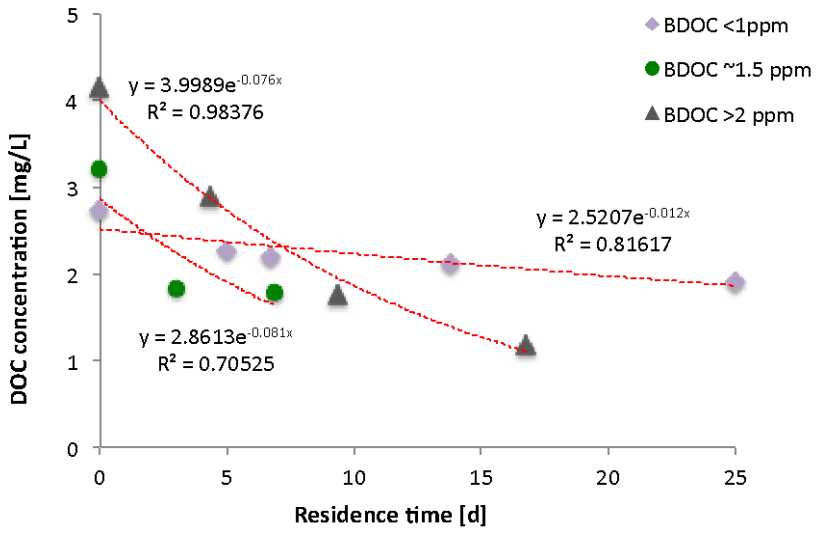


Figure 3.23. First-order removal rates for bulk organic carbon in soil column systems receiving different feed water quality.

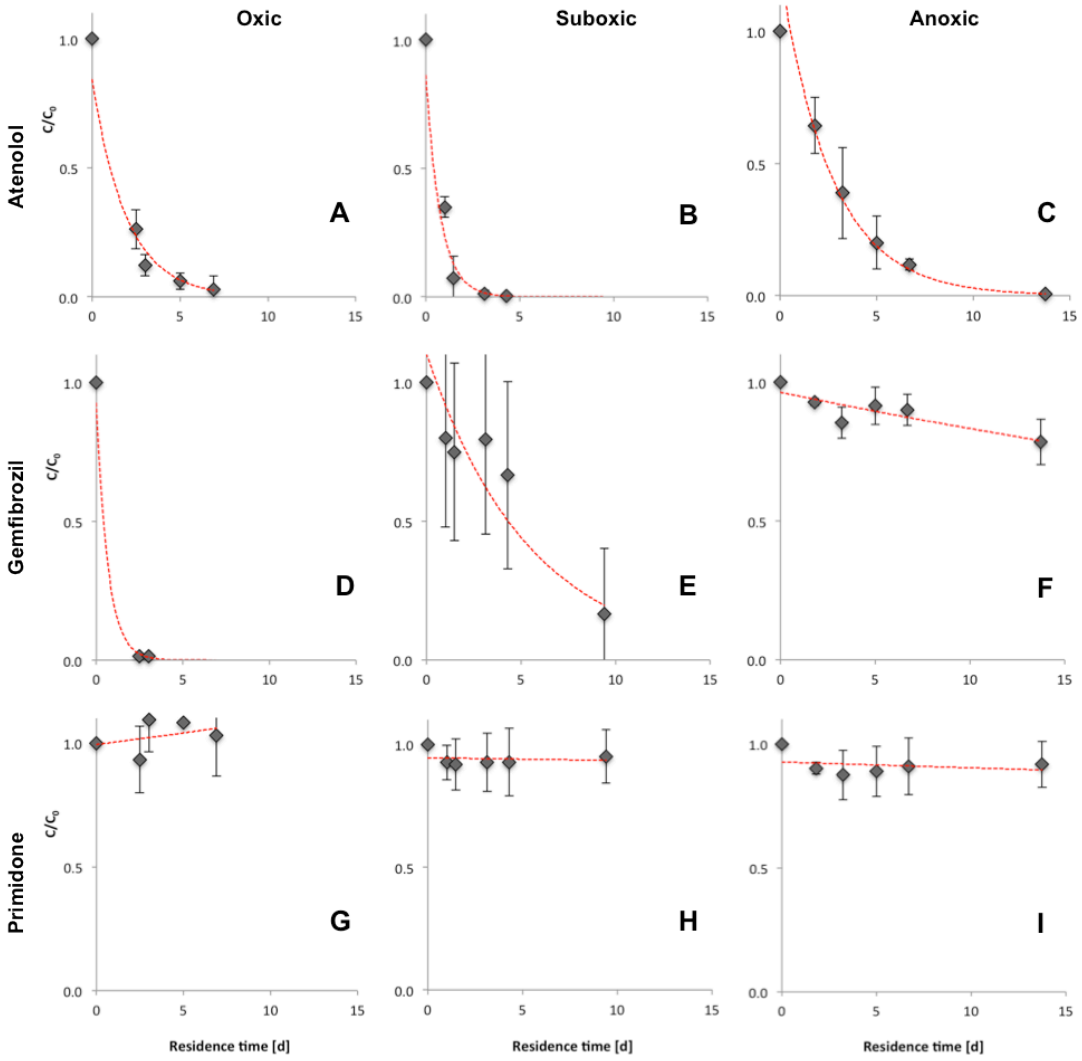


Figure 3.24. Fit of first-order kinetic to data sets of atenolol (A–C), gemfibrozil (D–F), and primidone (G–I) for three different redox conditions (oxic, suboxic, anoxic; n≥5 for each experimental data set).

The kinetic data for bins oxic, suboxic, and anoxic are used in the predictive contaminant transport model (STUMOD-MAR, Chapter 6). Experimental conditions are explained in detail in Section 2.5.1. The term DT_{50} describes the time required for 50% dissipation of initial compound concentration, as degradation cannot always be separated from other processes leading to compound attenuation under practical conditions (Beulke and Brown, 2001). A graphical example on how first-order kinetics were fit to the experimental data is given in Figure 3.24 for atenolol, gemfibrozil, and primidone under oxic, suboxic, and anoxic conditions (n≥5).

Table 3.10. First-Order Removal Rates and DT_{50} Values for Selected CECs Under Different Redox Conditions Based on Laboratory-Scale Soil Column Experiments

Redox Conditions^	Oxic			Suboxic			Anoxic			NF Suboxic		
	λ (d^{-1})*	R^2	DT_{50}	λ (d^{-1})	R^2	DT_{50}	λ (d^{-1})	R^2	DT_{50}	λ (d^{-1})	R^2	DT_{50}
Acesulfame	0.165	0.867	4.2	<0.001	1.000	>700	<0.001	1.000	>700	0.027	0.6926	25.4
Acetaminophen	0.360	0.780	1.9	0.402	0.963	1.7	0.486	0.937	1.4	0.231	0.8015	3.0
Atenolol	0.511	0.969	1.4	1.288	0.968	0.5	0.376	0.994	1.8	0.300	0.8015	2.3
Atrazine	0.010	0.755	73.0	0.014	0.659	48.8	0.007	0.874	103.4	<0.001	1.0000	>700
Caffeine	0.373	0.943	1.9	0.260	0.826	2.7	0.325	0.956	2.1	0.091	0.7549	7.6
Carbamazepine	<0.001	1.000	>700	0.020	0.764	35.2	0.007	0.657	106.6	<0.001	1.0000	>700
DEET	0.300	0.761	2.3	0.117	0.900	5.9	0.013	0.651	54.6	<0.001	1.0000	>700
Diclofenac	1.397	0.973	0.5	0.120	0.868	5.8	0.017	0.915	42.0	0.008	0.7264	92.4
Dilantin	0.051	0.736	13.6	0.012	0.729	56.3	0.019	0.828	37.3	0.003	0.7362	239.0
Fluoxetine	<0.001	1.000	>700	<0.001	1.000	>700	<0.001	1.000	>700	<0.001	1.000	>700
Gemfibrozil	1.490	0.973	0.5	0.183	0.900	3.8	0.015	0.764	47.5	0.011	0.7257	65.4
Iopromide	0.819	0.973	0.8	0.186	0.825	3.7	0.161	0.916	4.3	0.036	0.8572	19.0
Naproxen	1.443	0.973	0.5	0.166	0.899	4.2	0.082	0.876	8.5	0.009	0.7192	79.7
Primidone	<0.001	1.000	>700	<0.001	1.000	>700	<0.001	1.000	>700	<0.001	1.0000	>700
Sucralose	0.010	0.805	68.6	<0.001	1.000	>700	<0.001	1.000	>700	<0.001	1.0000	>700
Sulfamethoxazole	0.501	0.925	1.4	0.049	0.704	14.1	0.009	0.710	81.5	0.009	0.7395	80.6
TCEP	0.195	0.897	3.5	n.a.	n.a.	n.a.	<0.001	1.000	>700	<0.001	1.0000	>700
TCPP	0.177	0.780	3.9	0.044	0.758	15.9	0.011	0.731	64.8	<0.001	1.0000	>700
TDCP	0.124	0.632	5.6	0.039	0.996	17.8	0.006	1.000	121.6	0.027	0.7887	26.1
Trimethoprim	0.501	0.884	1.4	0.361	0.753	1.9	0.934	0.954	0.7	0.154	0.9006	4.5

Notes: ^Definition of redox conditions (experimental conditions): oxic=NH_4^+<0.5 mg/L, DOC<4 mg/L, BDOC<2 mg/L; suboxic=NH_4^+<1.5 mg/L, DOC 2–5 mg/L, BDOC 0.5–2 mg/L; anoxic=NH_4^+>1.5 mg/L, DOC 5–15 mg/L, BDOC 2–7 mg/L; NF suboxic=NH4+<1.5 mg/L, DOC<1 mg/L, BDOC<0.1 mg/L; *First-order decay=n≥5; soil column retention time 7–14 days (20 days for NF suboxic); soil properties: sand (93% sand, 2% silt, 5% clay); f_{OC}<0.5%;. DT_{50}=time required for 50% dissipation of initial concentration; DEET=N,N-Diethyl-meta-toluamide; TCEP=tris(2-carboxyethyl)phosphine; TCPP=tris(1-chloro-2-propyl)phosphate; TDCP=tris[2-chloro-1-(chloromethyl)ethyl]phosphate.

Chapter 4

Field Studies to Evaluate the Fate of Enteric Pathogen Survival in the Environmental Buffer

4.1. Enteric Pathogen Survival in the Environmental Buffer

A review of the literature on the survival of viruses in groundwater by John and Rose (2005) found that hepatitis A and the coliphage PRD-1 were the viruses with the slowest decay rates (Table 4.1). In updating data on the survival of enteric viruses in groundwater (Table 4.1), we found that it would appear that adenoviruses and coliphages ΦX-174 and PRD-1 are among the longest surviving viruses in groundwater (Tables 4.1 and 4.2). Inactivation rates of other viruses, coliform bacteria, and *Cryptosporidium parvum* appear to be higher.

Table 4.1. Survival of Microorganisms in Groundwater Versus Temperature

Organism	Temperature (°C)	Mean Inactivation Rate (log/day)	Inactivation Rate Range (log/day)
Poliovirus	0–10	0.02	0.005–0.05
	11–15	0.08	0.03–0.2
	16–20	0.1	0.03–0.2
	26–30	0.08	0.006–1.4
Hepatitis A virus	0–10	0.02	0–0.08
	20–30	0.04	0.009–0.1
Echovirus	11–15	0.1	0.05–0.2
	16–20	0.1	0.05–0.2
	21–25	0.2	0.06–0.6
Coxsackie virus	8–20	0.06	0.002–0.2
	25–30	0.1	0.007–0.3
Rotavirus*	3–15	0.4	one study
	23–2	0.03	one study
Adenovirus*	4	0.0076	one study
	12–22	0.028	0.01–0.047
Coliforms	0–10	0.07	0.03–0.4
	15–20	0.4	0.02–1.5
	21–37	0.3	0.007–2.5
*Cryptosporidium**	22	0.039	0.025–0.072

Source: Data from John and Rose (2009) and *this study.

Table 4.2. Biphasic Inactivation of Viruses in Groundwater (log/day)

Virus	Linear	First Phase	Second Phase
Adeno 2	0.010	0.489	0.002
Polio 3	0.073	0.143	0.019
Coxsackie B1	0.131	0.297	0.069
PRD-1	0.050	0.012	0.029
φX-174	0.050	0.086	0.047

Note: Temperature=12° C.

Source: Charles et al. (2005).

Bacteria have been found to survive significantly less in groundwater than viruses at MAR operations (Toze et al., 2010; Sidhu and Toze, 2012). In comparative studies, the die-off rate of *Salmonella* was 20 times that of rotavirus (Table 4.2). Usually, die-off rates of enteric bacteria in groundwater are 10 to more than 100 times greater than die-off rates of enteric viruses (Sidhu et al., 2010; Toze et al., 2010; Sidhu and Toze, 2012). *Cryptosporidium* survival is greater than that of enteric bacteria, but 5 to more than 10 times less than the survival rate of viruses (Table 4.1).

Considering that adenoviruses are generally the most abundant viruses in wastewater, it is probably best to use them to predict virus survival; however, because only a limited number of temperatures and groundwater types have ever been studied, it is difficult to select a general die-off constant for adenoviruses. At this time, it is recommended to select a die-off rate for adenoviruses closest to the groundwater temperature being studied.

4.2. Occurrence and Fate of Viruses During Full-Scale MAR

4.2.1. Field Monitoring Efforts

Upstream of the North Campus of the Prairie Waters Project in Brighton, secondary treated wastewater is discharged into the South Platte River and abstracted 18 miles downstream via an RBF well field located adjacent to the river. From the point of discharge, the wastewater takes approximately 18 to 20 h to reach the well field during low flow conditions in the river. During the sampling in fall 2012, there was little other water in the river except the effluent discharge. Adenoviruses and PMMoV were observed in the highest concentration in the discharged effluent (Table 4.3).

During travel down the river, the viruses decreased from 90 to 99% (1 to 2 log) on average. PMMoV has been detected in all of the RBF wells adjacent to the river and in the combined RBF water (the water from all operational producing wells is mixed), which is then conveyed to the subsequent ARR facility. Enteroviruses were detected in one of the RBF wells (PW-10) closest to the river (~5 days travel time) on one occasion (Well #1, Figure 2.1). This sample was tested for infectious viruses. The inoculated cell culture exhibited viral cytopathogenic effects (CPE). The cell culture exhibiting CPE was tested by PCR to identify the virus. The cell culture was positive for reoviruses, but negative for adenoviruses, enteroviruses, and aichiviruses.

Table 4.3. Occurrence of Viruses in Secondary Treated Wastewater, River Water, and RBF Wells (Including the Combined Collector for all Operational Wells) by qPCR at the Prairie Waters Project North Campus in Brighton

Sample Location	Date Collected	Adenovirus (copies/L)	Enterovirus (copies/L)	Aichivirus (copies/L)	Pepper Mild Mottle Virus (copies/L)	Travel Time (days)
Discharge at Metro plant	10/9/12	$3.22x10^5$	$5.42x10^3$	$1.23x10^4$	ND	-
	10/17/12	$1.83x10^5$	$3.19x10^3$	$1.05x10^4$	$5.84x10^5$	-
	10/30/12	$1.07x10^5$	$5.27x10^4$	$4.73x10^4$	$3.41x10^6$	-
South Plate River adjacent to well field	10/9/12	$1.82x10^3$	$6.89x10^2$	$3.51x10^3$	ND	-
	10/17/12	$9.56x10^4$	$3.35x10^1$	$2.81x10^3$	$2.06x10^5$	-
	10/30/12	$2.73x10^1$	$7.20x10^2$	$3.21x10^3$	$3.39x10^5$	-
	5/29/13	$8.59x10^2$	$2.52x10^2$	$2.44x10^4$	$1.75x10^5$	-
PW10	10/9/12	$<4.29*x10^0$	$5.00x10^1$	$<8.57x10^0$	$4.25x10^1$	~5
	10/17/12	$<4.29x10^0$	$<8.57x10^0$	$<8.57x10^0$	$3.91x10^2$	~5
	10/30/12	$<4.29x10^0$	$<8.57x10^0$	$<8.57x10^0$	$5.90x10^2$	~5
	5/29/13	$<6.00x10^0$	$<1.20x10^1$	$<1.20x10^1$	$3.56x10^1$	~5
PW11	10/30/12	$<5.25x10^0$	$<1.05x10^1$	$<1.05x10^1$	$8.55x10^2$	~5
PW18	5/29/13	$1.20x10^0$	$4.00x10^{-1}$	$4.00x10^{-1}$	$1.35x10^1$	>10
PW20	1/10/13	$<1.50x10^1$	$<3.00x10^1$	$<3.00x10^1$	$1.8x10^2$	>10
PW26	10/30/12	$<4.20x10^0$	$<8.40x10^0$	$<8.40x10^0$	$4.04x10^3$	>15
	1/10/13	$<9.00x10^0$	$<1.80x10^1$	$<1.80x10^1$	$<1.80x10^1$	>15
Combined 500*	1/10/13	$<1.20x10^1$	$<2.40x10^1$	$<2.40x10^1$	$<2.40x10^1$	5 to >15
Combined 1000*	1/10/13	$<6.00x10^0$	$<1.20x10^1$	$<1.20x10^1$	$<1.20x10^1$	5 to >15
Combined 400*	5/29/13	$<9.00x10^{-1}$	$<1.80x10^0$	$<1.80x10^0$	$1.02x10^2$	5 to >15

Notes: *=volume of water sampled in L; ND = not done.

Table 4.4 summarizes the results for the occurrence of viruses in the wastewater at the Tucson Water SWRF and the test basin of the Montebello Forebay Spreading Grounds. At the California site, only adenoviruses were detected at low concentrations of $1.2x10^2$ and $3.7x10^1$ genome copies per L (arithmetic mean: $7.8x10^1$) in the tertiary treated effluent used for recharge. The wastewater at this site receives the greatest amount of treatment prior to recharge compared to the sites in Colorado and Arizona, and this may explain the low numbers of virus in the samples collected. It could also be related to other factors such as incidence in the community of infections and seasonal differences. The PMMoV, which may have a potential use as a natural

tracer for virus transport and attenuation in the subsurface, was detected in monitoring Wells PR-9 and WP-Z at low concentrations but was not detected in PR-14 or PR-15. These results indicate that PMMoV was detected only in monitoring wells with relatively short travel times (PR-9=3 days and WP-Z=0.45 day) and not in those with longer subsurface travel times (PR-14=128.5 days and PR-15=49.5 days). The absence of PMMoV in the influent grab sample speaks to the high variability of the influent water quality as observed for geochemical parameters and CEC concentrations. Because the test basin is open to the public (including pet owners), the possibility of contributions of pathogens from other sources cannot be excluded.

At the Sweetwater Recharge site in Tucson, all the studied viruses were detected in the wastewater effluent in large concentrations (Table 4.4). Both aichiviruses and PMMoV were detected in one well with a 5 day travel time (MW-5). None of the viruses were detected in a well with a 14 day travel time (WR-069A). Unlike the other two sampling sites, attempts were made to sample the same effluent as it traveled from the basins to the monitoring well. The sampling was timed (synoptic sampling) so that the same body of water was sampled as it traveled through the subsurface. Samples showing the presence of any virus were assayed in cell culture; no infectious virus was detected in any of the samples from California or Arizona.

Table 4.4. Occurrence of Viruses in Wastewater and Wells by qPCR at the California and Arizona Sites

Sample Location	Adenovirus (copies/L)	Enterovirus (copies/L)	Aichivirus (copies/L)	Pepper Mild Mottle Virus (copies/L)	Travel Time (days)
Test Basin, Montebello Forebay, California					
Effluent	$8.07x10^{1}$	$<6.60x10^{1}$	$<6.60x10^{1}$	$<6.60x10^{1}$	-
Well WP-Z	$<6.50x10^{0}$	$<1.30x10^{1}$	$<1.30x10^{1}$	$7.59x10^{2}$	0.45
Well PR-9	$<6.90x10^{0}$	$<1.38x10^{1}$	$<1.38x10^{1}$	$2.10x10^{1}$	3.5
Well PR-15	$<6.30x10^{0}$	$<1.26x10^{1}$	$<1.26x10^{1}$	$<1.26x10^{1}$	44.5
Well PR-14	$<7.2x10^{0}$	$<1.44x10^{1}$	$<1.44x10^{1}$	$<1.44x10^{1}$	128.5
Sweetwater Recharge Site, Arizona					
Effluent	$9.37x10^{3}$	$3.46x10^{4}$	$4.76x10^{4}$	$5.15x10^{6}$	-
Well MW-5	$<8.40x10^{1}$	$<1.68x10^{2}$	$1.52x10^{4}$	$1.44x10^{6}$	5
Well WR-69A	$<3.56x10^{0}$	$<7.11x10^{0}$	$<7.11x10^{0}$	$<7.11x10^{0}$	~14

The relative amount of removal of the different viruses can be calculated for the different sites if virus was detected in the wastewater being recharged. This assumes that there is no other source of viruses in the vicinity of the facilities. Table 4.5 summarizes the degree of estimated removal of the different viruses at the three MAR sites in wells with different groundwater residence times. Determination of the degree of removal is limited by the concentration of the viruses in the wastewater being applied to the sites and the volume of concentrate assayed. It was usually easier to determine removal of PMMoV because it was usually present in the largest numbers in the reclaimed water. Aichiviruses and PMMoV were removed to a similar degree after a 5 day travel time at the Sweetwater Recharge site; however, the removal of aichiviruses exceeded 2.8 log after 14 days travel time, and PMMoV was removed by almost 5 log. Only the removal of adenoviruses could be detected at the San Gabriel Spreading Grounds test basin as it was the only virus detected in the recharged reclaimed water. It was reduced by at least 1 log in less than a day. It is interesting that PMMoV removal at the Colorado RBF site was almost identical for the three wells tested, in the 3 to 4 log range. At all of the sites, PMMoV appeared to be removed the least and could be considered as a conservative tracer of the enteric viruses studied.

Table 4.5. Log Removals of Viruses by Recharge at Three MAR Sites

Site/Well	Well Depth (ft)	Residence Time (days)	Adenovirus	Enterovirus	Aichivirus	Pepper Mild Mottle Virus
Arizona						
MW-5	30	5	>2.05	>2.31	0.50	0.55
WR-69A	152.2	~14	>3.42	>3.69	>3.83	>5.86
California						
WP-2	21.2	0.45	>1.09	ND	ND	ND
PR-9	35	3	>1.07	ND	ND	ND
15	40.5	49.5	>1.05	ND	ND	ND
14	70.5	128.5	>1.11	ND	ND	ND
Colorado						
PW-10*	30	~5	>2.63	1.15	>2.61	ND
1 (10/9/12)						
2 (10/17/12)			>4.35	ND	>3.07	2.72
3 (10/30/12)			>0.80	>2.70	>3.35	2.76
4 (5/29/13)			>2.16	ND	>3.31	3.69
PW11	29	~5	>0.72	>1.84	>2.49	2.60
PW26	24	>15	>0.81	>1.93	>2.58	1.92

Notes: *=this well was sampled on four different occasions; ND=not detected in reclaimed water.

4.2.2. Significant Findings and Relevance

- PMMoV appears to be a conservative indicator of human enteric virus removal during MAR. This is likely because of its occurrence in greater concentrations in wastewater than the human enteric viruses and perhaps longer survival and lower removal through soil. Absence of this virus suggests that human enteric viruses have been removed to below detection; however, the virus was also detectable in reclaimed water (secondary treated effluent) after passage through a 4.4 m long soil column (C3, ~16 days residence time) during laboratory-scale experiments simulating MAR.

- No human enteric viruses could be detected by qPCR after travel times of 10 days or greater at the three field sites. Enteric virus removal would generally appear to exceed 2 log during this time. A 5 day travel time resulted in a 2 to 3.7 log reduction of PMMoV.

- Reovirus was the only infectious virus detected in any of the groundwater wells. It was detected in RBF Well PW-10 at the Colorado site. This well had a 5 day travel time. It was also the only naturally occurring enteric virus found after travel through the 4.4 m long soil column C3 in a controlled laboratory-scale study. Reoviruses are among the most abundant and longest surviving viruses known in wastewater. They are also among the most common viruses detected in drinking water wells. Additional research on this virus would be useful to better define its removal by MAR.

- MS-2 virus removal was found to decrease with column length beyond 60 cm, supporting the hypothesis that virus removal rates decrease with travel distance. Thus, removal rate is not constant and cannot be described by a strict linear function. Pang (2009) described this type of removal as following a power law (or hyper-exponentially), with removal rates declining with greater travel distances. Removal rates are linear near the soil surface but then decline exponentially with time over distance traveled. No further significant removal of the virus occurred between 60 and 440 cm of travel through the soil column.

Chapter 5

Field Studies to Evaluate the Fate of Bulk Organic Carbon, Nitrogen, and CECs in the Environmental Buffer

5.1. Fate of TOC, CECs, and GR Activity During Full-Scale MAR

5.1.1. Case Study: San Gabriel Spreading Grounds

5.1.1.1. Bulk Parameters

Readings of field parameters (e.g., temperature, conductivity, pH, dissolved oxygen, standard redox potential E_0, water level) for all sampled wells and the test basin are summarized in Tables A.2a and A.2b (Appendix). The temperature of the reclaimed water in the test basin during the sampling campaign was on average 24.5° C (campaign #1) and 24.9° C (campaign #2). Temperature readings for all subsurface sampling locations except PR-15 and PR-14 were in the range of 23.0 to 24.9° C and 22.6 to 25.7° C, suggesting that most of the water present in monitoring wells was reclaimed water. In 2009, the background temperature of groundwater in the vicinity of the test basin (Well PR-10) prior to filling of the test basin was determined to be approximately 7° C lower than the receiving reclaimed water (Laws et al., 2011).

As PR-15 (travel time 49.5 days) and PR-14 (travel time 128.5 days) were not part of the synoptic sampling in December 2012, higher temperature readings at these wells might relate to higher influent water temperatures during previous recharge/wetting operations. The temperature reading of PR-14 (24.3° C) within the synoptic sampling in April 2013 was in the range of the influent water temperature about 130 days earlier, supporting the general applicability of the chosen synoptic sampling approach. Based on a comparison of chloride and sulfate concentrations (Figure 5.1), it appears that within each sampling campaign all of the groundwater samples beneath and downstream of the test basin originated from recharged reclaimed water. Nevertheless, daily differences in the influent water composition became obvious. In accordance, the sample collected at Well PR-14 during campaign #2 fits the chloride and sulfate ion signature of campaign #1.

Furthermore, analysis and comparison of the major cations (Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-}) have been used to determine if the samples collected beneath the test basin resulted from the same slug of infiltrating reclaimed water. As shown in Figure 5.2 for samples collected on December 10, 2012, the chemical matrix of the test basin influent matches the ion signature of sampling location WP-Z (travel time <0.5 day), although the NO_3^{-} concentration is slightly higher in the groundwater sample.

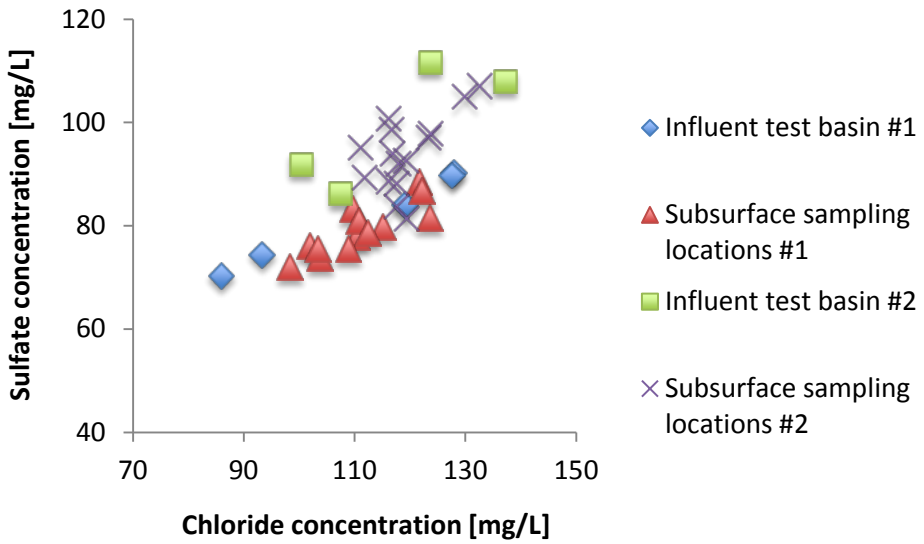


Figure 5.1. Comparison of sulfate and chloride concentrations in the test basin and groundwater monitoring wells during sampling campaigns #1 (December 2012) and #2 (April 2013).

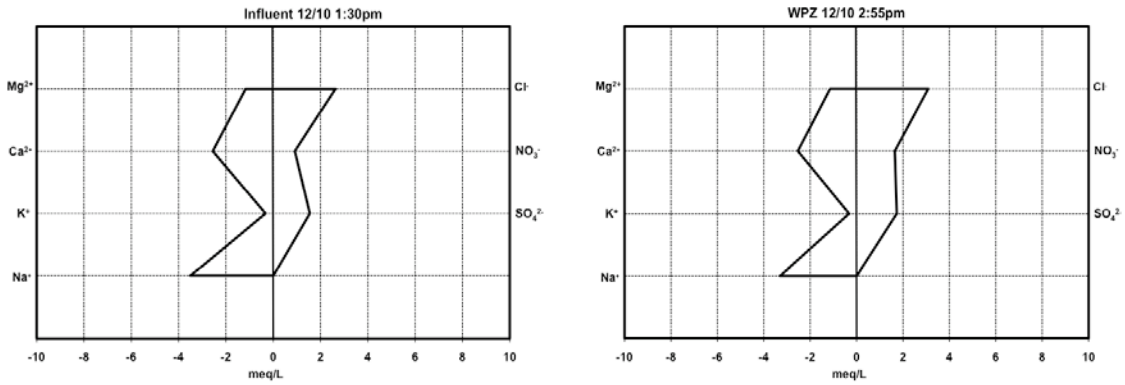


Figure 5.2. Stiff diagrams displaying chemical matrix of the test basin influent sample and subsurface sampling location WP-Z on December 10, 2012.

The geochemical composition of the receiving reclaimed water changed during both sampling campaigns as shown in the Stiff diagrams for selected influent samples (Figure 5.3). This might speak to a different blending of the tertiary treated effluent received by the test basin during the filling/recharge events. The highly variable influent water quality in terms of CECs and bulk parameter during both sampling campaigns was irrespective of daytime or weekday and complicated the interpretation of data obtained during the synoptic sampling as discussed in the SAT performance assessment section for CEC removal. It is noteworthy that the variability in quality was not due to variable treatment performance because operations staff confirmed that the reclamation plants providing the reclaimed water were working properly.

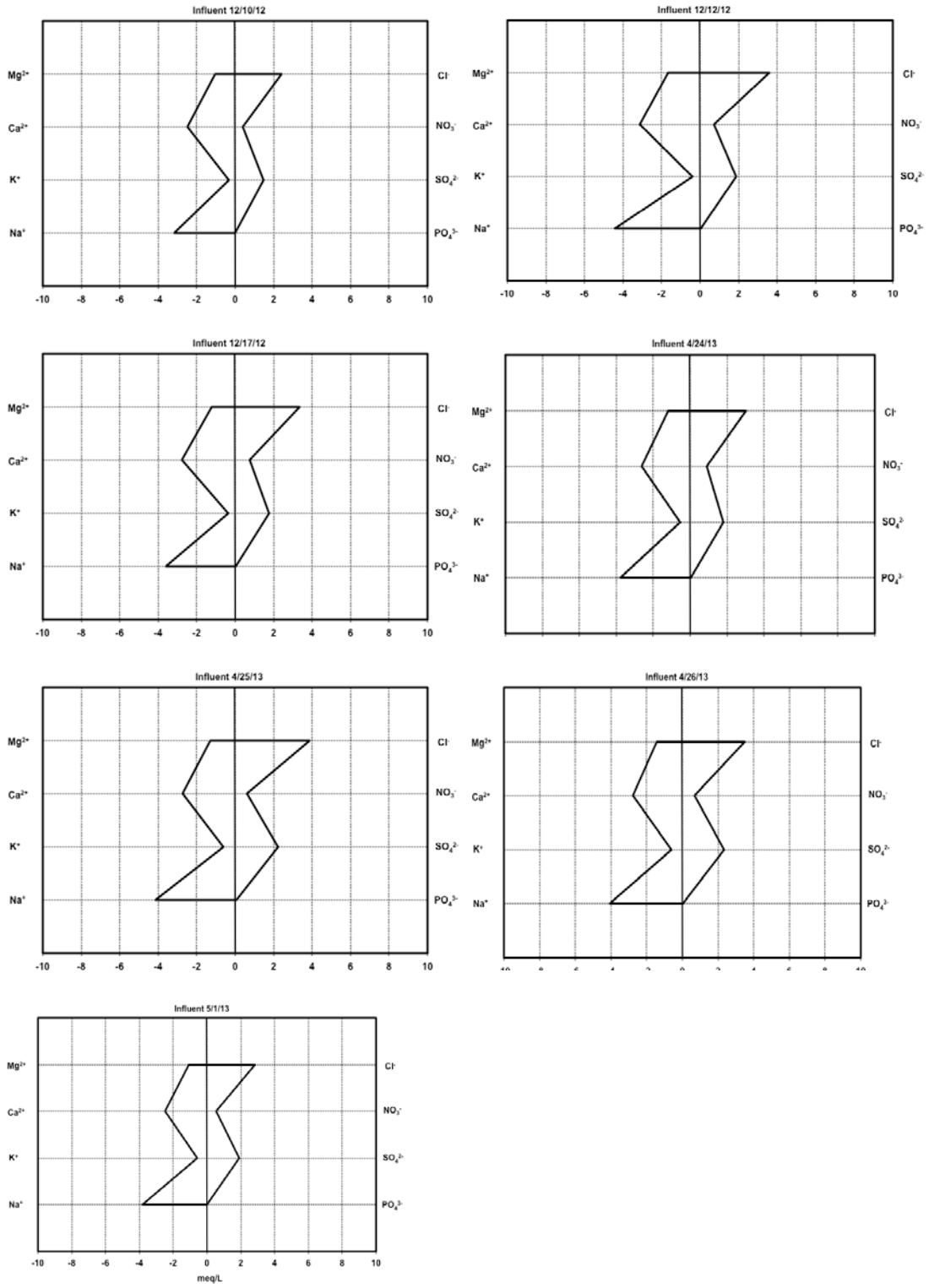


Figure 5.3. Stiff diagrams displaying chemical matrix of the test basin influent samples during sampling campaigns #1 and #2.

Note: X-axis represents meq/L.

During this study, nitrate concentrations in the aquifer were in general higher than nitrate levels in the nitrified–denitrified tertiary treated effluent applied to the basin (on average 4 mg/L N-NO_3). Even in the lower aquifer (PR-8 and PR-10), nitrate levels as N-NO_3 were 7.2 and 8 mg/L (campaign #1) and 9.5 and 8.6 mg/L (campaign #2). Although the test basin influent nitrate concentrations during both sampling campaigns are similar to those reported by Anders et al. (2004) and Laws et al. (2011), nitrate levels (organic and inorganic) in the lower aquifer exhibited higher concentrations compared to these previous studies. A fast movement of nitrate through the upper aquifer occurs during the recharge process. This is followed by more stagnant conditions in the aquifer and increased nitrate levels at greater depth after the filling of the test basin stops (Schroeder, 2003).

As the reclaimed water spills into the test basin during recharge operation, the infiltrate is rich in dissolved oxygen (~6–7 mg/L). Most of the oxygen is consumed within the vadose zone (<2.4 m), and dissolved oxygen concentrations drop to less than 1 mg/L after approximately 0.5 day of subsurface travel time in December 2012 and approximately 2 days of subsurface travel in April 2013. This indicates oxic to slightly suboxic redox conditions in the upper aquifer followed by anoxic redox conditions (e.g., release of manganese in PR-8 and PR-10) in the lower aquifer. Nitrate levels greater than 1 mg/L are typically sufficient to maintain anoxic conditions in the subsurface and prevent the aquifer from becoming anaerobic (Asano et al., 2006). The sulfate levels facilitate this assumption as concentrations remained relatively stable in the subsurface (Figure 5.1).

As the biodegradable portion of DOC is already consumed in the upper aquifer, as illustrated in Figure 5.4, not enough carbon is left for the denitrification of the remaining nitrate to N_2. This might result in a slight accumulation of nitrate in the lower aquifer; however, based on water quality monitoring data collected by WRD, no elevated nitrate concentrations were measured at production wells downstream of the site.

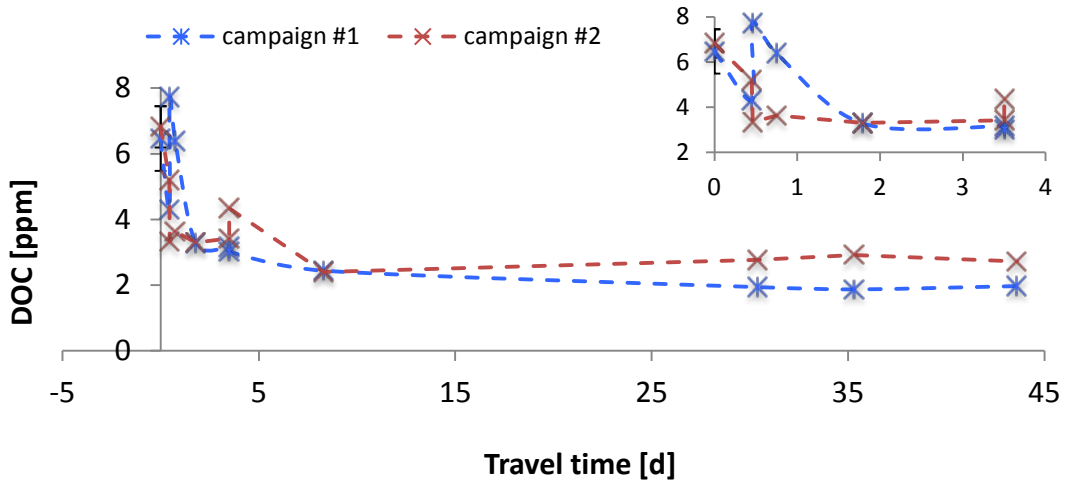


Figure 5.4. DOC removal in the subsurface during SAT using tertiary treated effluent (n≥4) at the Montebello Forebay Spreading Facility Test Basin.

Note: Details for shorter travel times shown in the upper right.

Influent DOC concentrations (6.46±0.98 mg/L and 6.82±0.63 mg/L) varied over time as reported in Tables A.2a and A.2b (Appendix). DOC results for all sampled wells are displayed in Figure 5.4. The presence of aerobic conditions in the vadose zone is favorable for the consumption of easily assimilable organic carbon. The DOC decreased below 2 mg/L in monitoring Wells PR-13, PR-8, and PR-10, with estimated travel times of 30, 35, and 44 days (Figure 5.4) during campaign #1 and below 2.9 mg/L during campaign #2. Approximately 50 to 51% and 62 to 65% of DOC was removed in the upper aquifer (travel times <4 and <9 days) during both campaigns, whereas overall removal with an increased travel time (>30 days) in the lower aquifer was up to 71%. The observed DOC spike after a travel time of 0.5 day during campaign #1 is most likely due to the variability in DOC influent concentrations as discussed earlier.

The proportion of BDOC in the upper aquifer is approximately 4 mg/L. The BDOC is considered to represent the portion of the DOC that can be mineralized by indigenous heterotrophic microorganisms. It is an operationally defined parameter that depends upon the underlying protocol of measurement and experimental conditions as described in the Independent Advisory Panel Final Report on BDOC as a performance measure by the National Water Research Institute (NWRI, 2012). In general, the BDOC value corresponds to the difference between the initial DOC and the minimum final concentration reached in a defined period, usually after an incubation or retention time of 30 days.

During this study, a subsurface travel time of about 8 days (PR-19) in the upper aquifer was sufficient to remove the biodegradable portion of the DOC. The first-order rate constant for BDOC disappearance was in the range of 0.11 d^{-1} (R^2=0.78). No significant difference in BDOC removal was observed between the campaigns. As the DOC level did not drop further in the lower aquifer, as indicated by the UV_{254nm} value of Well PR-14 (7.62 m^{-1} and 7.16 m^{-1}, travel time 129 days), the remaining organic carbon (1.9 and 1.8 mg/L) is likely composed of recalcitrant carbon fractions. The high DOC value obtained for Well WP-Z during the first sampling event in December 2012 might be related to released organic material deposited on the well screen and has been excluded from further considerations.

The overall results for DOC removal are similar to those observed by Laws et al. (2011) for the same field site and other studies cited therein. In agreement with those findings, no measurable BDOC was detected in the lower aquifer (travel times >30 days), indicating that the SAT system at the San Gabriel Spreading Grounds is functioning properly regarding removal of bulk organic matter.

5.1.1.2. Performance Assessment of SAT Operation—CECs

Similar to DOC, the data of both campaigns imply that attenuation of CECs main occurs during infiltration through the vadose zone and within the first 3 to 4 days in the aquifer. More easily biodegradable CECs, such as atenolol, caffeine, and gemfibrozil, are in the range of or below their respective detection limits after less than 4 days travel time. More hydrophobic compounds such as fluoxetine and diphenhydramine immediately sorb to the soil during infiltration and were not detected above their respective detection limits in any groundwater samples. Fluoxetine, an antidepressant drug, is poorly biodegradable and mobile in subsurface environments (Monteiro and Boxall, 2010). The significant attenuation of the flame retardants TCPP and TDCP within the first few meters of infiltration is most probably due to sorption effects to soil organic matter or clay materials. Anders et al. (2004) reported the accumulation of a thin layer of fine-grained, organic-rich sediment on the recharge test basin floor based on core material. Furthermore, a significant amount of fine-grained material (e.g., silt and clay) is present to a depth of about 0.7

to 1 m below surface. As both flame retardants have poor biodegradability, they are not further attenuated in the aquifer. Averaged concentrations for each sampling campaign (samples collected and analyzed in triplicate/duplicate for each sampling location) in ng/L and the respective standard deviations of 19 analyzed CECs are summarized in Tables A.3a and A.3b (see Appendix).

CEC concentrations in the influent of the test basin showed high fluctuations over time. Though high concentration variations in reclaimed water containing hospital effluents are known for X-ray contrast agents such as iopromide (no to little application on weekends), variations for some of the target analytes (e.g., acesulfame, sulfamethoxazole, gemfibrozil) were more significant than expected. Such variations in the source water quality have implications for the assessment of how changes in retention time or redox zone affect the degree of CEC removal achieved during SAT. The degree of CEC variability in the reclaimed water feeding the test basin was unexpected; however, as noted earlier, the variability was not caused by a variable performance of the upstream water reclamation facilities.

With the exception of summer 2009, as determined by Laws et al. (2011), dilution of recharged reclaimed water with native groundwater is negligible for all sampled wells. Laws et al. (2011) calculated a dilution of reclaimed water with native groundwater of approximately 40% based on primidone concentrations and temperature measurements. Concentrations of the conservative organic tracer primidone slightly increased from 181±24 ng/L (n=17) in the influent to 208±17 ng/L (n=5) at Well PR-11 (4 days travel time) and 187±12 ng/L (n=5) at Well PR-10 (44 days travel time). Results for carbamazepine, another compound with poor removal in natural subsurface systems, also imply negligible dilution (Tables A.3a and A.3b).

On the basis of the chloride measurements during recharge experiments, Schroeder (2003) calculated that the displacement of pre-existing water is completed within 2 days at the 5, 10, and 15 ft multilevel sampling ports underneath the test basin and within 3 to 4 days at a depth of 25 ft (PR-9 and PR-11). The observation that displacement of pre-existing water is rapid and nearly complete was confirmed by hydrogen and oxygen isotope ratios during their study (Schroeder, 2003); however, the dilution factor will likely increase during winter when stormwater and local runoff are expected at the recharge site. Furthermore, we found an indication that certain well screens (e.g., MLS-9, MLS-10) seem to have an impeded exchange with the surrounding groundwater and pull older water than implied by the estimated travel time or infiltration depth. For instance, all of the easily biodegradable compounds such as atenolol and trimethoprim are removed to below the detection limit
(10 ng/L) after less than 0.5 day of travel time while they are still present in low concentrations in wells with slightly longer travel times (MLS-14, travel time 0.75 day).

High variability in CEC concentration (e.g., DEET, dilantin, sulfamethoxazole, gemfibrozil, iopromide, sucralose) has been observed for wells with short travel times (<2 days) when samples have been collected on consecutive days. The differences in well travel times achieved by measurements and estimates during different studies at the test basin as indicated in Table 2.1 further complicated data interpretation.

The observed removal percentages of easily and intermediately biodegradable CECs for three different wells with travel times in the range of less than 0.5 day to more than 30 days is illustrated in Figure 5.5. No removal has been observed for the recalcitrant wastewater tracers primidone and carbamazepine. High concentrations of the insect repellent DEET in samples from Well PR-13 during campaign #1 indicated a contamination with this compound during the sampling process and led to an exclusion of these samples in terms of DEET removal calculation.

Results for sulfamethoxazole indicate a significant increase in concentration in the lower aquifer. This compound is known to be difficult to remove during SAT, and the formation of sulfamethoxazole reversible transformation products (e.g., 4-nitro-sulfamethoxazole) in aquifers under denitrifying conditions in controlled batch experiments has been reported by Barbieri et al. (2012) and might explain the increase in concentration. To support this assumption, the identification or quantitative analysis of transformation products will be necessary during future monitoring efforts.

None of the glucocorticoids was detected in the analyzed test basin influent sample analyzed during sampling campaign #2.

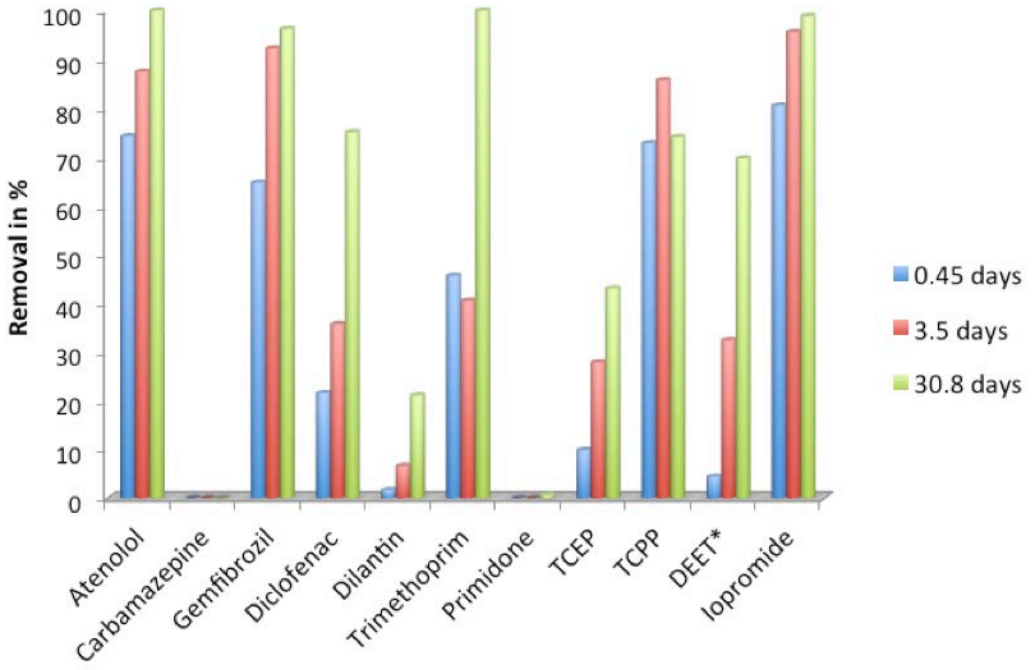


Figure 5.5. Average removal percentage of selected easy, intermediate, and recalcitrant biodegradable indicator compounds during SAT using tertiary treated effluent (n=17) based on subsurface travel times of 0.45 day (WP-Z, n=10), 3.5 days (PR-9, n=5), and 30.8 days (PR-13, n=5).

Note: *The green bar for DEET represents removal after 35.3 days (PR-8, n=5).

5.1.2. Case Study: Prairie Water Project, Aurora Water

5.1.2.1. Bulk Parameters

Readings of field parameters (e.g., temperature, conductivity, pH, dissolved oxygen) for all sampled wells at the RBF and ARR sites as well as the infiltration basins are summarized in Table A.4 (Appendix). The pH in all cases was neutral, and conductivity varied between 1077 and 1161 µS/cm at the ARR site and 988 and 1123 µS/cm at the RBF site. Groundwater temperature readings at the ARR site were in the range of 16.5 to 18.5° C. Both temperature and conductivity readings at groundwater wells located inside the slurry wall differed significantly from readings obtained at the background monitoring Well MW-20 outside the slurry wall (13.6° C and 1394 µS/cm).

The achieved DOC removal at the Prairie Waters Project site is on average more than 50% (Figure 5.6), from about 6 mg/L DOC in the South Platte River to less than 3 mg/L DOC in the water extracted from the RBF well field. A further drop in DOC of about 1 mg/L is achieved during infiltration of RBF water at the subsequent ARR facility (MW-25A, MW-28A). Overall, the RBF well field and ARR facility provided a stable water quality regarding DOC contents during the assessment. On the basis of previous investigations, the travel time between South Platte River and RBF Well 10A is estimated to be about 5 days. The retention time has been estimated to be 2 days in MW-25A and 5 days for MW-28A based on organic wastewater tracers (e.g., carbamazepine, primidone).

The large reduction of DOC during RBF coincides with dissolution of manganese, indicating a shift of redox conditions from oxic to anoxic during soil passage. After infiltration in the ARR basins, dissolved manganese is reduced by more than an order of magnitude through reoxygenation, suggesting that the ARR maintains oxic conditions throughout its infiltration depths (Figure 5.7). Based on these results, BDOC in the RBF is approximately 2.8 mg/L, and the redox condition is anoxic, whereas BDOC in the ARR is approximately 0.4 mg/L, and the redox condition is oxic.

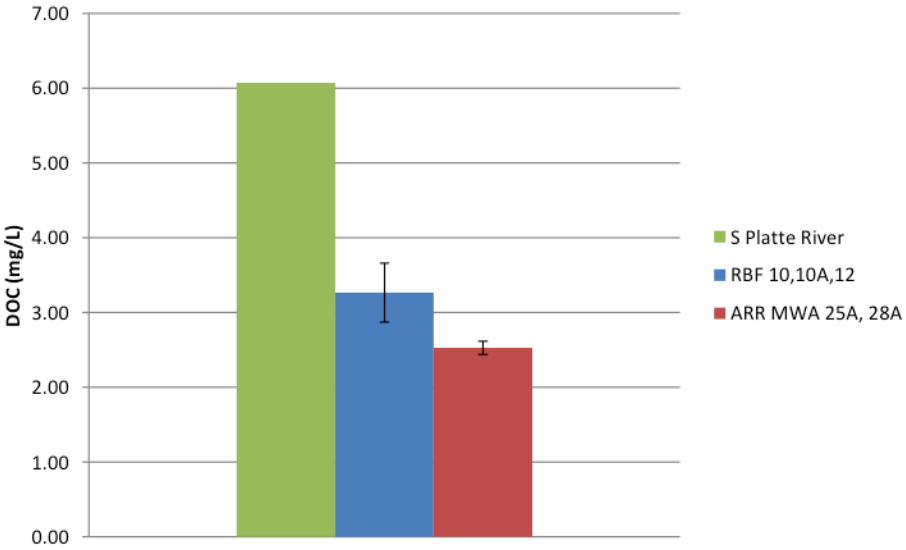


Figure 5.6. DOC concentrations in mg/L measured in the South Platte River, RBF production wells 10, 10A, and 12, and in ARR monitoring Wells MW-25A and 28A.

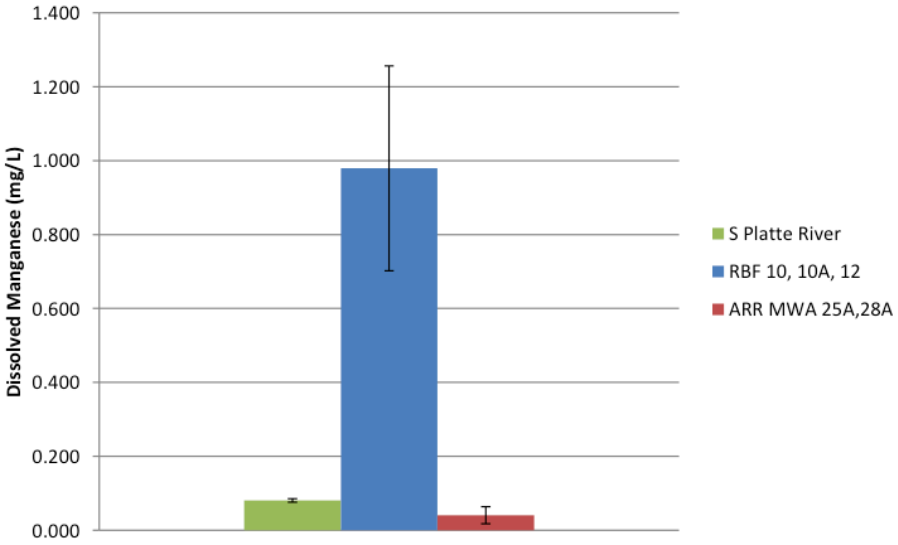


Figure 5.7. Dissolved manganese (Mn^{2+}) in mg/L as measured in the South Platte River, RBF production Wells 10, 10A, and 12, and in ARR monitoring Wells MW-25A and 28A.

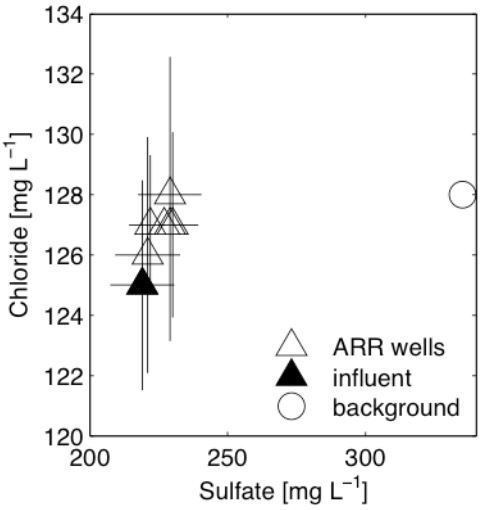


Figure 5.8. Ratio of chloride to sulfate used to demonstrate that the water inside the ARR is similar to the influent in comparison with the background.

The DOC concentration in the background monitoring Well MW-20 outside the ARR slurry wall was less than 2 mg/L. Nitrate concentration in the background well was elevated (4.9 mg/L N-NO_3) compared to the ARR wells (Table A.5, Appendix) because of agricultural land use in the environs of the ARR site. In general, nitrate dropped from 3.3 mg/L N-NO_3 in the recharged water to less than 2.8 mg/L N-NO_3 in the monitored ARR wells. Based on a comparison of the major cations (Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, NO^{3-}, SO_4^{2-}, PO_4^{3-}), it appeared that all of the groundwater samples collected at the ARR site originated from recharged reclaimed water, indicated by the clustering of data points with geochemical signature similar to the input water and different from the MW-20 water representative of the native groundwater. As indicated for chloride/sulfate concentrations in Figure 5.8, the ion signature of the native groundwater differed significantly from the recharged reclaimed water.

5.1.2.2. Performance Assessment of RBF and ARR Operation—CECs

The findings of the RBF performance assessment are shown in Table 5.1, summarizing the removal efficiencies for CECs of RBF Well 10A between 2009 and 2012. Based on previous investigations, the travel time between South Platte River and RBF Well 10A is estimated to be about 5 days. In general, the RBF performance regarding CEC removal improved significantly since start-up of the facility for CECs with intermediate removal classification (e.g., DEET, diclofenac, dilantin, TCPP).

Table 5.1. CEC Removal Efficiency (in %) of Well 10A at the RBF Well Field Between 2009 and 2012

	Removal Efficiency RBF (10A) in [%]		
CEC	**2009**	**2010**	**2012**
Atenolol	95	76	100
Atrazine	34	0	17
Caffeine	95	85	97
Carbamazepine	20	0	23
DEET	19	28	27
Diclofenac	26	21	51
Dilantin	1	5	20
Gemfibrozil	55	39	71
Meprobamate	5	3	14
Naproxen	86	90	89
Primidone	7	0	11
Sulfamethoxazole	46	0	37
TCEP	9	15	31
TCPP	22	12	39
Trimethoprim	95	86	97

Notes: DEET=N,N-Diethyl-meta-toluamide; RBF=riverbank filtration; TCEP=tris(2-carboxyethyl)phosphine; TCPP=tris(1-chloro-2-propyl)phosphate.

Geochemical measurements of bulk parameters and CECs along various ARR transects were used to estimate flow paths and travel times and assess the performance of the ARR site regarding water quality and quantity. The water quantity results imply that the water recovery of at least one basin located in the northeast is limited by the heterogeneous subsurface conditions at this field site. We identified three wells abstracting water (>50%) that does not originate from the infiltration basins based on water ion signatures and concentrations of conservative CECs. These wells have been excluded from the water quality assessment.

In general, significant water quality improvements are achieved within short travel times (<5 days) at this ARR site receiving RBF water for infiltration. As illustrated in Figure 5.9, indicator CECs representative of intermediate removal in natural treatment systems are completely removed (e.g., diclofenac) or significantly decreased (e.g., dilantin, meprobamate, sulfamethoxazole) during ARR following RBF. More easily biodegradable CECs such as gemfibrozil and naproxen are still present in RBF water but are completely removed after ARR treatment.

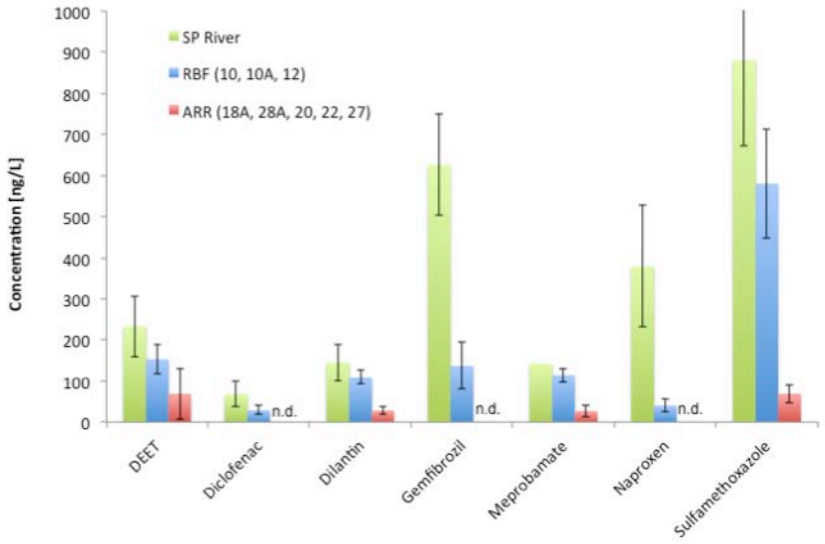


Figure 5.9. Average CEC concentrations determined in South Platte River water (n=4), RBF water (n=5; Wells 10, 10A, 12), and ARR filtered water (n=12; Wells 18A, 28A, 20, 22, 27) during fall 2012.

Note: n.d.=not detected

Refractory CECs such as the antiepileptic drugs carbamazepine and primidone are useful indicators because their persistence in subsurface systems can be used to estimate dilution. On average, the conservative organic tracers carbamazepine and primidone were reduced by less than 10% in RBF Wells 10, 10A, and 12. Presence of these compounds within the subsurface suggests that changes in concentration of less refractory compounds are not due to dilution but instead are a result of removal processes; however, the degree of dilution with native groundwater varied among the ARR wells.

Carbamazepine and primidone are excellent indicators for reclaimed water and were not present above their detection limits in native groundwater as verified in samples from background Well MW-20 outside the slurry wall. For primidone, sorption processes are negligible. For carbamazepine, minor attenuation due to soil sorption cannot be excluded (Scheytt et al., 2005). Normalized concentrations of both conservative CECs suggested dilution processes of less than 10% (Wells MW-25A, 28A) and less than 20% (Wells RW-22, MW-17A) at the Central Basin transect (Transect II, Figure 5.10). At the Southwest Basin transect (Transect I, Figure 5.11), dilution was calculated to be less than 25% (Well RW-1) and less than 15% (RW-2). Travel time for this well is approximately 2 weeks based on temperature and conductivity readings during infiltration experiments carried out in fall 2013. For Well MW-27A, dilution was considered to be less than 10% based on carbamazepine concentration (primidone was not available). The attenuation of CECs at both transects exceeded the observed decrease in carbamazepine and primidone based on dilution alone.

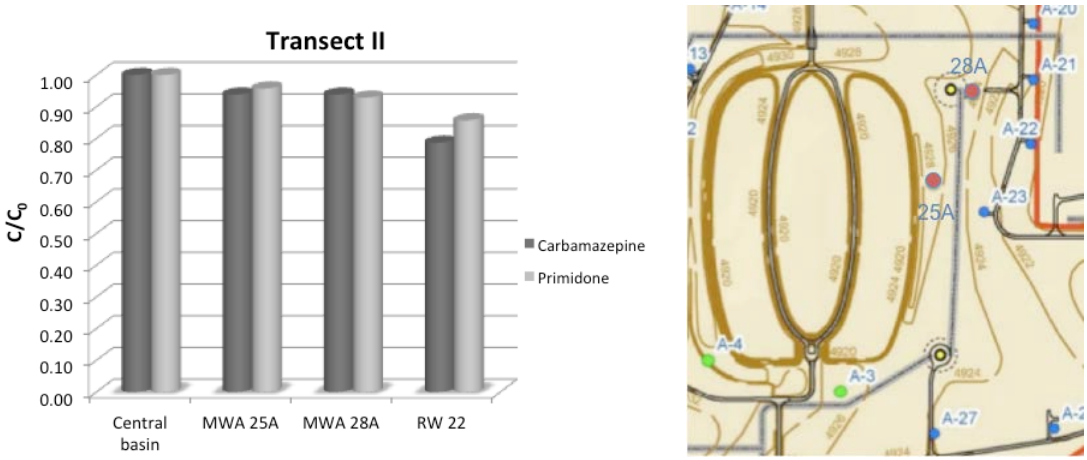


Figure 5.10. Normalized CEC tracer (carbamazepine, primidone) concentrations (n=4) along Transect II (e.g., infiltration basin and Wells 25A, 28A, 22) at the ARR field site.

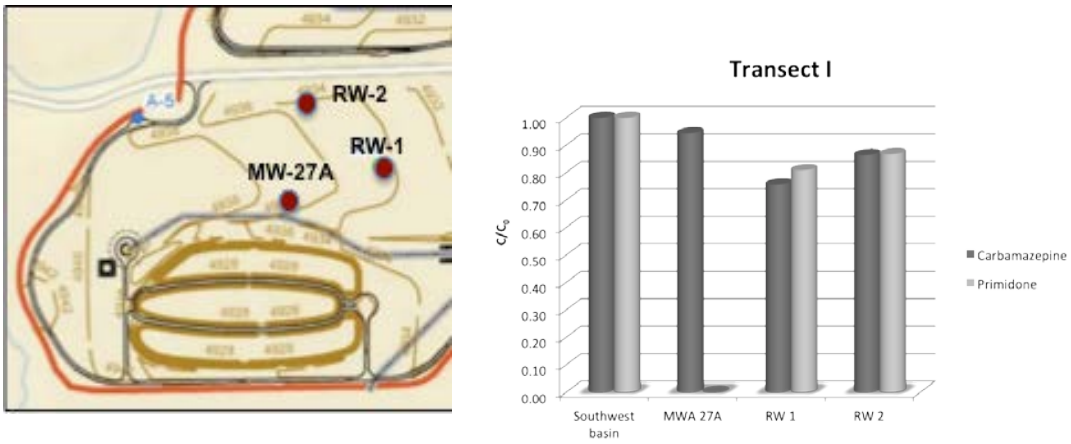


Figure 5.11. Normalized CEC tracer (carbamazepine, primidone) concentrations (n=4) along Transect I (e.g., infiltration basin and Wells 27A, 1, 2) at the ARR field site.

Removal between the river and RBF Wells 10, 10A, and 12 (2.8 mg/L BDOC/anoxic) was nearly 80% for gemfibrozil and just below 90% for naproxen (Figure 5.9). Removal of DEET was less than 45% during RBF and showed considerable variation in removal effectiveness. DEET removal ranged between 70 and 80% for all analyzed ARR wells but exhibited a high variability during different samplings; the compound was also present in the background groundwater. Sulfamethoxazole and diclofenac exhibited less than 25% removal during RBF. Removal efficiencies for sulfamethoxazole at the ARR site were in the range of 75% (MW-17A) to 94% (RW-2).

Between the RBF combined filtrate (ARR basin influent) and the closest monitoring wells, MW-25A and MW-28A (estimated travel time 2 and 5 days, respectively, and 0.4 mg/L BDOC/oxic), gemfibrozil and naproxen were consistently removed to below the detection limit. Diclofenac was present at low levels (<100 ng/L) in the river and poorly removed in RBF Wells 10, 10A, and 12. The RBF combined collector, which feeds the ARR and is diluted with native groundwater, contained approximately 20 ng/L diclofenac. The compound was not detected in

any ARR monitoring or production wells, but removal may have been due to photolysis, as diclofenac was not detected in a sample taken from the infiltration basin at the end farthest from the influent weirs (data not shown). Photolysis of diclofenac is well documented (Buser et al., 1998). Furthermore, diclofenac showed negligible sorption to the field soil or clay in batch sorption experiments.

Sulfamethoxazole was removed substantially better under low BDOC/oxic ARR conditions, being more than 80% removed compared to less than 25% on average during RBF characterized by high BDOC/anoxic conditions. This removal confirms reports that sulfamethoxazole is removed most effectively under oxic conditions (Wiese et al., 2011; Baumgarten et al., 2011) as well as the findings of the laboratory-scale soil column experiments.

DEET removal during ARR was highly variable and not significantly different than during RBF, although the variation shows that in some cases it was removed better during ARR. The attenuation of CECs at Transects I and II exceeded by far the observed decrease in carbamazepine and primidone based on dilution alone, as illustrated in Figure 5.12.

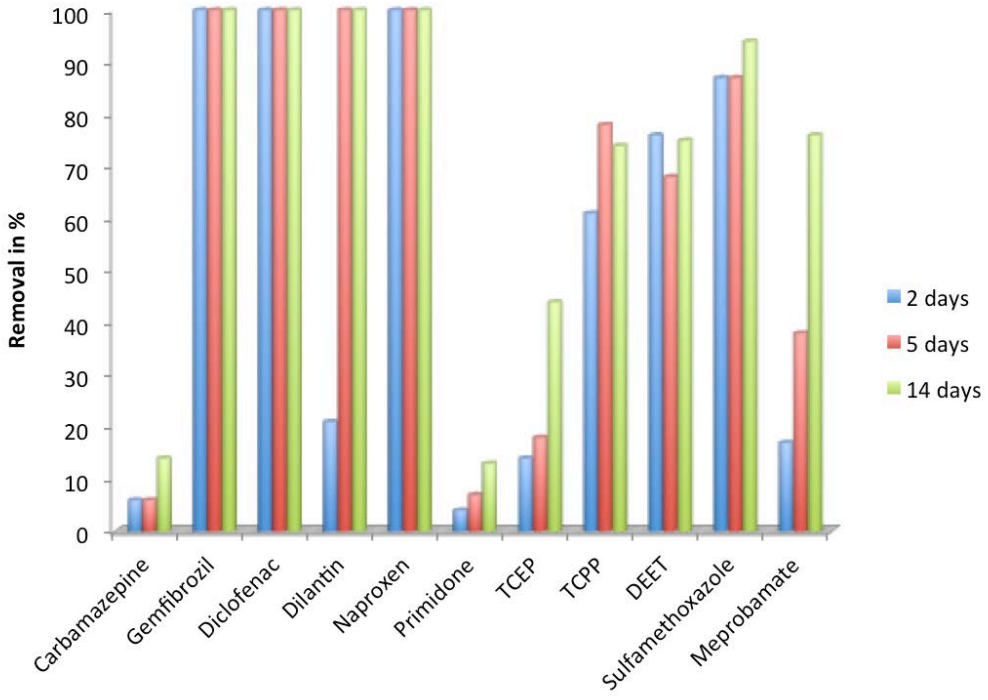


Figure 5.12. Average removal percentage of selected easy, intermediate, and recalcitrant biodegradable indicator compounds during surface spreading via ARR applying RBF (n=4) based on subsurface travel times of 2 days (MW-25A, n=4), 5 days (MW-28A, n=4), and 14 days (RW-2, n=3).

Diclofenac, gemfibrozil, and naproxen are immediately attenuated after infiltration at the ARR facility. The intermediate biodegradable compound dilantin exhibited a removal of 21% at monitoring Well MW-25A but was attenuated below detection limit in wells that are further away from the infiltration basins. The estimated travel times are about 2 days for MW-25A, 5 days for MW-28A, and 14 days for RW-2. The significant attenuation of the flame retardants TCEP and TCPP at the ARR site within short residence times (Figure 5.12) is most probably due to sorption effects to soil organic matter or clay materials, as all three flame retardants are characterized by poor biodegradability. Similar results have been observed in the laboratory batch sorption experiments using soil with different clay percentages from this field site as well as pure montmorillonite clay (bentonite). Furthermore, none of the glucocorticoids was detected in the analyzed South Platte River water sample collected in July 2013.

5.1.3. Case Study: Sweetwater Recharge Facility, Tucson Water

5.1.3.1. Bulk Parameters

Field readings and bulk parameters for all sampling locations are summarized in Tables A.7 and A.8 (Appendix). Based on a comparison of chloride and sulfate concentrations, it appears that the groundwater sample beneath the infiltration basin (MW-5) originated from recharged reclaimed water, whereas a significant impact from native groundwater is evident for the monitoring Well WR-069B sample (Figure 5.13). No significant differences in the geochemical influent water composition became obvious during the sampling on February 21, 2013. Influent water samples were collected at 8 am, 12 pm, and 4 pm. Analysis and comparison of the major cations (Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-}) have been used to determine if the samples collected beneath and downstream of the test basin resulted from the same slug of infiltrating reclaimed water.

As shown in Figure 5.14, the chemical matrix of the infiltration basin influent matches the ion signature of piezometer MW-5 (travel time ~5 days), which is located in the southeast corner of the infiltration basin. The geochemical composition of the WR-069B sample is influenced by dilution with native groundwater as well as an extended vadose zone of 120 ft at the well location (influence on nitrate concentration) and does not match closely with the recharged reclaimed water signature. Influent DOC concentrations were high and varied slightly during the day (16.16±0.44 mg/L). Approximately 52% (7.83 mg/L) of DOC is removed after 5 days of subsurface travel (MW-5). Release of manganese (≤1.22 mg/L) indicates anoxic redox conditions underneath the basin. At Well WR-069B (travel time 14 days), a DOC removal of approximately 93% (groundwater concentrations of 1.1 mg/L) is observed. Only traces of manganese (0.009 mg/L) were measured at this well, suggesting suboxic conditions.

The BDOC concentration, considering a residence time of 2 weeks in the aquifer, is approximately 15 mg/L. The first-order rate constant for BDOC disappearance during SAT is estimated to be 0.18 d^{-1} (R^2=0.98). On the basis of an earlier study, Drewes et al. (2011) also reported TOC removal in the range of 50 to 60% for monitoring Well MW-5.

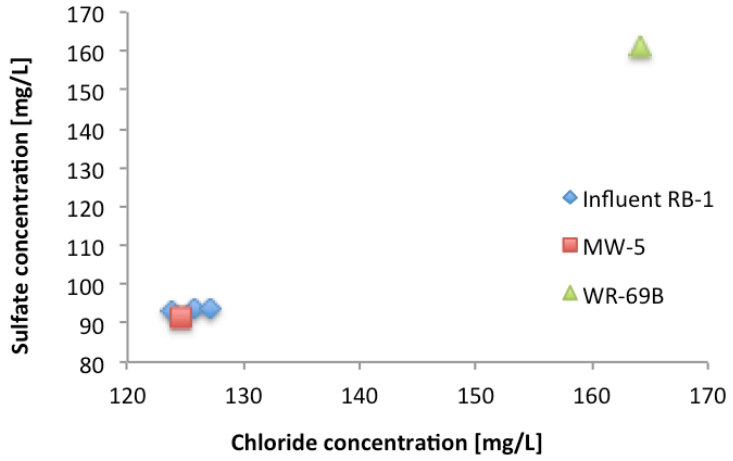


Figure 5.13. Comparison of sulfate and chloride concentrations in the surface-spreading basin RB-1, piezometer MW-5, and groundwater monitoring Well WR-69B during the sampling campaign in February/March 2013.

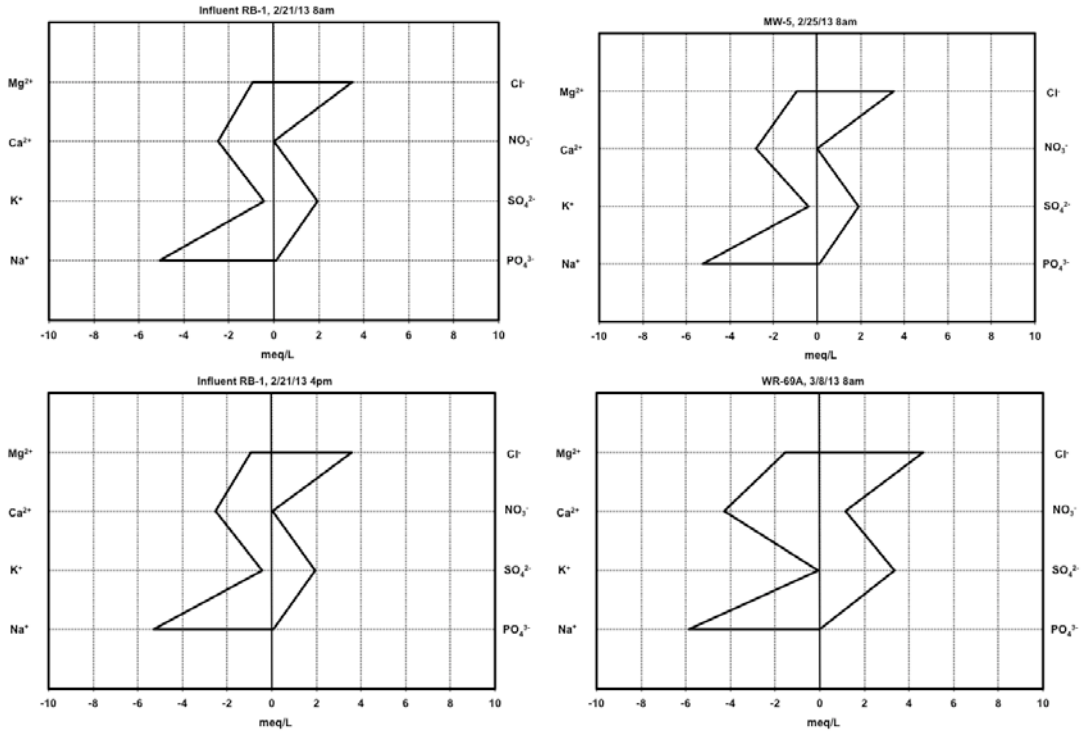


Figure 5.14. Stiff diagrams displaying chemical matrix of the infiltration basin influent (morning and afternoon sample) as well as piezometer MW-5 and monitoring Well WR-69B.

5.1.3.2. Performance Assessment of SAT Operation—CECs

Because of the high amount of BDOC available in reclaimed water at this site, the predominant redox conditions underneath the recharge basin (piezometer MW-5) become anoxic very quickly, resulting in less favorable conditions for CEC removal. CEC concentrations in the reclaimed water applied to the infiltration basin (secondary treated wastewater) are considerably higher than concentrations observed at the other study field sites (e.g., 13,900±754 ng/L for caffeine, 988±32 ng/L for trimethoprim, 5864±
602 ng/L for iopromide).

Removal efficiencies for selected CECs are summarized in Figure 5.15. The intermediate biodegradable compound DEET and the more easily biodegradable compound gemfibrozil exhibit almost no removal after 5 days of subsurface travel under these conditions. Easily biodegradable compounds such as caffeine, trimethoprim, and acetaminophen are still attenuated more than 90% within 5 days under anoxic conditions, whereas the removal of ibuprofen, iopromide, diclofenac, and naproxen is in the area of 32, 37, 55, and 66%, respectively.

More hydrophobic compounds such as amitriptyline, fluoxetine, diphenhydramine, and triclocarban immediately sorb to the soil during infiltration; however, fluoxetine and triclocarban were detected in the range of their detection limits in the analyzed MW-5 groundwater sample. No removal was observed for the flame retardants TCEP, TCPP, and TDCP or for dilantin, sucralose, or primidone. Sulfamethoxazole concentration at MW-5 (5467±404 ng/L) more than doubled compared to values observed in the influent to the recharge basin (2368±89 ng/L). This could suggest an accumulation of this compound in the upper aquifer under anoxic conditions.

After 2 weeks of subsurface travel, most of the easy and intermediate biodegradable compounds are attenuated (even flame retardants and sulfamethoxazole); however, Well WR-069B is considerably influenced by dilution with native groundwater. Based on sucralose and primidone concentrations, both recalcitrant wastewater tracers with negligible sorption potential, for this monitoring well at least 25 to 30% dilution of recharged reclaimed water can be assumed. The concentration of carbamazepine, another wastewater tracer, is slightly higher in Well WR-069B than in the influent.

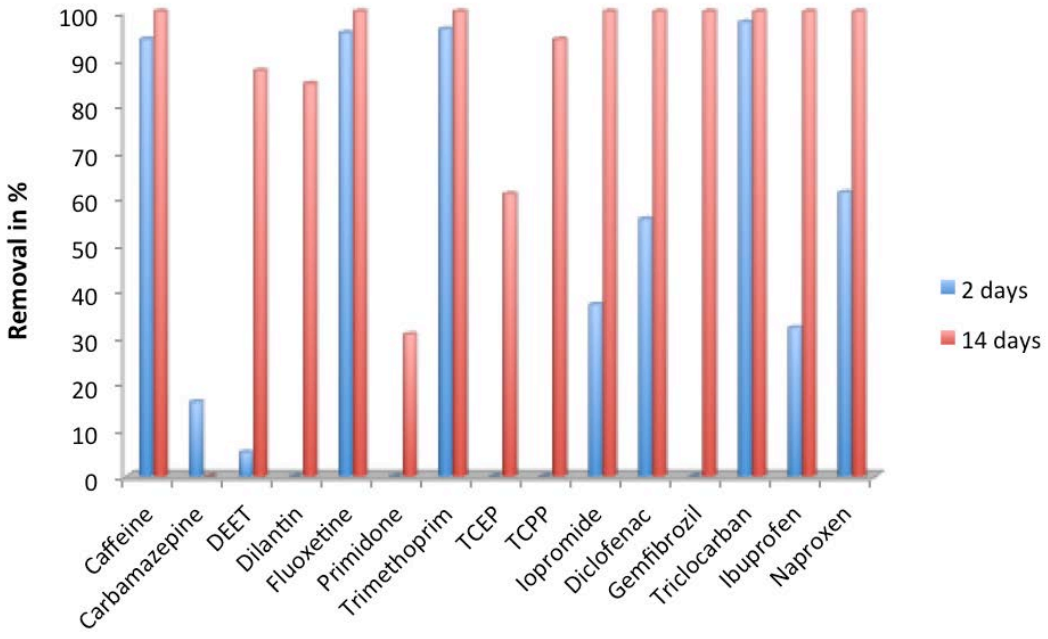


Figure 5.15. Average removal percentage of selected easy, intermediate, and recalcitrant biodegradable indicator compounds during soil–aquifer treatment applying secondary treated reclaimed water (n=3) based on subsurface travel times of 5 days (MW-5, n=1) and 14 days (WR-069B, n=1).

5.1.3.3. Performance Assessment of SAT Operation—GR Activity

All field samples collected at the SWRF were exposed in the GR assay at five different concentration fold (1.5625x, 3.125x, 6.25x, 12.5x, and 25x). The dose–response curve for all samples is shown in Figure 5.16. The recharge basin influent had significant GR activity at all three sampling times (8 am, 12 pm, 4 pm) throughout the course of a day. Only a very weak response was received from the piezometer sample (5 days residence time) at the highest enrichment fold, and no GR activity was observed in the sample from the monitoring well (WR-069B, 14 days residence time). The very weak response in the piezometer MW-5 sample indicates that GR activity disappears after a short infiltration passage and that the aquifer is efficient in removing GR activity. The results obtained at the full-scale SWRF site are in agreement with the results of the laboratory-scale soil column experiment.

The GR activity in the reclaimed water applied to the recharge basin shifted during the same sampling day. The DEX-EQ in the influent was 177 ng/L at 8 am in the morning and dropped to 111 ng/L at 4 pm in the afternoon (Table 5.2). This might be related to the usage pattern, degradation, or transformation of the target compounds and will require further investigation.

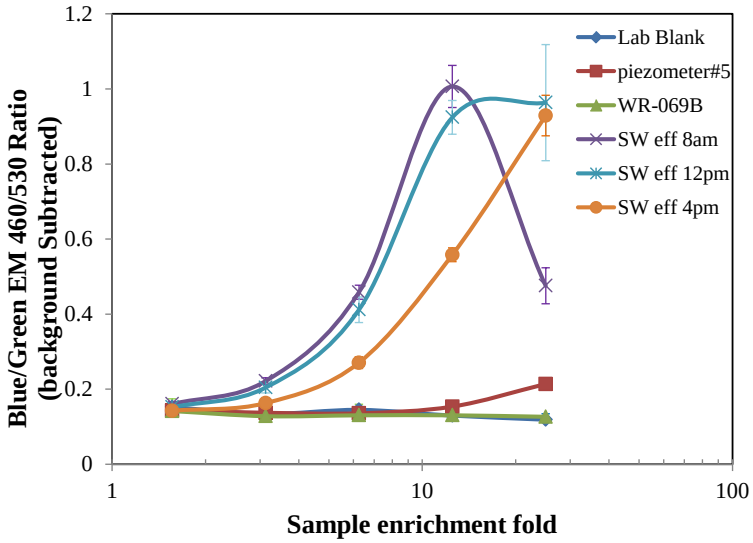


Figure 5.16. GR activity in basin influent and groundwater samples at the Sweetwater Recharge Facility.

Table 5.2. GR Activities Summary for the Sweetwater Recharge Facility Samples

Sample	EC_{10} (REF)	DEX-EQ (ng/L)
Piezometer#5	-	ND
WR-069B	-	ND
Sec. eff. 8am	5.1	177.0
Sec. eff. 12pm	5.6	161.2
Sec. eff. 4pm	8.1	111.4

Notes: ND=not detected under current enrichment fold; EC10 (REF): sample enrichment fold, where the activity is 10% of the maximum response in the same experiment day (% effect).

5.2. CEC Removal Kinetics—Comparison of Laboratory and Field Results

5.2.1. San Gabriel Spreading Grounds

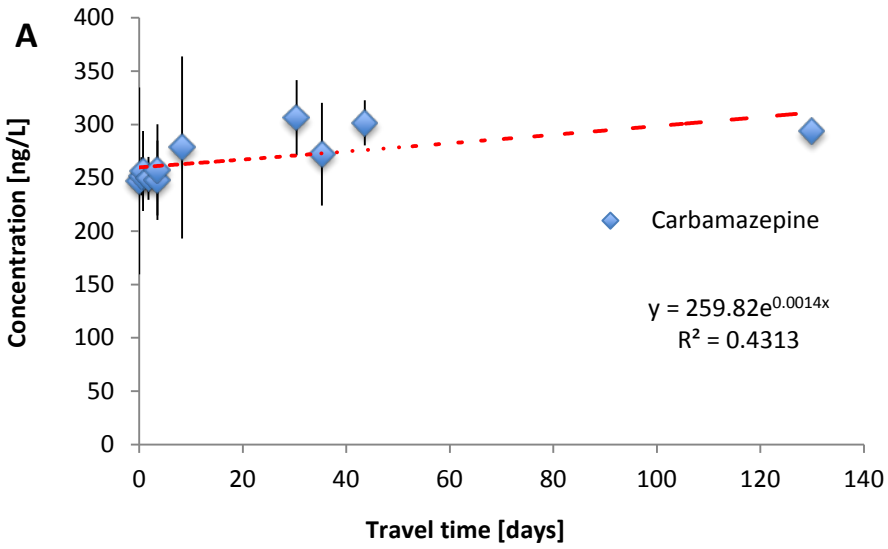
Previously derived removal kinetics for the analyzed suite of CECs using well acclimated, laboratory-scale soil column systems at CSM have been compared and validated with the data obtained from the field site during both sampling campaigns. The CEC removal kinetics for three defined redox conditions (oxic, suboxic, anoxic) are summarized in Table 3.10.

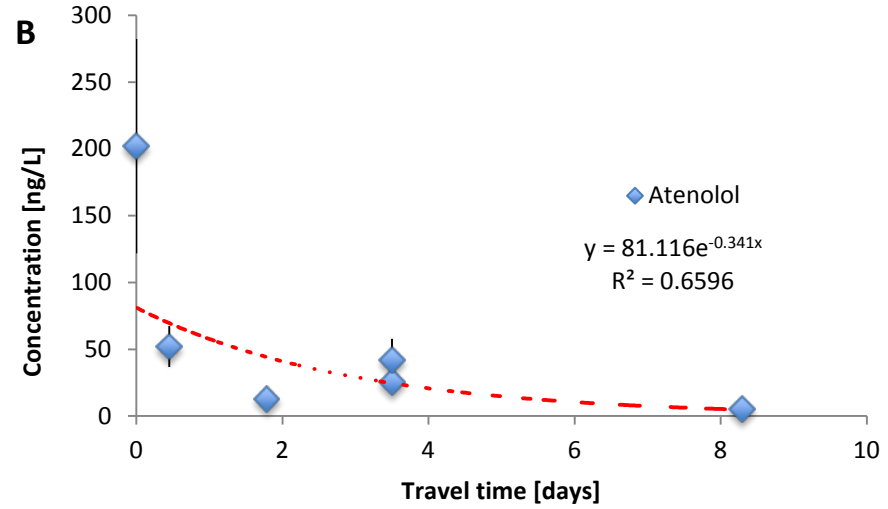
Determination of redox conditions is based on the concentration of certain bulk parameters (e.g., BDOC, ammonia/nitrate, manganese). The redox classification is further described in the footnote of Table 3.10. Averaged CEC concentrations for carbamazepine (recalcitrant), DEET, dilantin (intermediate biodegradable), atenolol, gemfibrozil, and trimethoprim (easily biodegradable) are illustrated versus subsurface travel time in Figure 5.17. First-order decay is assumed for the biodegradable compounds, as indicated in Figure 5.17. The large error bars are due to the high concentration variability in the feed water as discussed previously.

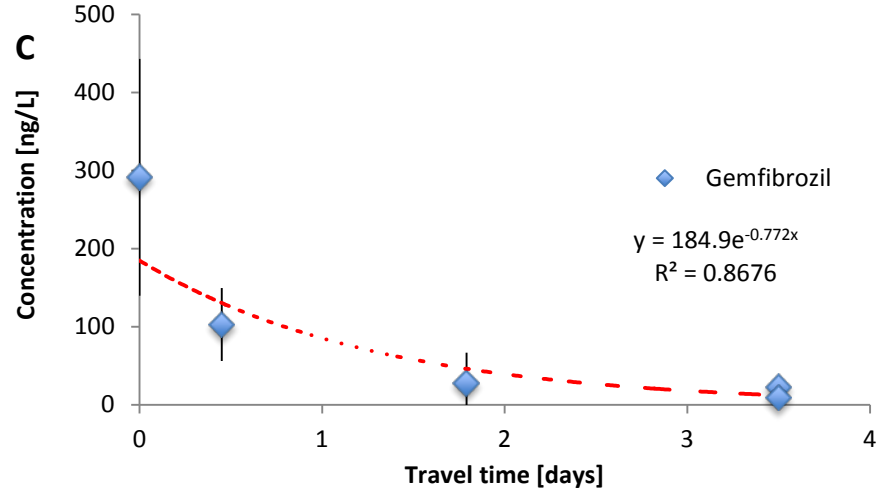
A slight increase in carbamazepine concentration indicates no removal or significant dilution process is occurring in the aquifer underneath the test basin. Conditions in the upper aquifer underneath the test basin can be classified as oxic with high BDOC levels that are transitioning to suboxic conditions after most of the dissolved oxygen in the recharged water is consumed. Simplified, the observed removal for the shown biodegradable compounds (Figure 5.17 B–F) during the first oxic soil passage largely matches the removal kinetic rates obtained in the laboratory-scale experiments, although DOC levels differ (high vs. low BDOC).

In laboratory soil column experiments, oxic conditions are difficult to maintain under high BDOC levels. In addition, performance under field conditions with travel times up to 44 days is dependent on a sequence of redox conditions and transient states that are usually not captured in the controlled laboratory-scale experiments. To be more precise, removal rates representative of the predominant redox conditions need to be applied over the appropriate travel distances to avoid over- or underestimation of compound removal with changing key factors in the subsurface (e.g., BDOC, redox). As shown in Table 3.10, the removal kinetics significantly change for certain CECs under different subsurface conditions.

In addition, considering the field data, compounds such as diclofenac undergo photolytic decay during ponding and are likely removed. Usually, this compound is more difficult to degrade, but oxic conditions under low BDOC levels significantly enhanced diclofenac removal in the soil column experiments. Furthermore, the unexpected high variability in CEC concentrations in the field data at the California site will require some additional research.


A
Concentration [ng/L]
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
120
140
Travel time [days]
Carbamazepine
y = 259.82e0.0014x
R² = 0.4313


B
Concentration [ng/L]
300
250
200
150
100
50
0
0
2
4
6
8
10
Travel time [days]
Atenolol
y = 81.116e-0.341x
R² = 0.6596


C
Concentration [ng/L]
500
400
300
200
100
0
0
1
2
3
4
Travel time [days]
Gemfibrozil
y = 184.9e-0.772x
R² = 0.8676

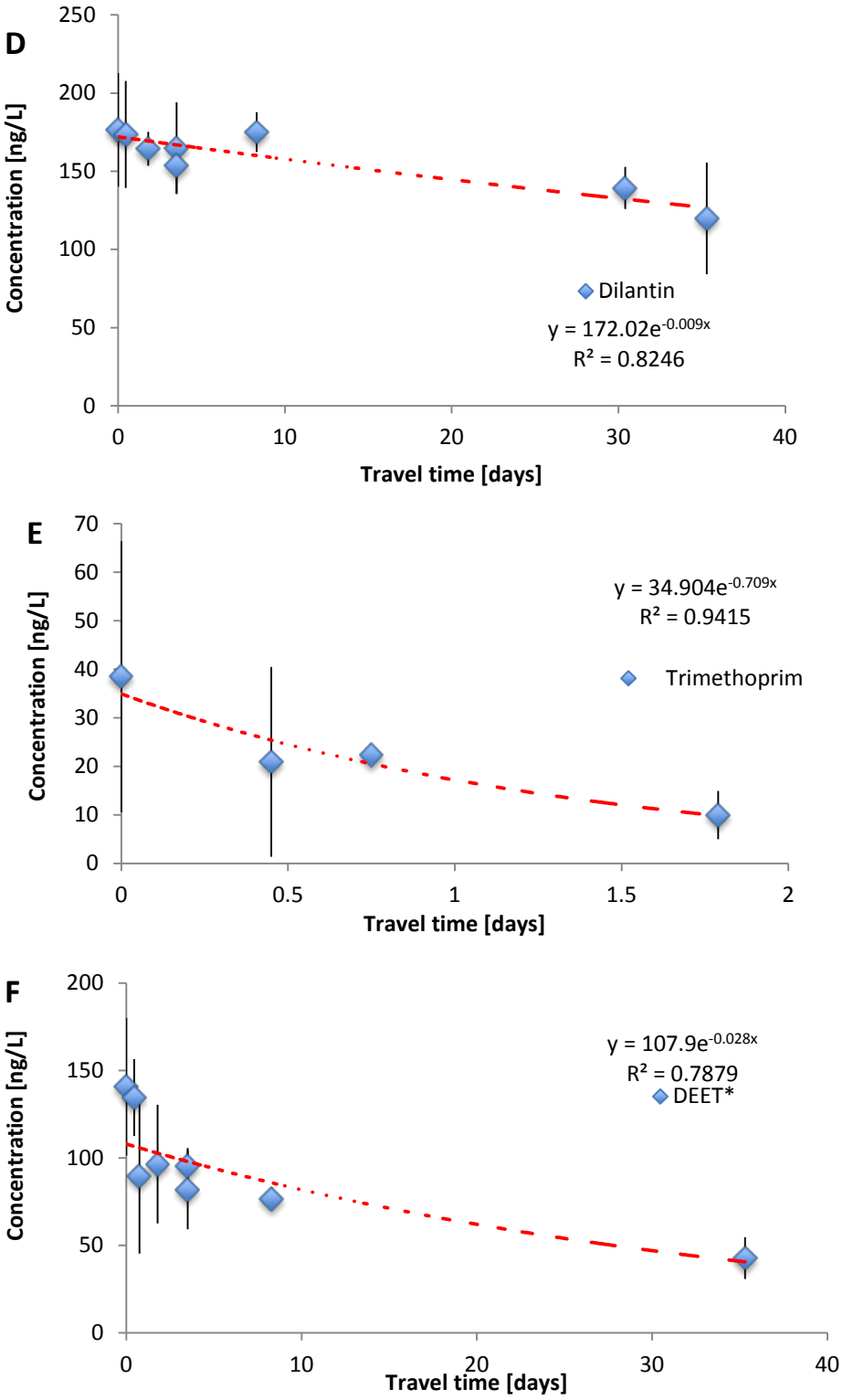


Figure 5.17. Averaged concentration of both Montebello Forebay test basin sampling campaigns (n≥5) at different travel times for A) carbamazepine, B) atenolol, C) gemfibrozil, D) dilantin, E) trimethoprim, F) DEET.

Note: Please note changes in scale; red dotted line indicates first-order decay fitted to the field data.

5.2.2. Prairie Waters Project, Aurora Water

The RBF soil passage in Colorado, although initially oxic, quickly became anoxic because of the high amount of BDOC (>3 mg/L) present in the South Platte River water. Thus, the RBF site is analogous to the laboratory-scale high BDOC/anoxic soil column system at CSM (C1 and C2, Experiment A). The ARR site, in contrast, exhibited conditions very similar to those tested in the low BDOC/oxic column experiment (C2, Experiment B). As seen in the soil column simulations (Table 2.1), low BDOC/oxic conditions facilitated exceptional removal of moderately biodegradable CECs within a shortest residence time (<10 days) as compared to anoxic conditions (Figure 5.17 and Table 3.10). The sequential operation at the Prairie Waters Project site (RBF followed by subsequent ARR) likely created a carbon-starving environment that resulted in significantly improved CEC removal (higher rate constants) compared to just extending travel times, as commonly practiced in conventional RBF systems (Figure 5.18).

5.2.3. Sweetwater Recharge Facility, Tucson Water

Anoxic conditions with high BDOC underneath the recharge basin are less favorable for the removal of CEC. DEET and gemfibrozil do not exhibit removal after 5 days of travel time under these conditions, confirming removal rates observed in the laboratory-scale soil columns (Table 3.10). CEC attenuation after 14 days (Well WR-069B) is partially due to dilution with native groundwater. Background concentrations of CECs in the native groundwater are not known; therefore, removal efficiencies were not modeled at this site.

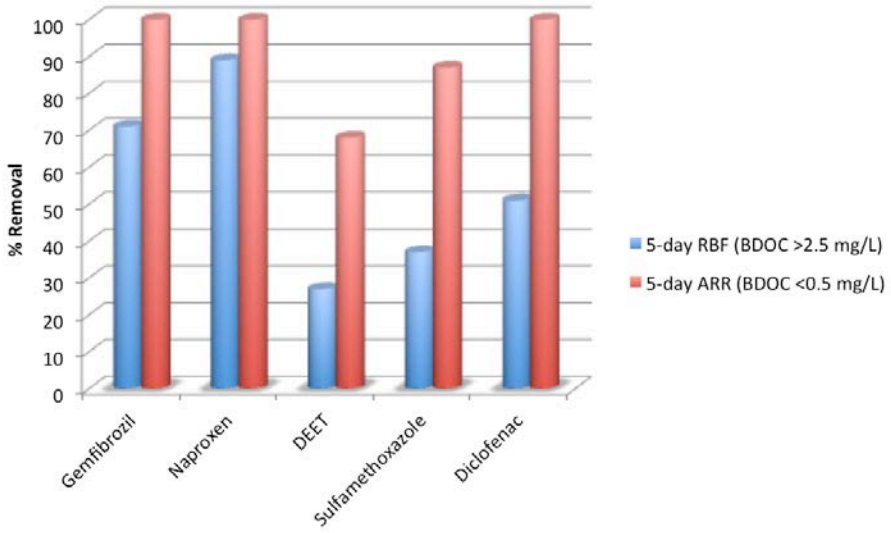


Figure 5.18. CEC removal efficiency of a full-scale RBF facility (blue bars) receiving high BDOC concentrations compared to an ARR (red bars) receiving low BDOC concentrations for an estimated travel time of 5 days.

Chapter 6

Modeling Framework to Assess MAR Performance

Reclaimed water contains chemical constituents such as DOC, nitrogen, CECs, and microbial contaminants (viruses and pathogenic bacteria). During MAR fed with reclaimed water, these contaminants may be partially or totally removed in the unsaturated (vadose) zone before reclaimed water reaches the underlying groundwater table. Once contaminants reach the water table, they are further transported through the groundwater driven by a hydraulic gradient and porous media properties. Thus, a modeling tool intended for estimating contaminant attenuation in MAR systems needs to consider contaminant transport and transformation in the unsaturated and saturated zone.

In this study, we adopted the Soil Treatment Unit Model (STUMOD) developed at CS M to predict fate and transport of nitrogen in the unsaturated zone of on-site systems. STUMOD had been extended to handle saturated and unsaturated zone flow and transport of DOC, CECs, pathogens, and nitrogen. The STUMOD for MAR Systems (STUMOD-MAR) is a one-dimensional formulation that is embedded into a spreadsheet model. The model considers advective movement, retardation via adsorption, dispersion, biotransformation of DOC and CECs, and inactivation of pathogens.

The Project Team intended to develop a user-friendly tool for assessing attenuation of microbial and chemical contaminants in MAR systems that is detailed enough to include relevant transport and transformation processes. STUMOD-MAR can be used as a screening tool to evaluate whether the impact of reclaimed water during MAR is a potential concern in IPR systems.

6.1. STUMOD-MAR: A Tool for Predicting Fate and Transport of Microbial and Chemical Contaminants in MAR

STUMOD-MAR is a physically based, user-friendly tool for estimating contaminant and pathogen removal in the unsaturated and saturated zones of MAR systems. STUMOD-MAR accounts for important fate and transport processes such as adsorption, nitrification and denitrification for nitrogen species, sorption and biodegradation for DOC and CECs, and inactivation for pathogens. The unsaturated zone is assumed to be predominantly vertical flow, and contaminants are transported mainly by advection. Thus, the effect of dispersion was ignored in the unsaturated zone. The computations are performed for steady-state conditions. The model also computes a soil moisture profile. The degree of saturation is used as a surrogate for the effect of aeration on aerobic and anaerobic processes of nitrification and denitrification. The soil moisture profile is also used in calculations of contaminant retardation due to sorption. The unsaturated zone model calculates concentration of nitrogen species, DOC, CECs, and pathogens reaching the groundwater table. This information is used as boundary input concentration to the subsequent saturated zone model. The saturated zone model implements a different model formulation than the unsaturated zone for hydraulics and chemical fate and transport.

6.1.1. Unsaturated Zone Hydraulics and Contaminant Transport

The overall procedures used to calculate removal efficiency are shown in Figure 6.1. The current version of the model is parameterized as one layer; however, STUMOD-MAR can handle up to four different soil layers in the unsaturated and saturated zone, each with different properties. In general, the first layer at the infiltrative surface is assigned biomat hydraulic properties as a bacteria layer forms over time during recharge of reclaimed water and results in a decrease of hydraulic conductivity. This biomat layer is typically in the range of 0.5 to 5 cm thickness (US EPA, 2002). The soil moisture content is calculated for each layer and based on wastewater loading rate and soil physical properties. The average vertical velocity is obtained by dividing the reclaimed water loading rate (cm/day) by the porosity. The calculations are made layer by layer.

For each layer, the travel time is estimated using velocity and the thickness of the layer. The travel time predicted by the model was compared to observed travel times in soil column studies at CSM with a reclaimed water loading rate of 1 mL/min and an inner soil column diameter of 15 cm. The travel time estimated by the model for 10 ft (3 m) travel distance was about 16 days, close to the observed travel time based on a conservative tracer (potassium bromide). The travel time is used in the model for the calculation of contaminant removal via nitrification/denitrification or biodegradation. Therefore, the reclaimed water loading rate should be known by the user with some degree of accuracy to obtain a reasonable estimate of travel time.

The application rate can be controlled by sizing the recharge area of MAR systems for known volumes (gpd) of reclaimed water. Thus, STUMOD-MAR can be used to guide sizing of the surface area for spreading operations given the volume of loading. In general, the unsaturated zone model can be run first to obtain or update input parameters for the saturated zone model and again to run the saturated zone model. These steps can be performed all at one time if the user prefers to run the saturated and unsaturated zone model in a single run. Users can also run the saturated zone model using an independent set of input parameters.

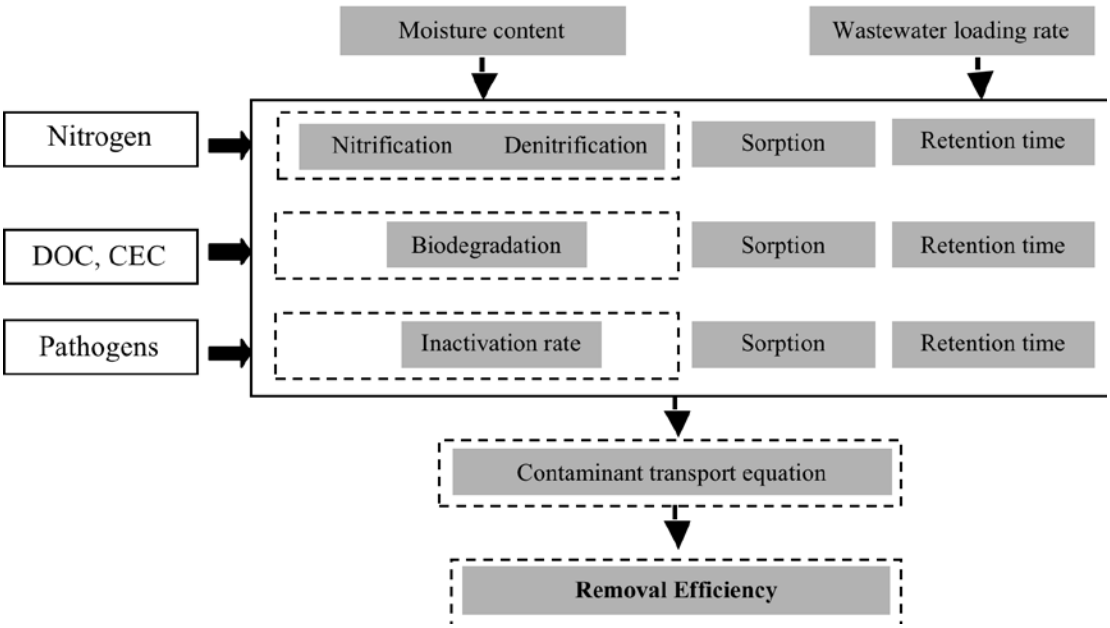


Figure 6.1. Flow chart of procedures in STUMOD-MAR.

6.1.1.1. Nitrogen

Nitrogen may not be a concern in MAR systems relative to other chemical and microbial contaminants because concentration of nitrate in the applied reclaimed water (depending on the level of treatment) could be less than the groundwater background level. STUMOD-MAR incorporates the fate and transport function for nitrogen as briefly discussed here. Nitrogen can be removed in the vadose zone through nitrification, denitrification, and sorption. Sorption retards the downward velocity and travel time of ammonium. In general, travel time affects the time available for reactions to occur that influence removal. The approach used for contaminant transport in STUMOD-MAR is a simplification of the general advection–dispersion equation (ADE) based on Huyakorn et al. (1985).

A first-order reaction is implemented in STUMOD-MAR for fate and transport of nitrogen species in MAR systems because nitrogen concentration in wastewater effluent is usually low. The equation is used for nitrification of ammonium and subsequent denitrification of nitrate. Based on the assumption that advection dominates dispersion and vertical flow dominates lateral flow in the unsaturated zone, dispersion and lateral flow are ignored in STUMOD-MAR and a steady state is assumed. The simplified ADE equation is given as:

$$C(z) = C_o \exp\left(-\frac{RK_{rmax} f_t f_{sw} f_c}{v_z} \Delta z \right) \qquad (6.1a)$$

or

$$C(z) = C_o \exp\left(-RK_{r\max} f_t f_{sw} f_c T \right) \qquad (6.1b)$$

where, Δz represents vertical distance, v_z is velocities in the vertical direction, $\Delta z/v_z$ represents the travel time (T) in each segment, C_o is effluent concentration, C is the

concentration of the dissolved constituent (M/L^3), R is the retardation factor (calculated based on sorption isotherm, density, and soil moisture content), K_{rmax} is maximum first-order nitrification or denitrification rate (1/d), f_t and f_{sw} are adjustment factors (between 0 and 1) to account for the effect of temperature and soil moisture on nitrification and denitrification, and f_c accounts for the effect of fraction of organic carbon on denitrification. Note that in equation (6.1b), $\Delta z/v_z$ is replaced by travel time (T). The rate K_{rmax} in the previous equation represents the maximum rate of nitrification or denitrification occurring at optimum condition. This maximum rate is adjusted for soil moisture, temperature, and carbon content.

6.1.1.2. DOC and CECs

The DOC and CEC module accounts for sorption and biodegradation of organic compounds. Similar to nitrification and denitrification processes, a first-order kinetic was used. The concentration C is expressed as a function of boundary input concentration C_o, depth, biodegradation rate, R_f, and velocity given by:

$$C(z) = C_o \exp\left(-\frac{RK_b}{v_z}\Delta z\right) \qquad (6.2a)$$

or

$$C(z) = C_o \exp\left(-RK_bT\right) \qquad (6.2b)$$

K_b is the first-order biodegradation rate coefficient. The R_f is described as a function of density, sorption, and soil moisture content. Note that in equation (6.2b), $\Delta z/v_z$ is replaced by travel time (T). The same equation is used to estimate the attenuation of pathogens, where R is the retardation factor for pathogens, T is the retention time, and an inactivation rate is used in place of K_b.

6.1.2. Saturated Zone Hydraulics and Contaminant Transport

One of the most popular analytical solutions used for modeling groundwater contaminant plumes is the Domenico (1987) solution. The saturated zone predicts change of concentration away from the source as a function of distance or retention time. The groundwater transport model has two components: flow and transport. The flow model computes groundwater flow velocity. Darcy's law is used to calculate the velocity given by:

$$v = \frac{k}{\theta}\frac{\Delta h}{\Delta x} \qquad (6.3)$$

where v [L/T] is the groundwater seepage velocity, k is the saturated hydraulic conductivity [L/T], θ is the porosity, and $\Delta h/\Delta x$ is the hydraulic gradient. Default values of k and θ are provided based on soil type in STUMOD-MAR. The hydraulic properties of the unsaturated zone in STUMOD-MAR were used as properties of the saturated zone model. The velocity is used in the steady and nonsteady groundwater fate and transport equations presented below (Equations 6.4 and 6.5).

Several approaches have been proposed to calculate transport in the saturated zone. The approaches range from analytical one-dimensional flow and contaminant transport codes to three-dimensional, multiphase, multicomponent reactive transport codes for the most complex sites and processes. We adapted analytical solutions in this study that provide computationally efficient tools for modeling the fate and transport of groundwater contaminant plumes (Aziz et al., 2000; Clement et al., 2002).

Several analytical solutions have been developed for subsurface flow and transport. Cleary and Ungs (1978) presented an analytical solution to a three-dimensional transport problem for a domain finite in y and z directions. Later, Sagar (1982) published an exact analytical solution to the transport problem considered by Domenico and Robbins (1985). Wexler (1992) extended the Sagar (1982) solution to include the effects of reaction and presented an exact analytical solution to the transport problem considered by Domenico (1987). Domenico (1987) solution is commonly used in several public domain design tools, including the U.S. Environmental Protection Agency tools BIOCHLOR and BIOSCREEN (Newell et al., 1996; Aziz et al., 2000).

In STUMOD-MAR, it is assumed that vertical percolation is the major flow pathway and that hydrodynamic dispersion was considered negligible during unsaturated zone transport. Dispersion is expected to be more important in the saturated zone; thus, the contaminant fate and transport module includes advection, sorption, dispersion and reaction (nitrogen), biotransformation (DOC and CEC), and inactivation (pathogens). The nitrate input concentration to the saturated zone is expected to be very low, and denitrification could be limited in this zone, depending on depth of water table and availability of a carbon source; however, some reduction in nitrate concentration may occur simply by dispersion. The same is true for refractory DOC or non-biodegradable CECs. It is further assumed that flow is predominantly lateral in the saturated zone. The saturated zone module in STUMOD-MAR estimates how far chemicals and pathogens travel laterally or how long they will persist in the subsurface.

The Domenico (1987) solution is the most commonly used analytical solution for modeling groundwater contaminant plumes. The model contains one-dimensional groundwater velocity, longitudinal, transverse, and vertical dispersion, the first-order degradation rate constant, finite contaminant source dimensions, and steady and non-steady source conditions. The model configuration is shown in Figure 6.1. It has options for both constant and instantaneous source boundary conditions. Both steady and non-steady solutions can be calculated. The steady model (given by Equation 6.4) produces the same results as the non-steady model (Equation 6.5) after some time interval.

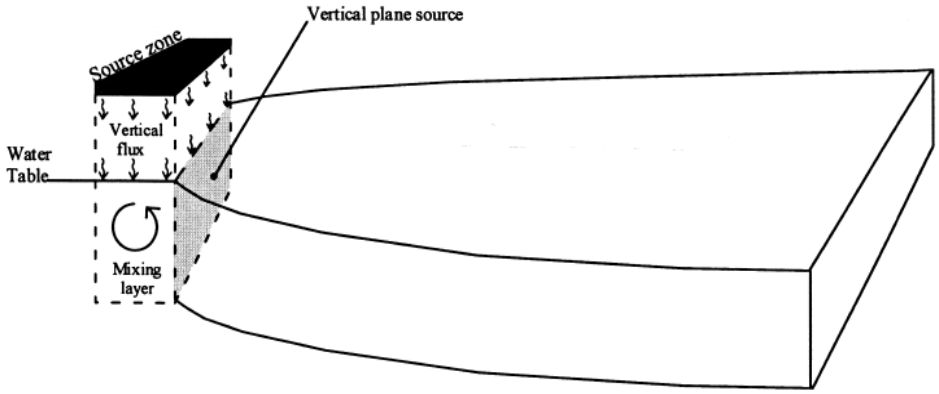


Figure 6.2. Model configuration for saturated zone module with assumptions about a mixing layer and source plane concentration.

Source: Guyonnet (2001).

The first form of Domenico solution is a one-dimensional Domenico steady-state constant source boundary condition given by:

$$\frac{C_x}{C_0} = exp\left\{\frac{x}{2\alpha_x}\left[1-\left(1+\frac{4\lambda\alpha_x}{v}\right)^{\frac{1}{2}}\right]\right\} erf\left[\frac{Y}{4(\lambda\alpha_y)^{\frac{1}{2}}}\right] erf\left[\frac{Z}{4(\lambda\alpha_z)^{\frac{1}{2}}}\right] \qquad (6.4)$$

Where

C_x = concentration downgradient at a well x along the plume centerline (mg/L),
C_0 = contaminant concentration in the source (mg/L),
x = centerline distance b/n downgradient point and source well (m),
α_x, α_y, and α_z = longitudinal, transverse, and vertical dispersivity (m)
λ = degradation rate constant (1/d),
ν = groundwater velocity (m/d),
Y = source width (m),
Z = source depth (m),
erf = error function,
exp = exponential function.

Equation 6.4 calculates the centerline concentration; however, concentrations off the centerline can be calculated by mapping a point off the centerline to a centerline point. This is done based on the assumption that the isoconcentration line follows the shape of an ellipse.

The second form of Domenico solution is a one-dimensional non-steady solution. For a continuous source and finite source dimensions with one-dimensional flow, longitudinal, transverse, and vertical dispersion, and a first-order degradation rate constant, the Domenico transient solution for the centerline concentration as a function of time is defined according to Domenico (1987) as:

$$C(x,0,0,t)=\frac{C_0}{2}\exp\left\{\frac{x}{2\alpha_x}\left[1-\left(1+\frac{4\lambda\alpha_x}{v}\right)^{\frac{1}{2}}\right]\right\}\times\left\{erfc\left[\frac{x-vt\left(1+\frac{4\lambda\alpha_x}{v}\right)^{\frac{1}{2}}}{2(\alpha_x vt)^{\frac{1}{2}}}\right]\right\}\times erf\left[\frac{Y}{4(\alpha_y x)^{\frac{1}{2}}}\right]\times erf\left[\frac{Z}{4(\alpha_z x)^{\frac{1}{2}}}\right] \quad (6.5)$$

Where

C(x, 0, 0, t) = concentration (M/L^3) at a downgradient location x at time t along the centerline
C_0 = steady state contaminant at source
α_x, α_y, and α_z = longitudinal, transverse, and vertical dispersivity (m)
λ = degradation rate constant (1/d)
v = groundwater velocity (m/d)
Y = source width (m)
Z = source depth (m)
erf and *erfc* = error and complementary error functions
exp = exponential function.

Model assumptions include a continuous release, source boundary, homogeneous aquifer properties, a one-dimensional groundwater flow, and no significant change in flow direction and velocity. Domenico and Robbins (1985), further modified by Domenico (1987) and Martin-Hayden and Robbins (1997), considered a three-dimensional model with first-order decay. The boundary condition assumes a vertically oriented, constant concentration source with source dimensions given in horizontal and vertical directions as y and z. The groundwater flow is in the longitudinal (x) direction, and dispersion occurs in all three dimensions.

6.1.3. Model Parameters for Nitrogen, DOC, CECs, and Pathogens

6.1.3.1. Hydraulic Parameters

To make it simple from a user perspective, a graphical user interface (GUI) was added to the spreadsheet model using Excel ™-VBA (Figure 6.3). The GUI allows users to choose a soil texture class, type of CEC, and type of pathogen as well as a groundwater temperature range for the selection of the inactivation rate for pathogens. Four sandy soil types typical for MAR systems were incorporated in the model. Based on the soil and CEC type, the model will automatically populate the default hydraulic and biodegradation parameters. The CEC K_b varies depending on redox conditions (three different bins reflecting oxic, suboxic, or anoxic redox conditions). The predominant redox condition in the subsurface is determined by the initial concentration of ammonia and DOC in the recharged water.

For a given CEC type, the model chooses the appropriate K_b based on the input concentration of ammonium and DOC provided by users; however, users can also populate the model with their own site-specific data (e.g., rate coefficient) if available. Users can simply input new data using the GUI to overwrite the default values automatically populated by the model. Model estimates of treatment performance with distance or retention time are obtained based on the default values or, if applied, user-specified inputs.

Table 6.1. STUMOD-MAR Hydraulic Parameters

Parameter	Units	Definition
HLR	cm d^{-1}	hydraulic loading rate
α_1	-	parameter [illegible] analytical equation for pressure distribution
α_2	-	parameter [illegible] in the
K_s	cm d^{-1}	saturated hydraulic conductivity (also referred to as K_{sat})
θ_1	-	residual soil moisture (also referred to as [illegible])
θ_2	-	saturated soil moisture (also referred to as [illegible])
N	-	parameter n in the soil water retention function
M	-	parameter m in the soil water retention function
L	-	tortuosity parameter

The hydraulic parameters listed in Table 6.1 are used to calculate the soil moisture profile in the unsaturated zone. As discussed in Section 6.1.1, the soil moisture profile is used as a surrogate for the effect of aeration on aerobic and anaerobic processes of nitrification and denitrification. The soil moisture profile is calculated using the van Genuchten (1980) approach. STUMOD-MAR default values for hydraulic properties of the four different soil texture classes commonly used in MAR systems (Table 6.2) were taken from the statistical database created by Schaap et al. (2001). This database provides data for hydraulic properties including saturated hydraulic conductivity, porosity, residual moisture content, and other parameters related to soil suction and capillarity.

The saturated hydraulic conductivity and porosity are used to calculate velocities both in the saturated and unsaturated zone. Saturated hydraulic conductivity for sandy soil from Schaap et al. (2001) is 6.5 m/d. Horizontal hydraulic conductivities ranged from 7.9 to 11.6 m/d for the MAR test site located at the Montebello Forebay (Laws et al., 2011). Data from this field site were used for the evaluation of STUMOD-MAR. An average value of 9.75 m/d was used for model evaluation. The infiltration rate of reclaimed water at the research basin was between 0.6 and 0.9 m/d. We used an average value of 0.75 m/d as hydraulic loading rate (HLR). A 2.4 m unsaturated zone existed beneath the basin at the time of the recharge experiment. This value was used as the thickness of the unsaturated zone in the STUMOD-MAR evaluation.

The soil moisture retention parameters in Table 6.2 (α_1, α_2, K_s, θ_1, θ_2, n, m, and l) are used to calculate the soil moisture content. The default values for STUMOD-MAR for these parameters are obtained from the same database as described earlier (Schaap et al., 2001). The remaining hydraulic parameters in Table 6.2 (e.g., HLR, saturated hydraulic conductivity, and porosity) are used in the calculation of travel time in the saturated and unsaturated zones and affect fate and transport of nitrogen, DOC, CEC, and pathogens.

Table 6.2. STUMOD-MAR Default Hydraulic Parameter Values

Parameters	Loamy Sand	Sand	Sandy Clay Loam	Sandy Loam
HLR	75	75	75	75
α_1	0.025	0.025	0.025	0.025
α_2	0.035	0.035	0.021	0.027
K_s	105.1	649	13.19	38.25
θ_1	*0.049*	0.053	0.063	0.039
θ_2	0.390	0.375	0.384	0.387
n	1.747	3.180	1.330	1.448
m	0.427	0.686	0.248	0.310
l	0.50	0.50	0.50	0.50

Note: Refer to Table 6.1 for definitions.

Source: The van Genuchten soil moisture retention parameters are obtained from Schaap et al. (2001), Rosetta program.

6.1.3.2. Contaminant Transformation Rate Parameters

Fate and transport of nitrogen in the unsaturated zone was modeled using Equation 6.1. Fate and transport for unsaturated and saturated zone DOC, CEC, and pathogen were modeled using Equation 6.2. Saturated zone fate and transport was modeled using Equation 6.5 for all constituents (nitrogen, DOC, CEC, and pathogens with biodegradation rates for DOC and CEC, denitrification rates for nitrogen, and inactivation rate for pathogens). Major parameters commonly used in microbial and chemical contaminant transport models are listed in Table 6.3.

Table 6.3. Parameters Used in Microbial and Chemical Contaminant Transport Models

Attenuation	Parameter
Pathogens	
Inactivation or decay	Primarily temperature dependent
Retardation	Depends on the nature of the soil; values as low as 0.5 have been observed for viruses
Velocity	Greater removal at lower flow velocities
Hydrodynamic dispersion	Dependent on the size of the organism
Sorption coefficient K_d	Dependent on soil organic matter, clay content, ion strength, and ph
Rate constant	Dependent on redox conditions
Trace Organic Chemicals	
Sorption coefficient K_d	Dependent on soil organic matter, clay content, ion strength, and ph
Rate constant	Dependent on redox conditions, availability of biodegradable organic carbon
Nitrogen Species	
Sorption coefficient K_d	Dependent on clay content and ph
Rate constant	Dependent on redox conditions and availability of organic carbon
	Temperature dependent

Contaminant transformation rate parameters for nitrogen are first-order nitrification and denitrification rates. These parameters were obtained from McCray et al. (2005). The median values reported for first-order nitrification and denitrification are 2.9 d^{-1} and 0.025 d^{-1}, respectively.

In general, sorption was assumed to be an insignificant removal mechanism for DOC. The behavior of DOC during MAR systems for reclaimed water demonstrated that the degradation rate decreases with decreasing concentration, and some fraction of the DOC was not biodegradable. Thus, in STUMOD-MAR, DOC biodegradation rates were classified into three categories based on an approach by Drewes and Jekel (1998): an easily biodegradable DOC fraction, a fraction with moderate biodegradation, and a non-degradable/refractory DOC fraction. This classification allowed a more precise calibration of STUMOD-MAR outputs to field DOC attenuation observations.

DOC removal results derived during the field monitoring study at the Montebello Forebay (Section 5.1.1) were used to determine the three rates; K_{b1}, $K_{b2,}$ and K_{b3} and the corresponding easily biodegradable, moderately degradable and refractory fractions using the Excel™ solver optimization approach. Thus, three different biotransformation rates (K_{b1}, $K_{b2,}$ and K_{b3}) were determined based on concentration remaining in the system as DOC migrates through the subsurface system. The biotransformation rate for the refractory fraction (K_{b3}) was set to zero, and the values obtained for K_{b1} and K_{b2} through optimization were $0.5\ d^{-1}$ and $0.1\ d^{-1}$, respectively. The fraction of the easily degradable portion was determined to be 25%, and the refractory fraction was 35%. The remaining fraction with intermediate biodegradation was 40%.

Table 6.4. Default CEC Parameters Used in STUMOD-MAR

	Biodegradation [K_b] by Redox Condition (1/day)			Sorption [K_d] by Soil Type (L/kg)*			
Compound	**Oxic**	**Suboxic**	**Anoxic**	**Sand**	**Loamy Sand**	**Sandy Clay Loam**	**Sandy Loam**
Acesulfame	0.165	0.001	0.001	0.00	0.00	0.00	0.00
Acetaminophen	0.360	0.402	0.486	5.00	2.60	2.80	1.00
Atenolol	0.511	0.444	0.376	1.20	8.10	5.30	20.42
Atrazine	0.010	0.014	0.007	0.01	0.01^	0.01	0.28
Caffeine	0.373	0.260	0.325	250.0	25.00^	25.00	44.00
Carbamazepine	0.001	0.020	0.007	0.03	1.43	0.51	6.03
DEET	0.300	0.117	0.013	0.01	1.00	1.00	0.00
Diclofenac	1.397	0.120	0.017	0.75	1.87	9.00	3.47
Dilantin	0.051	0.012	0.019	0.03	0.03^	0.03^	0.03^
Fluoxetine	0.001	0.001	0.001	18.00	490.00	616.60	8317.6
Gemfibrozil	1.490	0.752	0.015	0.40	1.00	1.56	1.00
Iopromide	0.819	0.186	0.161	0.00	0.00	0.00	0.00
Naproxen	1.443	0.166	0.082	0.00	1.00	11.00	1.65
Primidone	0.001	0.001	0.001	0.16	0.16	0.16	0.00
Sucralose	0.010	0.001	0.001	0.00	0.00	0.00	0.00
Sulfamethoxazole	0.501	0.049	0.009	2.00	2.00	8.00	2.00
TCEP	0.195	0.195	0.001	0.03	0.03	0.03	0.03
TCPP	0.177	0.044	0.011	8.70	8.70	8.70	8.70
TDCP	0.124	0.039	0.006	15.00^	15.00^	15.00^	15.00^
Trimethoprim	0.501	0.361	0.934	1.82	1.82	218.78	60.26

Notes: ^=No experimental/literature data available, data statistically derived by model;
DEET=N,N-Diethyl-meta-toluamide; TCEP=tris(2-carboxyethyl)phosphine; TCPP=tris(1-chloro-2-propyl)phosphate; TDCP=tris[2-chloro-1-(chloromethyl)ethyl]phosphate.

Sources: *Barron et al. (2009), Conkle et al. (2012), Lange et al. (2012), Lin et al. (2010), Loeffler et al. (2005), Scheytt et al. (2005), Xu et al. (2009), Yamamoto et al. (2009), Yu et al. (2009, 2013).

Biotransformation and sorption rates for different types of CECs are listed in Table 6.4. For CECs, 20 indicator compounds were included in the model database (Table 6.4). Sorption and biotransformation were determined as the major removal mechanisms, as discussed earlier. The values K_d and K_b vary based on the type of chemical constituent and soil type (Table 6.4). The model database comprises K_b values for three defined redox conditions: oxic, suboxic, and anoxic. Thus, for each CEC type, three rate coefficients can be chosen by the model based on the prevailing oxic, suboxic, and anoxic subsurface condition. The prevailing redox conditions are determined based on NH_4 and DOC input concentration and soil moisture zones.

To reflect the sequence of redox zones that evolves during recharge of reclaimed water in the subsurface, different rate coefficients were used for unsaturated and saturated zone. For the unsaturated zone, oxic rates are used for low initial NH_4 and DOC concentrations ($NH_4 \leq 1.5$ mg/l and DOC$\leq$10 mg/l), and suboxic rates are used for high initial effluent NH_4 and DOC concentrations ($NH_4 > 1.5$ mg/l and DOC>10 mg/l). For the saturated zone, suboxic rates are used for low initial effluent NH_4 and DOC concentrations, and anoxic values are used for intermediate and high initial NH_4 and DOC values. Even though this represents a simplification of the highly complex redox conditions occurring in the field, resulting model predictions are more accurate than just lumping biodegradation together into one single rate coefficient for the entire subsurface passage.

Data source (laboratory-scale soil column experiments under controlled conditions) and calculation of K_b are described in detail in Section 3.6. Compound-specific soil/sorption coefficients are provided for four soil types typically occurring in MAR schemes. Where soil sorption data were not available, based on results from this study literature data were applied as discussed in Section 3.5.2 and indicated in Table 6.4.

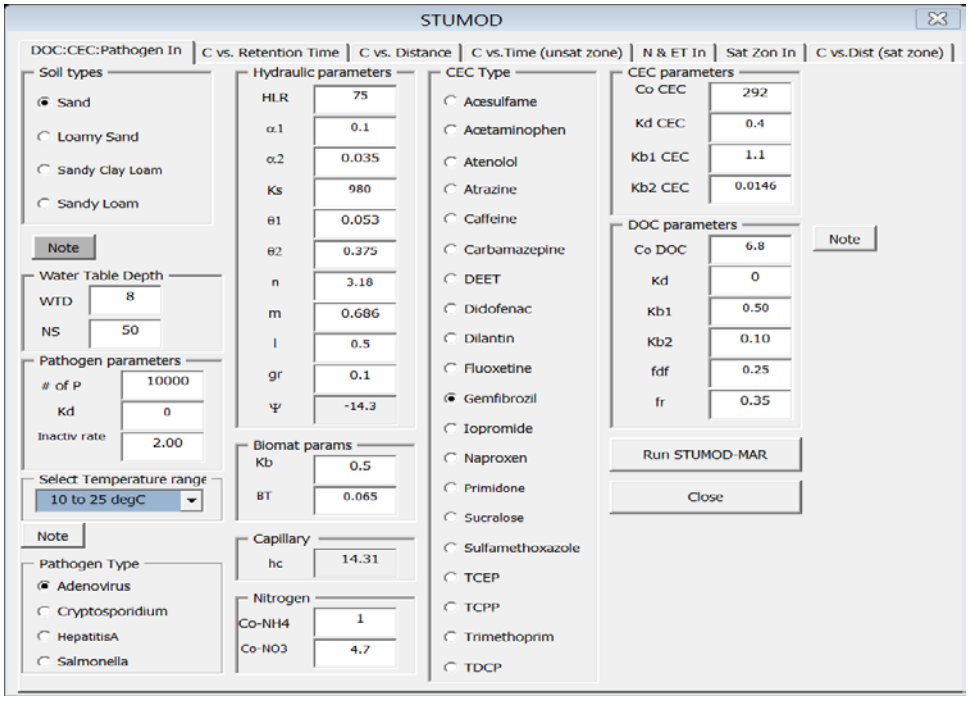


Figure 6.3. Graphical user interface for parameter inputs.

6.1.4. Model Calibration and Validation

CSM researchers conducted the first field sampling campaign (campaign #1) at the test basin from December 10 to 12, 2012, and a second campaign (campaign #2) from April 24 to 26, 2013. Both data sets were used for model calibration and validation of DOC removal in MAR systems. Data from campaign #1 were used for the calibration process, and data from campaign #2 were used for the model validation. A comparison of DOC concentrations predicted by the model and observed in the field based on travel time for campaign #1 is shown in Figure 6.4. A scatter diagram of model predicted versus observed values is shown in Figure 6.5.

The model fit (coefficient of determination; R^2) achieved during model calibration was R^2=0.8. R^2 values greater than 0.5 are considered to be acceptable for model fits (Santhi et al., 2001). Model validation was accomplished using data from the same field site but measured during a different time period (data set campaign #2). Simulated and measured DOC concentrations versus retention time for the validation period are displayed in Figure 6.6. A scatter diagram of model predicted versus observed DOC values for the validation period is shown in Figure 6.7. The model fit obtained for the validation period is R^2=0.67.

In contrast to DOC parameterization, where degradation rates were determined through calibration, CEC biodegradation rates were not calibrated; instead, biodegradation rates for CEC for the three conditions (oxic, suboxic, and anoxic) were calculated from experimental data (Table 6.4) as presented earlier. Model performance was evaluated for each travel time based on average CEC concentrations from both field campaigns. R^2 values were calculated for most of the selected compounds (Table 6.5). The model fit obtained was acceptable for most of the compounds (R^2>0.5); however, for some of the compounds, the R^2 value was less than 0.5, thus, further calibration with different data sets may be needed to improve the model performance. An example output to illustrate the comparison of model predicted and field observed CEC concentrations versus retention time is shown in Figure 6.8 for gemfibrozil. A scatter diagram of model predicted versus observed concentration values for gemfibrozil is provided in Figure 6.9.

The model considers pathogen attenuation for two types of viruses (e.g., hepatitis A, adenovirus), bacteria (e.g., *Salmonella*), and protozoa (e.g., *Cryptosporidium*; Table 6.6). Inactivation rates reported were specified for three groundwater temperature ranges. A discussion on available data and constraints in modeling pathogen attenuation (linear vs. biphasic) is provided in Chapter 4 and the literature review (Regnery, et al., in review). Of the four considered pathogens, only adenovirus was analyzed within this study. Model results were compared with results obtained from the California and Arizona field sites. Because of limited data availability, a comprehensive validation of the model output for pathogen attenuation based on field observations will need some further research and model improvements. At the moment, the model uses linear inactivation rates for three different groundwater temperature ranges (Table 6.6) and does not consider biphasic decay of certain pathogens. Model performance was evaluated based on linear inactivation rate for adenovirus (Figure 6.10).

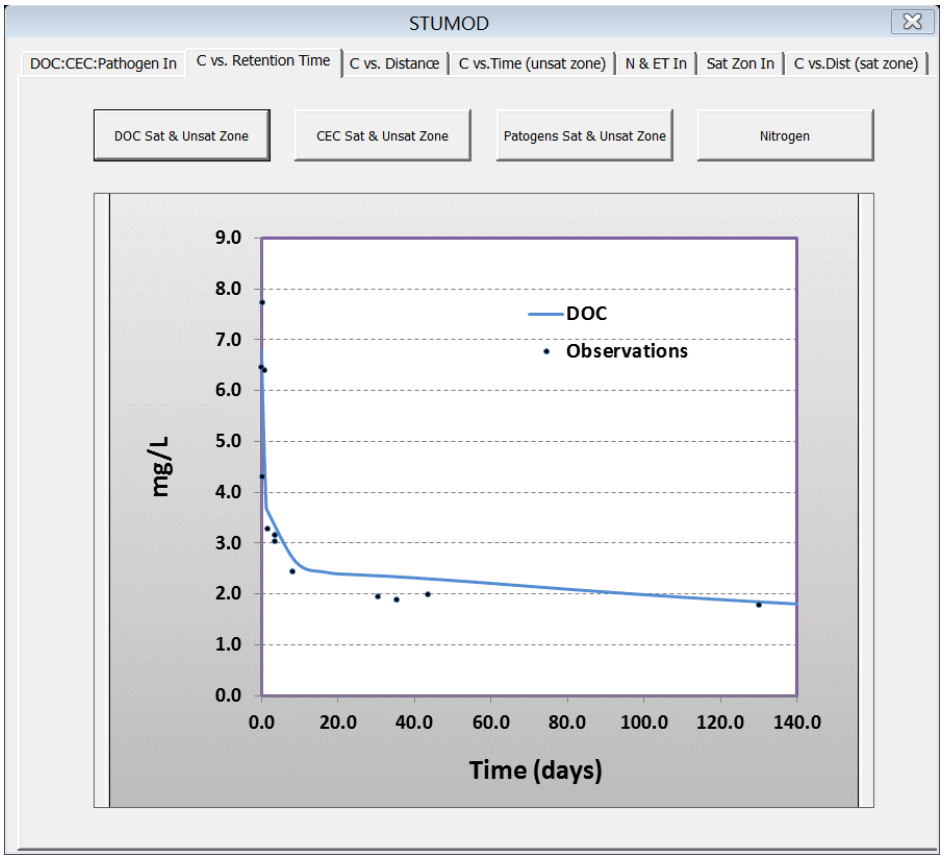


Figure 6.4. Output for DOC concentration (mg/L) vs. retention time (calibration period).

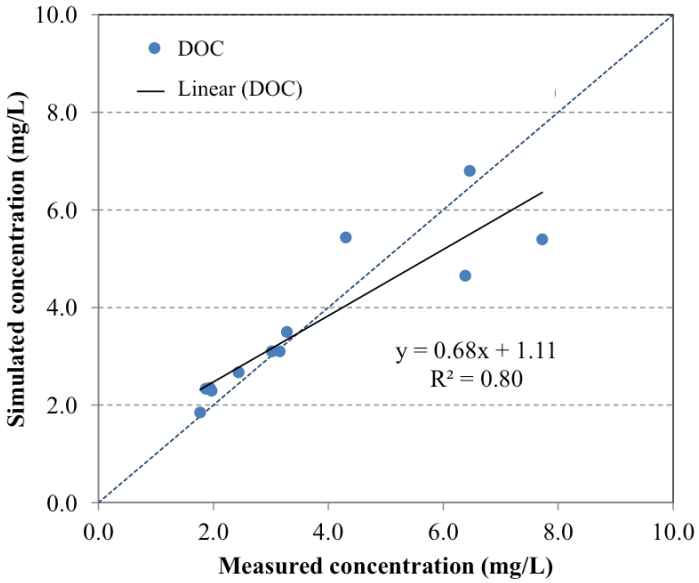


Figure 6.5. STUMOD-MAR simulated DOC concentration (mg/L) vs. measured DOC concentrations (calibration period).

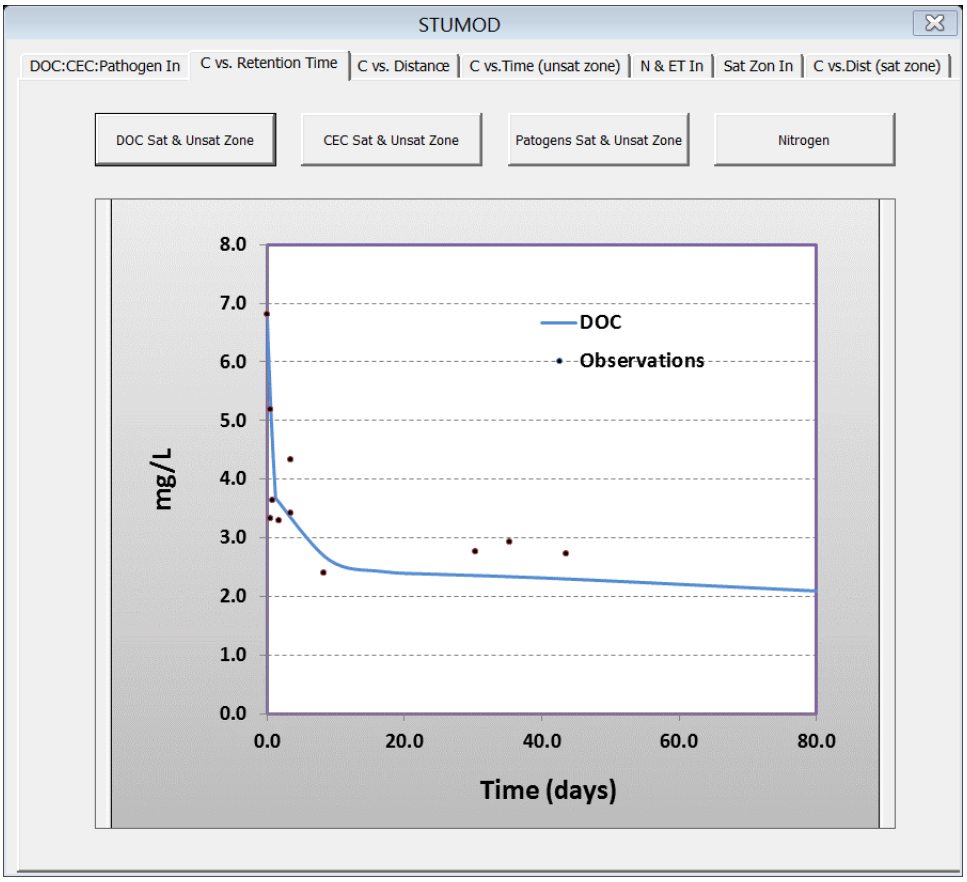


Figure 6.6. Output for DOC concentration (mg/L) vs. retention time (validation period).

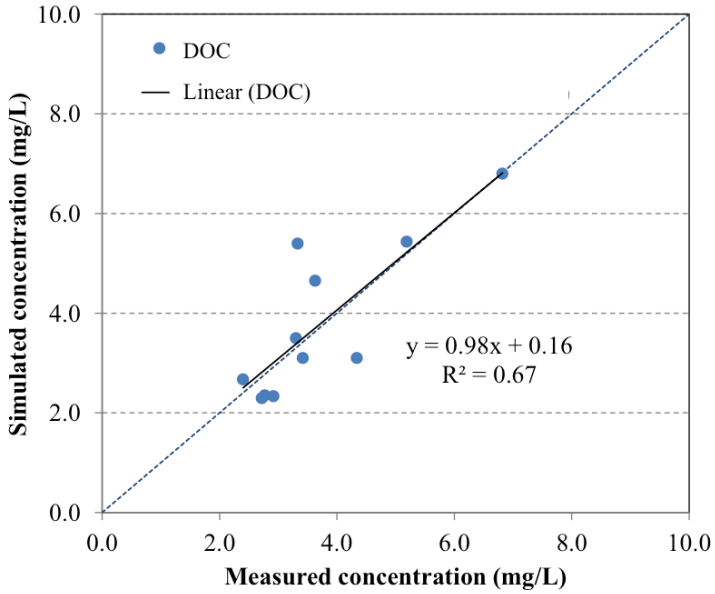


Figure 6.7. STUMOD-MAR simulated vs. measured DOC concentration (mg/L; validation period).

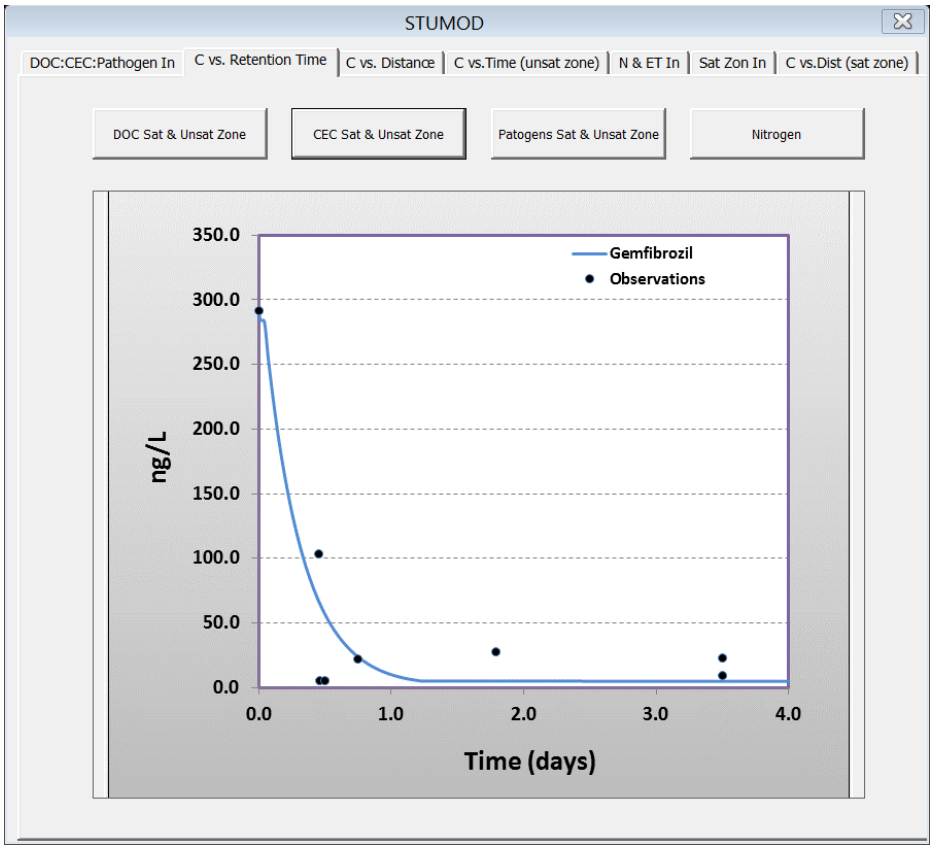


Figure 6.8. Example output for the decrease in concentration (ng/L) of the selected CEC (gemfibrozil) vs. retention time.

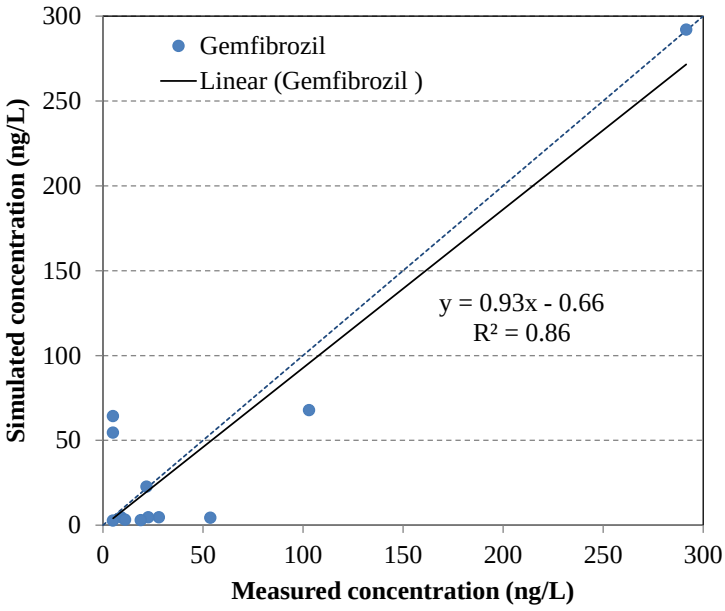


Figure 6.9. STUMOD-MAR simulated vs. measured concentration (ng/L) for the selected CEC (gemfibrozil).

Table 6.5. Calculated Coefficient of Determination for Selected CECs

CEC Type	R^2
Atenolol	0.90
Carbamazepine	0.34
DEET	0.25
Diclofenac	0.61
Gemfibrozil	0.86
Iopromide	0.40
TCEP	0.57
TCPP	0.87
TDCP	0.89
Trimethoprim	0.40

Notes: DEET=N,N-Diethyl-meta-toluamide; TCEP=tris(2-carboxyethyl)phosphine; TCPP=tris(1-chloro-2-propyl)phosphate; TDCP=tris[2-chloro-1-(chloromethyl)ethyl]phosphate.

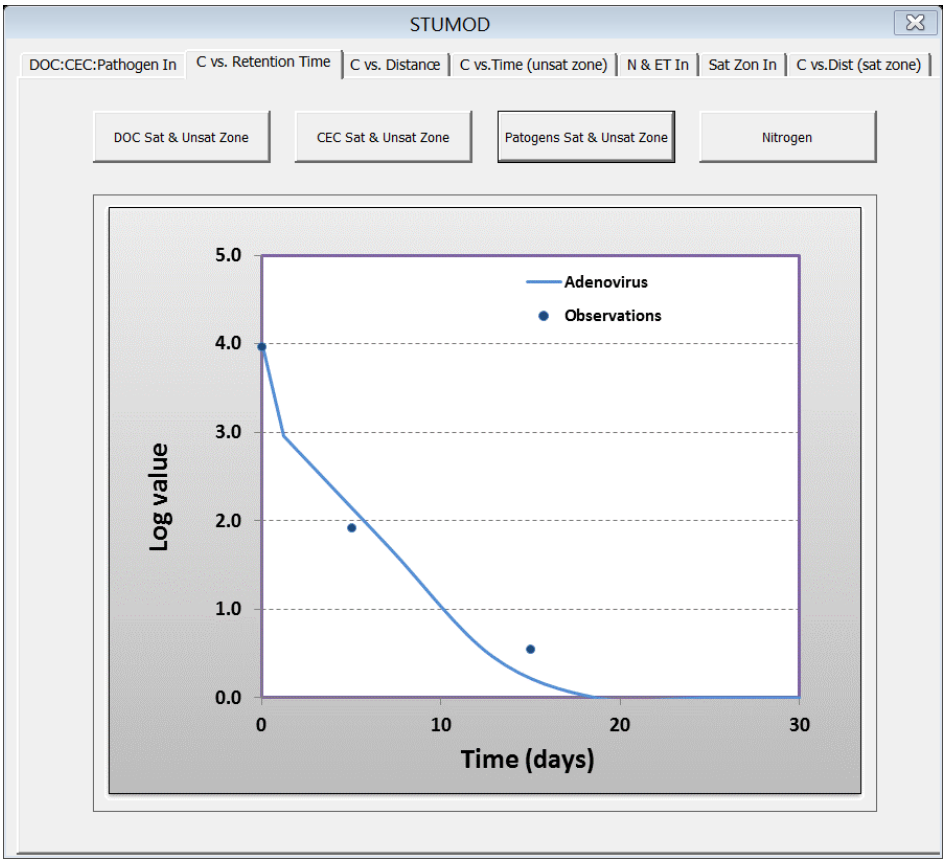


Figure 6.10. Example output for pathogen removal (adenovirus) over retention time.

Table 6.6. Default Pathogen Parameters Used in STUMOD-MAR

(Model) Pathogen	Removal/Inactivation Rate log_{10}/day			Mean (linear) log_{10}/day	Biphasic Removal log_{10}/day	
Temp. ° C	**4 to 10**	**11 to 20**	**21 to 30**	**5 to 30**	**Vadose Zone**	**Saturated Zone**
Hepatitis A	0.02 [b)]	0.02	0.04	0.02 [b)]		
Adenovirus^	0.0076	0.028	0.047	0.01	0.489	0.002
Salmonella sp.	0.04 [b)]	0.1 [b)]	0.6 [b)]; 0.8102			
Cryptosporidium sp. ^		0.0254	0.039	0.044 [a)]	0.0824 [c)]	0.0682 [c)]

Note: ^=biphasic behavior (data provided for groundwater temperature range 11–25° C).

Sources: a=Ives et al. (2007); b=John and Rose (2005); c=Toze et al. (2010)

6.1.5. Summary and Conclusion

STUMOD-MAR is a user-friendly tool that can provide a quick evaluation of the efficiency of chemical and microbial contaminant attenuation in MAR systems. Modeling fate and transport of contaminants is based on simplification of the general advection dispersion equation. Although the model is easy to use, it is detailed enough to account for important fate and transport processes such as advection, sorption, biotransformation (DOC and CECs), pathogen inactivation, and nitrification and denitrification (nitrogen). The model is parameterized for the evaluation of chemical and microbial contaminant removal in MAR systems. The input parameters for transport and transformation were derived based on a thorough literature review and experimental data generated during this study.

STUMOD-MAR outputs were compared to field observation. STUMOD-MAR predictions were similar to laboratory- and field-scale observations for DOC, CECs, and nitrogen. Pathogen removal validation was limited by insufficient data as a function of travel time. STUMOD-MAR predicted relatively higher removal with distance at lower reclaimed water loading rates because of increased travel times in the subsurface. At higher loading rates, the retention time was reduced, resulting in a lower overall removal with distance or depth. Thus, designers of MAR systems can get valuable insight regarding the surface area needed for a system that is designed to receive a certain flow.

6.2. Remarks on Model Use

6.2.1. Input and Output

- Open the spreadsheet model. Click anywhere on the screen to display the user input form. STUMOD-MAR input page for DOC, CECs, and pathogens is displayed. The inputs for nitrogen and plant uptake (for nitrogen) are listed on a separate page.
- Enter NH_4 and DOC reclaimed water concentrations first. The model automatically populates CEC biodegradation rates for oxic, suboxic, and anoxic conditions based on CEC type, NH_4, and DOC input concentration.
- Similarly, pathogen inactivation rates are populated automatically when pathogen type and temperature range are selected.
- Choose soil type. Hydraulic parameters are updated based on type of soil chosen by the user.
- Choose value for HLR (cm/day). HLR affects travel time; thus, estimates have to be as accurate as possible. Default values are added but can be changed by user.
- After all values have been entered, click on “Run STUMOD-MAR” to execute the saturated and unsaturated zone models. The model will produce outputs for unsaturated and saturated zones based on outputs and parameters from the unsaturated zone. Users should follow the instruction below the “Saturated Zone” button if they need to run the saturated zone model independent of the unsaturated zone model.

- Go to “C vs. Retention Time” and “C vs. Distance” pages and evaluate the graphical outputs of constituent concentrations versus travel time and distance. Users can also view the results separately for the saturated and unsaturated zone (see the tabs for saturated and unsaturated zone outputs on the GUI).

6.2.2. Saturated Zone Model

The saturated zone model can be run with either input or parameters from the unsaturated zone or by direct user input.

- Go to the “Saturated Zone Inputs” page to input saturated zone input parameters. Click on “Help” and read instructions. Click “Update” to get input data from the unsaturated zone model. This allows output from the unsaturated zone to be used as input to the saturated zone model.
- Users can modify the input parameters for the saturated zone and run the model if input values and parameters are different from the unsaturated zone model.
- After all values have been entered, click on "Sat Zon In" to run the saturated zone model.
- Go to “Sat Zon Out” tab and evaluate the graphical outputs of constituent concentrations.
- For more information about parameters, place cursor on the input box within the “Input User's Form,” or see the "Parameter Definition" worksheet.

Chapter 7

Conclusions and Recommendations

7.1. Role of Retention Time, Redox Conditions, and Primary Substrate

This study investigated the role of retention time in the environmental buffer of IPR systems utilizing MAR to augment groundwater supplies. The main goal of this research project was to develop and validate relationships between the removal and inactivation of pathogens and attenuation of chemical contaminants by the environmental buffer as a function of retention time, system characteristics, and operating conditions. The study employed a series of laboratory-scale soil column experiments with different flow conditions and feed water compositions simulating MAR. These experiments simulated different predominant redox conditions, availability of a primary substrate, and retention time. Validation of laboratory findings occurred through monitoring campaigns at three full-scale MAR facilities in California, Colorado, and Arizona. These facilities allowed a high resolution of retention time utilizing a dense network of lysimeters and monitoring wells.

7.1.1. Relationships Between Pathogen Attenuation and Retention Time

In this study, viruses were primarily targeted as the most relevant pathogen for MAR applications. Virus attenuation was mainly quantified by PCR, a highly sensitive tool that cannot determine infectivity. Therefore, potentially both infectious and noninfectious viruses are detected by PCR; however, the detection of the virus's nucleic acid presents the issue that if it can be detected, an infectious virus could be present. Thus, PCR is a more conservative measure of virus presence than cell culture techniques. Absence of virus detection by PCR indicates that viruses are not present.

The following relationships were identified for the attenuation of pathogens and retention times for MAR systems fed with reclaimed water.

- A review of the literature on the survival of viruses in groundwater revealed that adenoviruses, coliphages ΦX-174, and PRD-1 are among the longest surviving viruses in groundwater. Inactivation rates of coliform bacteria and *Cryptosporidium parvum* during MAR, however, appeared to be much higher. Considering that adenoviruses are generally one of the most abundant viruses in wastewater, this study focused on adenoviruses and other indicator viruses to study and predict virus survival in MAR systems.

- PMMoV appeared to be a conservative indicator of human enteric virus removal during MAR, likely because it occurs in greater concentrations in wastewater than the human enteric viruses and perhaps survives longer and is more difficult to remove in porous media. Absence of this virus suggests that human enteric viruses have been removed to below detection limit. The virus was also detectable in reclaimed water (secondary treated effluent) after passage through a 4.4 m long soil column (~16 days residence time) during laboratory-scale experiments.

- No human enteric viruses could be detected by qPCR after travel times of 10 days or greater in groundwater samples collected at any of the three field sites. Enteric virus removal would generally appear to exceed 2 log during this time. Based on field monitoring data, a 5 day travel time resulted in a 2 to 3.7 log reduction of PMMoV.

- Reovirus was the only infectious virus detected in groundwater wells. It was detected in an RBF well at the Colorado site with a travel time of 5 days. It was also the only naturally occurring enteric virus found after travel through the 4.4 m long laboratory-scale soil column. Reoviruses are among the most abundant and longest surviving viruses known in wastewater. They are also among the most common viruses detected in drinking water wells. Additional research on this virus would be useful to better understand its removal by MAR.

- MS-2 virus removal decreased with column length beyond 60 cm, supporting the hypothesis that virus removal rates decrease with travel distance. Thus, removal rate is not constant and cannot be described by a strict linear function. Pang (2009) described this type of removal as following a power law (or hyperexponentially) with removal rates declining with greater travel distances. Removal rates were linear near the soil surface but then declined exponentially with time over distance traveled. No further significant removal of the virus occurred between 60 and 440 cm of travel through the soil column experiment.

- This study in general confirmed findings reported by Pang (2009) that removal rates are specific to the physical and chemical properties of the microbes, subsurface media, solution chemistry, transport scale, type of contaminated source (e.g., wastewater vs. surface water), and duration of contamination (years of operation).

- Where MAR conditions are similar to conditions investigated in this study, determined inactivation rates can be used to conservatively estimate removal efficiencies for pathogens similar to those targeted in this study. These are also embedded in STUMOD-MAR. Only a limited set of conditions were investigated; however, inactivation rates closest to the conditions likely to occur in the field (flow velocity, porous media properties, temperature) should be selected.

7.1.2. Relationships Between Trace Organic Chemical Attenuation and Retention Time

The following relationships were identified for the attenuation of trace organic chemicals and retention times for MAR systems fed with reclaimed water.

- Soil properties, in particular the sorptive capacity, can have a significant impact on CEC attenuation in MAR systems. Although the sorptive capacity of soil is well known for hydrophobic CECs, findings of this study suggest that also more hydrophilic, water soluble CECs can be attenuated by sorption depending on soil properties. The target compounds atenolol, caffeine, and trimethoprim exhibited complete or nearly complete removal to below detection in the presence of bentonite clay. The field soil taken from the initial layer of an infiltration basin was able to sorb 70% of atenolol, 91% of caffeine, and 70% of trimethoprim. The field clay sorbed a greater percentage of atenolol and trimethoprim than the field soil and removed 84% and 93% of these two compounds, respectively.

- Sorption of diclofenac, gemfibrozil, naproxen, and sulfamethoxazole to bentonite clay was less than 30%. DEET was removed by 58% through sorption to bentonite. The field soil provided little sorptive capacity for these compounds, as removal was within the standard deviation of 10%. The field clay removed 15 to 25% of all five compounds. The chlorinated flame retardants sorbed strongly to bentonite, which removed greater than 75% on average; 57% of carbamazepine and 38% of primidone were removed in the presence of bentonite. Therefore, in order to elucidate CEC attenuation under field conditions, a proper characterization of subsurface conditions, including soil properties, is essential.
- Concentrations of TCEP and TCPP did not decrease in the presence of field soil, whereas the concentration of the more hydrophobic TDCP was reduced by 57%. TDCP concentration was reduced by 71% on average by the field clay, which removed 37 and 56% of TCEP and TCPP, respectively. These results suggest that clay, rather than organic carbon, is the dominant sorbent for these CECs in subsurface systems.
- Biotransformation is another key mechanism for CEC attenuation in MAR systems. A determining factor for the biotransformation of trace organic chemicals in these systems is the redox condition prevailing in the subsurface. As electron acceptors are depleted during metabolism of organic matter (DOC) while reclaimed water is infiltrating, the redox state of the system transitions from an oxic setting towards suboxic to an anoxic redox state. The depletion of DOC and subsequent shift in redox conditions both have direct impacts on the performance of the microbial community and therefore attenuation of CECs.
- It is noteworthy that DOC removal was not affected by changes in temperature, indicating that the microorganisms responsible for DOC degradation were not sensitive to temperature changes within the studied range (8–30° C).
- Li et al. (2012, 2013) demonstrated that the diversity of the microbial community increased as BDOC is depleted when reclaimed water infiltrates. For some CECs, in particular those that are characterized as moderately degradable, this low BDOC environment (carbon starving) also resulted in better attenuation. Although microbial diversity may converge with depth, the redox state of the system will differ depending on the amount and makeup of carbon present in the initial feed. Both of these factors affected the degree of biotransformation, in particular for moderately degradable CECs.

- In general, biotransformation of CECs under carbon-starving and specific redox conditions was compound specific. Under low BDOC and suboxic conditions, atenolol was removed by greater than 95% in 3 days. The compound was removed less efficiently under oxic conditions (~85% removal) but notably less under high BDOC/anoxic conditions (<60% removal). Caffeine exhibited good removal (≥70%) under all redox and carbon conditions; however, trimethoprim was removed significantly faster under high BDOC conditions, the only compound to perform best under this condition throughout the study. Atenolol was very sensitive to BDOC concentrations and less sensitive to redox conditions.
- Moderately degradable compounds, with the exception of sulfamethoxazole, were removed significantly better under carbon-starving conditions than under high BDOC (>2 mg/L) conditions. Under oxic, carbon-starving conditions in controlled column experiments, complete removal was demonstrated for diclofenac, gemfibrozil, and naproxen within a retention time of 3 days. Sulfamethoxazole and DEET were removed more than 80% on average under oxic conditions during this study. Under field conditions, diclofenac and gemfibrozil exhibited good removal of greater than 70% on average after 9 days of travel under carbon-starving conditions but under carbon-rich conditions exhibited little to no removal after 14 days of travel. In the field, naproxen was completely removed within 9 days with carbon-starving conditions, compared to an average removal of only 60% after 14 days with carbon-rich feed. Carbon-starving conditions improved DEET removal by more than 40% on average, even with 5 fewer days of travel time. These results confirm that carbon-starving conditions characterized by low BDOC (~0.15–0.25 mg/L) improve removal efficiency of CECs.
- Enhanced removal was also demonstrated for the anticonvulsant dilantin (34%), the artificial sweetener acesulfame (64%), and the flame retardants TCEP (72%), TCPP (65%), and TDCP (58%) under low BDOC/oxic conditions after 7 days residence time, whereas no removal occurred during suboxic (14 days residence time) or anoxic soil column conditions with up to 42 days retention time.
- Overall, with the exception of a couple of compounds, lower temperatures did not significantly decrease CEC attenuation. Two of the compounds studied, trimethoprim and oxybenzone, were better removed as the operating temperature of the columns was reduced. Lower temperatures would have been expected to decrease microbial activity, in turn reducing CEC attenuation. This suggests that for compounds that are chemically related different microbial groups might be responsible for their transformation.

7.2. Lessons Learned

Findings of this study confirmed the high reliability and efficiency of MAR and in particular SAT in removing bulk organic carbon and trace organic chemicals as well as pathogens. Specific conclusions and recommendations are discussed below:

- Controlled laboratory studies simulating MAR conditions confirmed that pathogen inactivation does not fit linear filtration models. Inactivation and transport rates are often not constant and may slow down with distance. Laboratory and field data suggest that linear–log functions best describe pathogen removal.

- Findings from controlled laboratory studies confirmed by field monitoring campaigns revealed that reducing travel time in SAT to values of less than 30 days does not seem to result in a compromised water quality regarding chemical contaminants. During this study, a subsurface travel time of about 8 days in the aquifer was sufficient to remove the biodegradable portion of the DOC. As the character of the remaining DOC in the lower aquifer did not change significantly, based on UV_{254} absorbance values, the remaining organic carbon is likely composed of recalcitrant carbon fractions. In agreement with those findings, no measurable BDOC was detected in the lower aquifer (travel times >30 days), indicating that (1) the SAT system at the San Gabriel Spreading Grounds is functioning properly regarding removal of bulk organic matter; and (2) travel times of approximately 10 days are expected to result in sufficient performance. If denitrification of remaining nitrate concentrations during SAT is desired, slightly longer travel times (10–30 days) might be needed where anoxic conditions can prevail. The overall results for DOC removal confirm those observed by Laws et al. (2011) for the same field site.

- Similar to DOC, the data of sampling campaigns at the three field sites imply that attenuation of biodegradable CECs is mainly occurring during infiltration through the vadose zone and within the first 3 to 4 days in the saturated aquifer, especially where oxic to suboxic conditions prevail. More easily biodegradable CECs, such as atenolol, caffeine, and gemfibrozil, are in the range of or below detection limits after less than 4 days travel time. More hydrophobic compounds, such as fluoxetine and diphenhydramine, immediately sorb to the soil during infiltration and were not detected above detection limits in any groundwater samples at any site. The significant attenuation of the flame retardants TCPP and TDCP within the first few meters of infiltration is most probably due to sorption effects to soil organic matter or clay materials. As both flame retardants have poor biodegradability, they are not further attenuated in the aquifer, except where carbon-starving/oxic conditions prevail.

- Utilizing biotransformation rate constants for select CECs derived for predominant redox conditions (oxic, suboxic, anoxic) in controlled laboratory-scale studies allowed an accurate prediction of CEC removal under field conditions during short travel times in SAT (<30 days).

7.3. Implementations

In 2013, the SWRCB endorsed a concept proposed by Drewes et al. (2008) and Dickenson et al. (2009) following the recommendations of a Science Advisory Committee to ensure proper performance of MAR operations regarding the removal of CECs (Drewes et al., 2013). The SWRCB suggested a combination of appropriate surrogate parameters and health- and performance-based indicator chemicals for monitoring of SAT projects. These studies demonstrated that changes in bulk parameters (e.g., BDOC) did correlate with changes of indicator CECs in the subsurface (Drewes et al., 2011). Basically, selecting multiple indicators representing a broad range of properties and amenability for biotransformation permits the study of how changes in retention time or redox zone affect the degree of removal achieved during MAR.

The concept of using health- and performance-based indicators has been adopted for this study and augmented with additional compounds proposed by Laws et al. (2011) that are relevant for a performance assessment of MAR field sites (e.g., artificial sweetener: acesulfame; pharmaceuticals: atenolol, carbamazepine, diclofenac, gemfibrozil, meprobamate, primidone, sulfamethoxazole, trimethoprim; flame retardants: TCEP, TCPP; stimulant: caffeine; X-ray contrast media: iopromide).

On the basis of these concepts, we recommend monitoring the easy to intermediate biodegradable compounds iopromide, atenolol, and gemfibrozil as performance indicator compounds to ensure the achievement of the 90% removal during SAT required by the California Department of Public Health, which could be achieved in less than 30 days travel time based on the findings of this study.

Refractory CECs, such as primidone and carbamazepine, are very suitable organic conservative tracers to assess the impact of dilution from native groundwater. These CECs should be included in monitoring programs to assure that observed removal is not due to dilution with native groundwater.

Shorter travel times would have the advantage of increasing the total recharge capacity of SAT facilities. If SAT systems with shorter retention times are being favored to remove BDOC and CECs, monitoring wells should be selected that represent relative accurate travel times (with a narrow flow path distribution). These can be calibrated using the reported biotransformation rate constants for performance indicator compounds, and a removal percentage for these wells can be defined. Subsequent monitoring should include these performance indicators and conservative tracers (e.g., primidone) to verify the expected removal percentage and assure proper performance during long term SAT. After proper performance has been demonstrated for a specified period of time, production wells with shorter travel times could be utilized.

CEC concentrations in the influent of the test basin at the California site exhibited high fluctuations over time. Variations for some of the target analytes (e.g., acesulfame, sulfamethoxazole, gemfibrozil) were more significant than expected, and further research is needed to explain the reason for this variability; however, such variations in the source water quality have implications for the assessment of how changes in retention time or redox zone affect the degree of CEC removal achieved during SAT, especially for sites where shorter travel times are desired. Field monitoring results revealed that feed water variations for biodegradable CECs were buffered during SAT and did not seem to affect the observed performance considering travel times of approximately 30 days.

Varying operational factors can have adverse effects for the attenuation of pathogens. Changing water compositions with different ion strengths (alternating stormwater and reclaimed water in the same spreading basin) have the potential to mobilize previously retained microorganisms, allowing greater transport. Where shorter subsurface retention times are implemented, steady groundwater velocities should be maintained, suggesting a well pumping regime with steady extraction volumes and flow rates.

References

Abel, C. D. T.; Sharma, S. K.; Malolo, Y. N.; Maeng, S. K.; Kennedy, M. D.; Amy, G. L. Attenuation of Bulk Organic Matter, Nutrients (N and P), and Pathogen Indicators During Soil Passage: Effect of Temperature and Redox Conditions in Simulated Soil Aquifer Treatment (SAT). *Water Air Soil Poll.* **2012,** *223,* 5205–5220.

Ahmed, W.; Wan, C.; Goonetileke, A.; Gardner, T. Evaluating sewage-associated JCV and BKV polyomaviruses for sourcing human fecal pollution in a coastal river in Southeast Queensland, Australia. *J. Environ. Qual.* **2010,** *39,* 1743–1750.

Alidina, M.; Hoppe-Jones, C.; Yoon, M.; Hamadeh, A.; Li, D.; Drewes, J. E. Occurrence of Trace Organic Chemicals in Wastewater Effluent in Western Saudi Arabia. *Sci. Total Environ.* **2014,** *478,* 152–162.

Alidina, M.; Li, D.; Ouf, M.; Drewes, J. E. Role of Primary Substrate Composition and Concentration on Attenuation of Trace Organic Chemicals in Managed Aquifer Recharge Systems. *J. Environ. Manage.* **2014**, *144*, 58–66.

American Public Health Association (APHA). Standard methods for the examination of water and wastewater. Washington, DC, **2012**.

Amy, G.; Drewes, J. E. Soil–aquifer treatment (SAT) as a natural and sustainable wastewater reclamation/reuse technology: Fate of wastewater effluent organic matter (EfOM) and trace organic compounds. *Environ. Monit. Assess.* **2007,** *129*, 1–3, 19–26.

Anders, R.; Yanko, W. A.; Schroeder, R. A.; Jackson, J. L. Virus fate and transport during recharge using recycled water at a research field site in the Montebello Forebay, Los Angeles County, California, 1997–2000. U.S. Geological Survey Scientific Investigations Report 2004-5161. **2004**, 65 pp.

Anderson, P.; Denslow, N.; Drewes, J. E.; Olivieri, A.; Schlenk, D.; Snyder, S. Final Report Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water Recommendations of a Science Advisory Panel, State Water Resources Control Board, Sacramento, CA. **2010**.

Asano, T.; Burton, F.; Leverenz, H.; Tsuchihashi, R.; Tchobanoglous, G. *Water Reuse Issues, Technologies, and Applications*. McGraw Hill, 1st ed. **2006**.

Aurora Water. Prairie Waters Project Fact Sheet. **2012**. https://www.auroragov.org/cs/groups/public/documents/document/002347.pdf

Aziz, C. E.; Newell, C. J.; Gonzales, J. R.; Haas, P.; Clement, T. P.; Sun, Y. BIOCHLOR: Natural attenuation decision support system v. 1.0, User's manual. U.S. EPA Report EPA/600/R-00/008. Cincinnati, Ohio: U.S. Environmental Protection Agency. **2000**.

Bales, R. C.; Gerba, C. P.; Grondin, G. H.; Jensen, S. L. Bacteriophage transport in sandy soil and fractured turf. *Appl. Environ. Microbiol.* **1989,** *55*, 2061–2067.

Barbieri, M.; Carrera, J.; Ayora, C.; Sanchez-Vila, X.; Licha, T.; Nödler, K.; Osorio, V.; Pérez, S.; Köck-Schulmeyer, M.; López de Alda, M.; Barceló, D. Formation of diclofenac and sulfamethoxazole reversible transformation products in aquifer material under denitrifying conditions: Batch experiments. *Sci. Total Environ.* **2012,** *426,* 256–263.

Barron, L.; Havel, J.; Purcell, M.; Szpak, M.; Kelleher, B.; Paull, B. Predicting sorption of pharmaceuticals and personal care products onto soil and digested sludge using artificial neural networks. *Analyst* **2009,** *134*(4), 621–808.

Baumgarten, B.; Jahrig, J.; Reemtsma, T.; Jekel, M. Long term laboratory column experiments to simulate bank filtration: Factors controlling removal of sulfamethoxazole. *Water Res.* **2011,** *45*, 211–220.

Beulke, S.; Brown, C. D. Evaluation of methods to derive pesticide degradation parameters for regulatory modeling. *Biol. Fertil. Soils* **2001,** *33*, 558–564.

Bovee, T. F. H.; Helsdingen, R. J. R.; Hamers, A. R. M.; Brouwer, B. A.; Nielen, M. W. F. Recombinant cell bioassays for the detection of (gluco)corticosteroids and endocrine-disrupting potencies of several environmental PCB contaminants. *Anal. Bioanal. Chem.* **2011,** *401*(3), 873–882.

Burke, V.; Richter, D.; Hass, U.; Duennbier, U.; Greskowiak, J.; Massmann, G. Redox-dependent removal of 27 organic trace pollutants: compilation of results from tank aeration experiments. *Environ. Earth Sci.* **2013,** DOI 10.1007/s12665-013-2762-8.

Buser, H.; Poiger, T.; Muller, M. Occurrence and Fate of the Pharmaceutical Drug Diclofenac in Surface Waters: Rapid Photodegradation in a Lake. *Environ. Sci. Technol.* **1998,** *32*(22), 3449–3456.

Charles, K. J.; Shore, J.; Sellwood, J.; Laverick, M.; Hart, A.; Pedley, S. Assessment of the stability of human viruses and coliphage in groundwater by PCR and infectivity methods. *J. Appl. Microbiol.* **2005,** *106*, 1827–1837.

Chu, Y.; Jin, Y.; Baumann, T.; Yates, M. V. Effect of soil properties on saturated and unsaturated virus transport through columns. *J. Environ. Qual.* **2003**, *32*, 2017–2025.

Cleary, R.; Ungs, M. J. Analytical models for groundwater pollution and hydrology. Report No. 78-WR-15. Princeton, NJ: Water Resources Program, Princeton University. **1978**.

Clement, T. P.; Truex, M. J.; Lee, P. A case study for demonstrating the application of U.S. EPA's monitored natural attenuation screening protocol at a hazardous waste site. *J. Contamin. Hydrol.* **2002,** *59*(1–2), 133–162.

Conkle, J. L.; Gan, J.; Anderson, M. A. Degradation and sorption of commonly detected PPCPs in wetland sediments under aerobic and anaerobic conditions. *J. Soils Sediments* **2012,** *12*, 1164–1173.

Cory, R. M.; McKnight, D. M. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environ. Sci. Technol.* **2005,** *39*, 8142–8149.

Dickenson, E. R. V.; Drewes, J. E.; Sedlak, D. L.; Wert, E.; Snyder, S. A. Applying Surrogates and Indicators To Assess Removal Efficiency of Trace Organic Chemicals During Chemical Oxidation of Wastewater. *Environ. Sci. Technol.* **2009,** *43*, 6242–6247.

Dickenson, E.; Drewes, J. E.; Snyder, S. A.; Sedlak, D. L. Indicator Compounds: An Approach for Using Monitoring Data To Quantify the Occurrence and Fate of Wastewater-Derived Contaminants in Surface Waters. *Water Res.* **2011,** *45,* 1199–1212.

Domenico, P. A. An analytical model for multidimensional transport of a decaying contaminant species. *J. Hydrol.* **1987,** *91,* 49–58.

Domenico, P. A.; Robbins, G. A. A new method of contaminant plume analysis. *Ground Water* **1985,** *23*(4), 476–485.

Drewes, J. E. Final Report: Performance Assessment of Surface Spreading Operations Receiving Different Blends of Tertiary/RO Treated Waters. Water Replenishment District of Southern California, Lakewood, CA, **2010**.

Drewes, J. E.; Jekel, M. Behavior of DOC and AOX using advanced treated wastewater for groundwater recharge. *Water Res.* **1998,** *32,* 3125–3133.

Drewes, J. E.; Fox, P. Effect of drinking water sources on reclaimed water quality in water reuse systems. *Water Environ. Res.* **2000,** *72*(3), 353–362.

Drewes, J. E.; Khan, S. Water Reuse for Drinking Water Augmentation. Edzwald, J., Ed.; *Water Quality and Treatment* (6th ed.). American Water Works Association. Denver, CO. **2010**.

Drewes, J. E.; Heberer, T.; Rauch, T.; Reddersen, K. Fate of Pharmaceuticals During Ground Water Recharge. *Ground Water Monit. R.* **2003,** *23,* 64–72.

Drewes, J. E.; Hoppe, C.; Jennings, T. Fate and transport of N-nitrosamines under conditions simulating full-scale groundwater recharge operations. *Water Environ. Res.* **2006,** *78,* 13, 2466–2473.

Drewes, J. E.; Sedlak, D. L.; Snyder, S.; Dickenson, E. R. V. Development of indicators and surrogates for chemical contaminant removal during wastewater treatment and reclamation. WateReuse Foundation, Alexandria, VA, **2008**.

Drewes, J. E.; Dickenson, E. R. V.; Snyder, S. Development of surrogates to determine the efficacy of groundwater recharge systems for the removal of trace organic chemicals. WateReuse Research Foundation, Alexandria, VA, **2011**.

Drewes, J. E.; Anderson, P.; Denslow, N.; Olivieri, A.; Schlenk, D.; Snyder, S. A.; Maruya, K. A. Designing Monitoring Programs for Chemicals of Emerging Concern in Potable Reuse—What to include and what not to include? *Water Sci. Technol.* **2013,** *67*(2), 433–439.

Fox, P.; Houston, S.; Westerhoff, P.; Drewes, J. E.; Nellor, M.; Yanko, W.; Baird, R.; Rincon, M.; Arnold, R.; Lansey, K.; Bassett, R.; Gerba, C.; Karpiscak, M.; Amy, G.; Reinhard, M. Soil–aquifer treatment for sustainable water reuse. American Water Works Association and AWWA Research Foundation, Eds. Tempe, AZ, **2001**.

Gerba, C. P. Virus occurrence and survival in the environmental waters in Bosch, A., Ed.; *Human Viruses in Water*. Elsevier: Amsterdam, **2007**, pp. 91–108.

Gerba, C. P.; Yates, M. Y., Yates, S. R. Quantitation of factors controlling viral and microbial transport in the subsurface in Hurst, C., Ed.; *Modeling the Environmental Fate of Microorganisms*. American Society for Microbiology, Washington, DC, **1991**, pp. 77–88.

Gregory, J. B.; Litaker, R. W.; Noble, R. T. Rapid one-step quantitative reverse transcriptase PCR assay with competitive internal positive control for detection of enteroviruses in environmental samples. *Appl. Environ. Microbiol.* **2006,** *72,* 3960–3967.

Grünheid, S.; Amy, G.; Jekel, M. Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. *Water Res.* **2005,** *39,* 3219–3228.

Guyonnet, D. An analytical model for estimating impact of pollutant sources on groundwater. MISP_v1. User's guide. BRGM report RP-51040-FR, **2001**.

Haramoto, E.; Katatyama, H.; Ohgaki, S. Detection of noroviruses in tap water in Japan by means of a new method for concentrating enteric viruses in large volumes of freshwater. *Appl. Environ. Microbiol.* **2004,** *70,* 2154–2160.

Haramoto, E.; Katatyama, H.; Oguma, K.; Ohgaki, S. Recovery of naked viral genomes in water by virus concentration methods. *J. Virol. Methods* **2007,** *142,* 169–173.

Heim, A.; Ebnet, C.; Harste, G.; Pring-Akerblom, P. Rapid and quantitative detection of human adenovirus DNA by real-time PCR. *J. Med. Virol.* **2003,** *70,* 228–239.

Hinsby, K.; McCay, L. D.; Jorgensen, P.; Lenczewski, M.; Gerba, C. P. Fracture aperture measurements and migration of solutes, viruses, and immiscible creosote in a column of clay-till. *Ground Water* **1996,** *34,* 1065–1075.

Hoppe-Jones, C.; Oldham, G.; Drewes, J. E. Attenuation of total organic carbon and unregulated trace organic chemicals in U.S. riverbank filtration systems. *Water Res.* **2010,** *44,* 4643–4659.

Hoppe-Jones, C.; Dickenson, E.; Drewes, J. E. Role of Microbial Adaptation and Bioavailable Substrate on the Attenuation of Trace Organic Chemicals during Groundwater Recharge. *Science of the Total Environment* **2012**, *437,* 137–144.

Hua, J.; An, P.; Winter, J.; Gallert, C. Elimination of COD, microorganisms and pharmaceuticals from sewage by trickling through sandy soil below leaking sewers. *Water Res.* **2003,** *37,* 4395–4404.

Huyakorn, P. S.; Mercer, J. W.; Ward, D. S. Finite element matrix and mass balance computational schemes for transport in variably saturated porous media. *Water Resour. Res.* **1985,** *21,* 346–358.

Ikner, L. A.; Soto-Beltran, M.; Bright, K. R. New method using a positively charged microporous filter and ultrafiltration for concentration of viruses from tap water. *Appl. Environ. Microbiol.* **2011,** *77,* 3500–3506.

Ives, R. L.; Kamarainen, A. M.; John, D. E.; Rose, J. B. Use of Cell Culture To Assess Cryptosporidium parvum Survival Rates in Natural Groundwaters and Surface Waters. *Appl. Environ. Microbiol.* **2007,** *73*(18), 5968–5970.

John, J. E.; Rose, J. B. Review of Factors Affecting Microbial Survival in Groundwater. *Environ. Sci. Technol.* **2005,** *39,* 7345–7356.

Jothikumar, N.; Kang, G.; Hill, V. R. Broadly reactive TaqMan assay for real-time RT-PCR detection of rotavirus in clinical and environmental samples. *J. Virol. Methods* **2009,** *155,* 126–131.

Kageyama, T.; Kojima, S.; Shinohara, M.; Uchida, K.; Fukushi, S.; Hoshino, F. B.; Takeda, N.; Katayama, K. Broadly reactive and highly sensitive assay for Norwalk-like

viruses based on real-time quantitative reverse transcription-PCR. *J. Clin. Microbiol.* **2003,** *41,* 1548–1557.

Kitajima, M.; Oka, T.; Takagi, H.; Tohya, Y.; Katayama, H.; Takeda, N.; Katayama, K. Development and application of a broadly reactive real-time reverse transcription-PCR assay for detection of murine noroviruses. *J. Virol. Methods* **2010,** *169,* 269–273.

Kitajima, M.; Hata, A.; Yamashita, T.; Haramoto, E.; Minagawa, H.; Katayama, H. Development of a reverse transcription-quantitative PCR system for detection and genotyping of Aichi viruses in clinical and environmental samples. *Appl. Environ. Microbiol.* **2013,** *79,* 3952–3958.

Kitajima, M.; Iker, B. C.; Pepper, I. L.; Gerba, C. P. Relative abundance and treatment reduction of viruses during wastewater treatment processes—identification of potential viral indicators. *Sci. Total Environ.* **2014,** doi:10.1016/j.scitotenv.2014.04.087.

Kugathas, S.; Sumpter, J. P. Synthetic Glucocorticoids in the Environment: First Results on Their Potential Impacts on Fish. *Environ. Sci. Technol.* **2011,** *45*(6), 2377–2383.

Lance, J. C.; Gerba, C. P.; Melnick, J. L. Virus movement in soil columns flooded with secondary sewage effluent. *Appl. Environ. Microbiol.* **1976,** *32,* 520–526.

Lange, F. T.; Scheurer, M.; Brauch, H. J. Artificial sweeteners—a recently recognized class of emerging environmental contaminants: a review. *Anal. Bioanal. Chem.* **2012,** *403,* 2503–2518.

Laws, B. V.; Dickenson, E. R. V.; Johnson, T. A.; Snyder, S. A.; Drewes, J. E. Attenuation of contaminants of emerging concern during surface-spreading aquifer recharge. *Sci. Total Environ.* **2011,** *409,* 1087–1094.

Leary, T. P.; Erker, J. C.; Chalmers, M. L.; Cruz, A. T.; Wetzel, J. D.; Desai, S. M.; Mushahwar, I. K.; Dermody, T. S. Detection of mammalian reovirus RNA by using reverse transcription-PCR: sequence diversity within the lambda3-encoding L1 gene. *J. Clin. Microbiol.* **2002,** *40,* 1368–1375.

Li, D.; Sharp, J. O.; Saikaly, P. E.; Ali, S.; Alidina, M.; Alarwi, M.; Keller, S.; Hoppe-Jones, C.; Drewes, J. E. Dissolved Organic Carbon Influences Microbial Community Composition and Diversity in Managed Aquifer Recharge Systems. *Appl. Environ. Microbiol.* **2012,** *78*(19), 6819–6828.

Li, D.; Alidina, M.; Ouf, M.; Sharp, J. O.; Saikaly, P.; Drewes, J. E. Microbial community evolution during simulated managed aquifer recharge in response to different biodegradable dissolved organic carbon (BDOC) concentrations. *Water Res.* **2013,** *47,* 2421–2430.

Lin, A. Y. C.; Lin, C. A.; Tung, H. H.; Chary, N. S. Potential for biodegradation and sorption of acetaminophen, caffeine, propranolol and acebutolol in lab-scale aqueous environments. *J. Hazard. Mater.* **2010,** *183,* 242–250.

Loeffler, D.; Römbke, J.; Meller, M.; Ternes, T. A. Fate of pharmaceuticals in water/sediment systems. *Environ. Sci. Technol.* **2005,** *39,* 5209–5218.

Maeng, S. K.; Ameda, E.; Sharma, S. K.; Grützmacher, G.; Amy, G. L. Organic micropollutant removal from wastewater effluent-impacted drinking water sources during bank filtration and artificial recharge. *Water Res.* **2010,** *44*(14), 4004–4014.

Maeng, S. K.; Sharma, S. K.; Lekkerkerker-Teunissen, K.; Amy, G. L. Occurrence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: a review. *Water Res.* **2011,** *45,* 3015–3033.

Mahalanabis, M.; Reynolds, K. A.; Pepper, I. L.; Gerba, C. P. Comparison of multiple passage integrated cell culture-PCR and cytopathogenic effects in cell culture for the assessment of poliovirus in water. *J. Food Environ. Virol.* **2010,** *2,* 225–230.

Maier, R. M.; Pepper, I. L.; Gerba, C. P. *Environmental Microbiology* (2nd ed.). Academic Press: San Diego, CA, **2009**.

Martin-Hayden, J.; Robbins, G. A. Plume Distortion and Apparent Attenuation Due to Concentration Averaging in Monitoring Wells. *Ground Water* **1997,** *35*(2), 339–346.

Massmann, G.; Greskowiak, J.; Dünnbier, U.; Zuehlke, S.; Knappe, A.; Pekdeger, A. The impact of variable temperatures on the redox conditions and the behaviour of pharmaceutical residues during artificial recharge. *J. Hydrol.* **2006,** *328,* 141–156.

Massmann, G.; Dünnbier, U.; Heberer, T.; Taute, T. Behaviour and redox sensitivity of pharmaceutical residues during bank filtration—Investigations of residues of phenazone-type analgesics. *Chemosphere* **2008,** *71,* 1476–1485.

McCray, J. E.; Kirkland, S. L.; Siegrist, R. L.; Thyne, G. D. Model parameters for simulating fate and transport of onsite wastewater nutrients. *Ground Water* **2005,** *43*(4), 628–639.

Monteiro, S. C.; Boxall, A. B. A. Factors affecting the degradation of pharmaceuticals in agricultural soils. *Environ. Toxicol. Chem.* **2010,** *28,* 2546–2554.

Montgomery-Brown, J.; Reinhard, M.; Drewes, J. E.; Fox, P. Behavior of alkylphenol polyethoxylate metabolites during soil aquifer treatment. *Water Res.* **2003,** *37,* 3672–3681.

National Water Research Institute (NWRI). Regulatory Aspects of Direct Potable Reuse in California. A White Paper. Fountain Valley, CA. **2010**.

NWRI. BDOC as a performance measure for organics removal in groundwater recharge of recycled water. Independent Advisory Panel Final Report NWRI-2012-05, California Department of Public Health, Fountain Valley, CA, **2012**.

Newell, C. J.; McLeod, R. K.; Gonzales, J. R. BIOSCREEN: Natural attenuation decision support system user's manual. EPA/600/R-96/087. Ada, OK, Robert S. Kerr Environmental Research Center, **1996**.

Odermatt, A.; Gumy, C.; Atanasov, A. G.; Dzyakanchuk, A. A. Disruption of glucocorticoid action by environmental chemicals: Potential mechanisms and relevance. *J. Steroid Biochem. Mol. Biol.* **2006,** *102*(1–5), 222–231.

Oka, T.; Katayama, K.; Hansman, G. S.; Kageyama, T.; Ogawa, S.; Wu, F. T.; White, P. A.; Takeda, N. Detection of human sapovirus by real-time reverse transcription-polymerase chain reaction. *J. Med. Virol.* **2006,** *78,* 1347–1353.

Oldham, G. Characterization and modeling of the transport of selected organic micropollutants at laboratory and field scales in a riverbank filtration system. MSc. Thesis, Dept. of Civil and Environmental Engineering. Colorado School of Mines, Golden, CO, **2008**.

Pang, L. Microbial removal rates in subsurface media estimated from published studies of field experiments and large soil cores. *J. Environ. Qual.* **2009,** *38,* 1531–1559.

Pietikäinen, J.; Pettersson, M.; Bååth, E. Comparison of temperature effects on soil respiration and bacterial and fungal growth rates. *FEMS Microbiol. Ecol.* **2005**, *52,* 49–58.

Quanrud, D.; Arnold, R.; Wilson, L. G.; Gordon, H.; Graham, D.; Amy, G. Fate of organics during column studies of soil aquifer treatment. *J. Environ. Eng.* **1996,** *122,* 314–321.

Quanrud, D. M.; Carroll, S. M.; Gerba, C. P.; Arnold, R. G. Virus removal during simulated soil–aquifer treatment. *Water Res.* **2003,** *37,* 753–762.

Quezada, C. R.; Clement, T. P.; Lee, K. K. Generalised Sagar, B. 1982. Dispersion in three dimensions: Approximate analytical solutions. *ASCE J. Hydraulic Div.* **2004,** *108,* 47–62.

Rauch, T.; Drewes, J. E. Assessing the removal potential of soil–aquifer treatment systems for bulk organic matter. *Water Sci. Technol.* **2004,** *50*(2), 245–253.

Rauch, T.; Drewes, J. E. Quantifying biological organic carbon removal in groundwater recharge systems. *J. Environ. Eng.* **2005,** *131,* 909–923.

Rauch-Williams, T; Drewes, J. E. Using soil biomass as an indicator for the biological removal of effluent-derived organic carbon during soil infiltration. *Water Res.* **2006,** *40,* 961–968.

Rauch-Williams, T.; Hoppe-Jones, C.; Drewes, J. E. The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge. *Water Res.* **2010,** *44,* 449–460.

Regnery, J.; Mazahirali, A.; Wing, A. D.; Gerba, C. P.; Dickenson, E. R. V.; Snyder, S. A.; Drewes, J. E. Attenuation of Microbial and Chemical Contaminants During Groundwater Recharge in Indirect Potable Reuse Systems: A Review. *Crit. Rev. Env. Sci. Tec.* (in review).

Rosario, K.; Symonds, E. M.; Sinigalliano, C.; Stewart, J.; Breitbart, M. Pepper Mild Mottle Virus as an Indicator of Fecal Pollution. *Appl. Environ. Microbiol.* **2009,** *75,* 7261–7267.

Sagar, B. Dispersion in three dimensions: Approximate analytic solutions, *J. Hydraul. Div. Proc. Am. Soc. Civ. Eng.*, **1982,** *108 HY1*, 47–62.

Santamaría, J.; Brusseau, M. L.; Araujo, J.; Orosz-Coghlan, P.; Blanford, W. J.; Gerba, C. P. Transport and Retention of Cryptosporidium Parvum Oocysts in Sandy Soils. *J. Environ. Qual.* **2012,** *41,* 1246–1252.

Santhi, C.; Arnold, J. G.; Williams, J. R.; Dugas, W. A.; Srinivasan, R.; Hauck, L. M. Validation of the SWAT model on a large river basin with point and nonpoint sources. *J. Am. Water Resourc. Assoc.* **2001,** *37*(5), 1169–1188.

Sargis, R. M.; Johnson, D. N.; Choudhury, R. A.; Brady, M. J. Environmental endocrine disruptors promote adipogenesis in the 3T3-L1 cell line through glucocorticoid receptor activation. *Obesity* **2010,** *18*(7), 1283–1288.

Schaap, M. G.; Leij, F. J.; van Genuchten, M. T. Rosetta: a computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions. *J. Hydrol.* **2001,** *251,* 163–176.

Scheytt, T.; Mersmann, P.; Lindstädt, R.; Heberer, T. Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. *Chemosphere* **2005,** *60,* 245–253.

Schroeder, R. A. Water-quality changes and organic-carbon characterization during recharge with recycled water at a research basin in Montebello Forebay, Los Angeles County, California, 1991–1996. U.S. Geological Survey Scientific Investigations Report 03-4146, **2003,** p. 279.

Sidhu, J. P. S.; Toze, S. Assessment of pathogen survival potential during managed aquifer recharge with diffusion chambers. *J. Appl. Microbiol.* **2012,** *113*(3), 693–700.

Sidhu, J. P. S.; Toze, S.; Hodgers, L.; Shackelton, M.; Barry, K.; Page, D. Pathogen inactivation during passage of stormwater through a constructed reedbed and aquifer transfer, storage and recovery. *Water Sci. Technol.* **2010,** *62,* 1190–1197.

Sotelo, J.; Ovejero, G. Study of Natural Clay Adsorbent Sepiolite for the Removal of Caffeine from Aqueous Solutions: Batch and Fixed-Bed Column Operation. *Water Air Soil Poll.* **2013,** *224*(1466), 1–15.

State of California. Recycled Water Policy. Attachment A. Requirements for Monitoring Constituents of Emerging Concern for Recycled Water. Sacramento, CA. 17 January **2013**.

Stavreva, D. A.; George, A. A.; Klausmeyer, P.; Varticovski, L.; Sack, D.; Voss, T. C.; Schiltz, R. L.; Blazer, V. S.; Iwanowicz, L. R.; Hager, G. L. Prevalent Glucocorticoid and Androgen Activity in US Water Sources. *Sci. Rep.* **2012,** *2,* 937.

Taylor, R.; Cronin, A.; Pedley, S.; Barker, S.; Atkinson, T. The implication of groundwater velocity variation on microbial transport and wellhead protection— review of field evidence. *FEMS Microbiol. Ecol.* **2004,** *49,* 17–26.

Teerlink, J. Occurrence and fate of trace organic chemicals in soil treatment units associated with onsite wastewater treatment. PhD Dissertation, Dept. of Civil and Environmental Engineering. Colorado School of Mines, Golden, CO, **2012**.

Teerlink, J.; Hering, A.; Higgins, C.; Drewes, J. E. Variability of trace organic chemical concentrations in raw wastewater at three distinct sewershed scales. *Water Res.* **2012,** *46,* 3261–3271.

Toze, S.; Bekele, E.; Page, D.; Sidhu, J.; Shackelton, M. Use of static Quantitative Microbial Risk Assessment to determine pathogen risks in an unconfined carbonate aquifer used for Managed Aquifer Recharge. *Water Res.* **2010,** *44,* 1038–1049.

Trujillo, A. A.; McCaustland, K. A.; Zheng, D. P.; Hadley, L. A.; Vaughn, G.; Adams, S. M.; Ando, T.; Glass, R. I.; Monroe, S. S. Use of TaqMan real-time reverse transcription-PCR for rapid detection, quantification, and typing of norovirus. *J. Clin. Microbiol.* **2006,** *44,* 1405–1412.

U.S. Environmental Protection Agency (US EPA). Onsite Wastewater Treatment Systems Manual. Cincinnati, OH, **2002**.

Vaidya, S. R.; Chitamber, S. D.; Arankalie, V. A. Polymerase chain reaction–based prevalence of hepatitis A, hepatitis E and TT viruses in sewage from an endemic area. *J. Hepatol.* **2002,** *37,* 131–136.

Van Genuchten, M. T. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* **1980,** *44*(5), 892–898.

Vanderford, B. J.; Snyder, S. A. Analysis of pharmaceuticals in water by isotope dilution liquid chromatography/tandem mass spectrometry. *Environ. Sci. Technol.* **2006,** *40,* 7312–7320.

Wexler, E. J. Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow. USGS—TWRI Book 3, Chapter B7. United States Geological Survey: Reston, VA, **1992**.

Wiese, B.; Massmann, G.; Jekel, M.; Heberer, T.; Dünnbier, U.; Orlikowski, D.; Grützmacher, G. Removal Kinetics of Organic Compounds and Sum Parameters under Field Conditions for Managed Aquifer Recharge. *Water Res.* **2011,** *45,* 4939–4950.

Wilson, L. G.; Amy, G. L.; Gerba, C. P.; Gordon, H.; Johnson, B.; Miller, J. Water quality changes during soil aquifer treatment of tertiary effluent. *Water Environ. Res.* **1995,** *67,* 371–376.

Wing, A. D. Enhanced removal of emerging contaminants during managed aquifer recharge using optimized operating conditions. MSc thesis, Dept. of Civil and Environmental Engineering. Colorado School of Mines, Golden, CO, **2013**.

Xu, J.; Wu, L.; Chang, A. C. Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. *Chemosphere* **2009,** *77,* 1299–1305.

Yamamoto, H.; Nakamura, Y.; Moriguchi, S.; Nakamura, Y.; Honda, Y.; Tamura, I.; Hirata, Y.; Hayashi, A.; Sekizawa, J. Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments. *Water Res.* **2009,** *43,* 351–362.

Yu, L.; Fink, G.; Wintgens, T.; Melin, T.; Ternes, T. A. Sorption behavior of potential organic wastewater indicators with soils. *Water Res.* **2009,** *43,* 951–960.

Yu, L.; Liu, Y.; Wu, L. Sorption and degradation of pharmaceuticals and personal care products (PPCPs) in soils. *Environ. Sci. Poll. Res.* **2013,** *20,* 4261–4267.

Zhang, T.; Breitbart, M.; Lee, W. H.; Run, J. Q.; Wei, C. L.; Soh, S. W.; Hibberd, M. L.; Liu, E. T.; Rohwer, F.; Ruan, Y. RNA viral community in human feces: prevalence of plant pathogenic viruses. *PLoS Biol.* **2006,** *4,* e3.

Zwiener, C.; Frimmel, F. H. Short-term tests with a pilot sewage plant and biofilm reactors for the biological degradation of the pharmaceutical compounds clofibroc acid, ibuprofen, and diclofenac. *Sci. Total Environ.* **2003,** *309,* 201–211.

Appendix

Table A.1. Recoveries for chemicals of emerging concern analyzed at CSM.

Compounds (ESI^+)	Recovery CSM* (%)	Compounds (ESI^-)	Recovery CSM* (%)
Acetaminophen	85 ± 15	Acesulfame	<30
Amitriptyline	<30	Bisphenol A	73 ± 7
Atenolol	100 ± 10	Diclofenac	71 ± 18
Atrazine	58 ± 7	Gemfibrozil	116 ± 11
Benzophenone	97 ± 8	Ibuprofen	67 ± 15
Caffeine	72 ± 7	Ketoprofen	54 ± 13
Carbamazepine	81 ± 8	Methylparaben	n.a.
DEET	70 ± 6	Naproxen	71 ± 10
Diazepam	58 ± 8	Propylparaben	81 ± 13
Dilantin	76 ± 9	Sucralose	85 ± 17
Diphenhydramine	47 ± 16	Triclocarban	<30
Fluoexetine	<30	Triclosan	<30
Iopromide	123 ± 8		
Meprobamate	102 ± 12		
Oxybenzone	n.a.		
Primidone	80 ± 18		
Sulfamethoxazole	90 ± 12		
TCEP	68 ± 12		
TCPP	68 ± 12		
TDCP	68 ± 12		
Trimethoprim	114 ± 10		

Table A.2a. Field parameter readings of sampled wells and test basin at the San Gabriel Spreading Grounds during campaign #1.

Sample	Date	Time	Water level [ft]	Travel time [d]	Conductivity [µS/cm]	O_2 [mg/L]	Temp. [˚C]	pH	E_0 [mV]
Influent	12/10/12	1:52 PM	n.a.	n.a.	806	7.3	24.8	7.3	246
Influent	12/10/12	4:00 PM	n.a.	n.a.	797	7.1	24.5	7.1	n.a.
Influent	12/11/12	8:45 AM	n.a.	n.a.	971	6.1	24.3	6.8	n.a.
Influent	12/12/12	10:40 AM	n.a.	n.a.	946	n.a.	24.3	7.2	n.a.
Influent	12/17/12	1:00 PM	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
WP-Z	12/10/12	2:38 PM	18.3	0.45	810	0.9	23.9	6.8	211
WP-Z	12/11/12	9:00 AM	18.6	0.45	922	0.8	23.0	6.7	n.a.
MLS-9	12/11/12	11:15 AM	n.a.	0.46	896	n.a.	23.7	7.4	n.a.
MLS-14	12/10/12	3:10 PM	n.a.	0.75	810	2.0	24.4	6.8	303
MLS-14	12/11/12	11:35 AM	n.a.	0.75	805	1.4	24.4	7.0	229
MLS-20	12/11/12	11:56 AM	n.a.	1.79	844	0.4	24.2	7.0	232
PR-9	12/12/12	9:35 AM	19.4	3.50	851	0.4	23.7	7.0	286
PR-11	12/12/12	10:31 AM	21.2	3.50	838	0.3	23.5	7.0	265
PR-19	12/17/12	12:50 PM	21.9	8.30	889	1.4	24.6	7.6	n.a.
PR-13	1/7/13	11:40 AM	12.7	30.80	932	4.6	23.5	7.7	n.a.
PR-8	1/11/13	1:50 PM	14.5	35.30	948	0.8	24.9	7.8	n.a.
PR-10	1/22/13	12:00 PM	22.1	43.60	894	2.0	24.9	7.6	n.a.
PR-15	12/11/12	10:00 AM	26.4	49.50	925	0.8	26.2	7.6	n.a.
PR-14	12/11/12	9:45 AM	26.6	128.50	917	0.5	27.6	7.8	n.a.

n.a. = Data not available

Table A.2b. Field parameter readings of sampled wells and test basin at the San Gabriel Spreading Grounds during campaign #2.

Sample	Date	Time	Water level [ft]	Travel time [d]	Conductivity [µS/cm]	O_2 [mg/L]	Temp. [˚C]	pH	E_0 [mV]
Influent	4/24/13	1:50 PM	n.a.	n.a.	904	4.0	24.8	6.9	n.a.
Influent	4/25/13	9:10 AM	n.a.	n.a.	998	5.6	25.0	6.9	n.a.
Influent	4/26/13	10:00 AM	n.a.	n.a.	996	5.2	24.9	7.0	n.a.
Influent	5/1/13	2:30 PM	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
WPZ	4/24/13	2:30 PM	19.7	0.45	923	3.3	22.6	7.2	212
WPZ	4/25/13	8:50 AM	n.a.	0.45	995	2.1	23.9	6.9	210
MLS-10	4/24/13	2:07 PM	n.a.	0.50	928	1.2	n.a.	6.9	n.a.
MLS-10	4/25/13	8:40 AM	n.a.	0.50	970	3.3	24.1	6.8	271
MLS-14	4/24/13	3:00 PM	n.a.	0.75	944	3.3	23.8	6.9	267
MLS-14	4/25/13	9:50 AM	n.a.	0.75	1002	2.6	24.0	6.9	n.a.
MLS-20	4/24/13	3:20 PM	n.a.	1.79	915	0.7	24.3	6.9	278
MLS-20	4/25/13	11:30 AM	n.a.	1.79	946	0.7	25.0	6.9	260
PR-9	4/26/13	9:30 AM	20.1	3.50	946	0.7	24.5	6.9	256
PR-11	4/26/13	8:30 AM	22.1	3.50	963	n.a.	24.2	6.9	265
PR-19	5/1/13	2:25 PM	24.7	8.30	944	3.0	24.9	6.3	216
PR-13	4/24/13	11:08 AM	35.5	30.80	947	2.1	23.3	6.8	223
PR-8	5/29/13	10:45 AM	29.9	35.30	931	n.a.	25.7	6.9	398
PR-10	6/5/13	3:00 PM	12.9	43.60	937	1.7	25.4	7.2	212
PR-14	4/25/13	10:40 AM	25.7	128.50	888	0.2	24.3	6.8	265

n.a. = Data not available

Table A.2a. Bulk water quality analysis of groundwater and test basin samples at the San Gabriel Spreading Grounds, CA (campaign #1).

Sample	Date	$N\text{-}NO_3$ [mg/L]	PO_4 [mg/L]	DOC [mg/L]	UV_{254} [m^{-1}]	SUVA [L/mg m]	Fe [mg/L]	Mn [mg/L]
Influent	12/10/12	2.9	1.9	5.8	13.12	2.27	0.175	0.008
Influent	12/10/12	2.7	1.6	5.5	11.78	2.14	0.070	0.027
Influent	12/11/12	5.4	1.4	8.0	12.72	1.58	0.005	n.a.
Influent	12/12/12	4.9	2.4	6.5	14.24	2.18	0.139	0.049
Influent	12/17/12	5.4	2.0	6.5	13.41	2.07	0.033	0.007
WP-Z	12/10/12	5.2	3.3	17.5	23.75	1.36	0.051	0.008
WP-Z	12/11/12	8.6	2.5	4.3	10.10	2.35	0.099	0.016
MLS-9	12/11/12	9.0	3.2	7.7	10.82	1.40	0.022	0.001
MLS-14	12/10/12	7.9	4.2	n.a.	9.36	n.a.	0.027	0.070
MLS-14	12/11/12	10.5	4.6	6.4	12.98	2.03	0.036	0.002
MLS-20	12/11/12	8.3	3.1	3.3	8.70	2.65	0.049	0.005
PR-9	12/12/12	6.6	3.9	3.2	10.09	3.20	0.013	0.015
PR-11	12/12/12	7.9	3.8	3.0	10.69	3.54	0.023	0.001
PR-19	12/17/12	9.0	1.7	2.4	8.87	3.64	0.055	0.005
PR-13	1/7/13	n.a.	n.a.	1.9	6.88	3.55	0.036	0.013
PR-8	1/11/13	7.2	1.4	1.9	8.25	4.41	0.010	1.681
PR-10	1/22/13	8.0	2.0	2.0	9.22	4.68	0.036	1.318
PR-15	12/11/12	5.8	1.5	4.2	12.15	2.87	n.a.	n.a.
PR-14	12/11/12	7.3	1.3	n.a.	7.62	n.a.	n.a.	n.a.

n.a. = Data not available

Table A.2b. Bulk water quality analysis of groundwater and test basin samples at the San Gabriel Spreading Grounds, CA (campaign #2).

Sample	Date	$N\text{-}NO_3$ [mg/L]	PO_4 [mg/L]	DOC [mg/L]	UV_{254} [m^{-1}]	SUVA [L/mg m]	Fe [mg/L]	Mn [mg/L]
Influent	4/24/13	6.4	4.4	6.1	12.77	2.10	0.188	0.069
Influent	4/25/13	4.3	5.4	7.2	13.11	1.83	0.041	0.004
Influent	4/26/13	4.7	3.0	7.2	12.39	1.72	0.032	0.022
Influent	5/1/13	3.8	1.6	5.6	n.a.	n.a.	0.022	0.003
WPZ	4/24/13	7.8	1.4	5.2	16.04	3.11	0.314	0.012
WPZ	4/25/13	6.0	2.8	5.2	17.46	3.34	0.093	0.008
MLS-10	4/24/13	11.9	2.1	3.2	12.55	3.98	0.113	0.156
MLS-10	4/25/13	8.3	3.3	3.5	11.76	3.35	0.067	0.002
MLS-14	4/24/13	14.1	1.6	3.1	9.70	3.16	0.015	0.001
MLS-14	4/25/13	6.1	3.8	4.2	16.84	4.01	0.027	0.001
MLS-20	4/24/13	5.5	3.0	3.5	10.33	2.99	0.025	0.688
MLS-20	4/25/13	11.4	2.8	3.1	9.84	3.13	0.012	0.014
PR-9	4/26/13	14.7	2.4	3.4	10.25	2.99	0.026	0.003
PR-11	4/26/13	4.9	2.4	4.3	10.25	2.36	0.136	0.034
PR-19	5/1/13	6.9	2.0	2.4	n.a.	n.a.	0.017	0.015
PR-13	4/24/13	8.5	1.5	2.8	8.29	2.99	0.038	0.037
PR-8	5/29/13	9.5	1.0	2.9	7.83	2.68	0.008	2.441
PR-10	6/5/13	8.6	1.3	2.7	4.96	1.82	0.005	1.066
PR-14	4/25/13	5.4	1.2	1.8	7.16	3.98	0.014	0.272

n.a. = Data not available

Table A.3a. Average concentrations (ng/L; n = 3) and respective standard deviations of indicator compounds in the test basin and subsurface sampling locations at San Gabriel Spreading Grounds, CA during the December 2012 sampling campaign.

Sample	Date	Travel time [d]	Acesulfame [ng/L]	Atenolol [ng/L]	Caffeine [ng/L]	Carbamazepine [ng/L]	Diclofenac [ng/L]	Gemfibrozil [ng/L]	Iopromide [ng/L]
Influent	12/10/12	n.a.	997 ± 171*	150 ± 13	<LOD	259 ± 6	49 ± 23	147 ± 1	62 ± 5
Influent	12/11/12	n.a.	2540 ± 170	255 ± 3	<LOD	197 ± 1	26 ± 3	483 ± 4	2383 ±110
Influent	12/12/12	n.a.	3438 ± 665	199 ± 16	<LOD	206 ± 11	48 ± 2	383 ± 8	1753 ± 29
Influent	12/17/12	n.a.	2113 ± 584	247 ± 9	<LOD	170 ± 2	87 ± 3	392 ± 10	900 ± 36
WPZ	12/10/12	0.45	1261 ± 146	63 ± 2	<LOD	256 ± 5	37 ± 3	89 ± 3	25 ± 2
WPZ	12/11/12	0.45	1640 ± 797	57 ± 9	<LOD	229 ± 11	40 ± 5	113 ± 1	206 ± 13
MLS-9	12/11/12	0.41	1286 ± 61	<LOD	<LOD	234 ± 2	14 ± 2	<LOD	46 ± 1
MLS-14	12/10/12	0.75	1731 ± 599	10 ± 2	<LOD	219 ± 7	26 ± 4	24 ± 1	<LOD
MLS-14	12/11/12	0.75	791 ± 207	12 ± 0	11 ± 3	244 ± 8	17 ± 3	10 ± 1	34 ± 1
MLS-20	12/11/12	1.79	741 ± 216	10 ± 1	11 ± 4	231 ± 3	<LOD	<LOD	<LOD
PR-9	12/12/12	3.50	1241 ± 396	31 ± 0	<LOD	222 ± 11	18 ± 3	26 ± 1	57 ± 1
PR-11	12/12/12	3.50	1313 ± 320	31 ± 2	<LOD	226 ± 2	19 ± 5	12 ± 0	49 ± 4
PR-19	12/17/12	8.30	1418 ± 478	<LOD	<LOD	216 ± 10	11 ± 0	65 ± 1	86 ± 10
PR-13	1/7/13	30.80	938 ± 116	<LOD	<LOD	281 ± 1	<LOD	15 ± 0	<LOD
PR-8	1/11/13	35.30	3131 ± 346	19 ± 0	<LOD	237 ± 3	<LOD	28 ± 1	37 ± 1
PR-10	1/22/13	43.60	1928 ± 709	<LOD	<LOD	287 ± 8	17 ± 1	<LOD	77 ± 2
PR-14	4/25/13	128.50	n.a.	<LOD	<LOD	294 ± 6	<LOD	<LOD	<LOD
LOD [ng/L]			250	10	10	25	10	10	25

* Average concentration ± standard deviation [n=3]

Table A.3a continued.

Sample	Date	Travel time [d]	Primidone [ng/L]	Sulfamethoxazole [ng/L]	TCEP [ng/L]	TCPP [ng/L]	Trimethoprim [ng/L]	Diphenhydramine [ng/L]
Influent	12/10/12	n.a.	170 ± 3	124 ± 9	561 ± 8	2322 ± 31	12 ± 1	43 ± 7
Influent	12/11/12	n.a.	170 ± 5	176 ± 6	452 ± 14	1840 ± 57	37 ± 1	75 ± 0
Influent	12/12/12	n.a.	142 ± 11	342 ± 6	337 ± 17	1200 ± 120	64 ± 3	65 ± 4
Influent	12/17/12	n.a.	169 ± 7	577 ± 14	513 ± 10	2008 ± 56	94 ± 1	91 ± 1
WPZ	12/10/12	0.45	161 ± 6	165 ± 3	486 ± 10	545 ± 52	<LOD	<LOD
WPZ	12/11/12	0.45	201 ± 15	306 ± 14	397 ± 22	354 ± 4	<LOD	<LOD
MLS-9	12/11/12	0.41	200 ± 4	189 ± 8	298 ± 17	166 ± 58	<LOD	<LOD
MLS-14	12/10/12	0.75	179 ± 9	258 ± 6	347 ± 12	140 ± 5	12 ± 0	<LOD
MLS-14	12/11/12	0.75	220 ± 6	234 ± 8	339 ± 19	145 ± 17	12 ± 0	<LOD
MLS-20	12/11/12	1.79	185 ± 3	350 ± 7	350 ± 10	146 ± 9	<LOD	<LOD
PR-9	12/12/12	3.50	186 ± 8	290 ± 7	370 ± 18	229 ± 17	11 ± 1	<LOD
PR-11	12/12/12	3.50	196 ± 7	402 ± 12	369 ± 6	195 ± 11	13 ± 1	<LOD
PR-19	12/17/12	8.30	200 ± 2	625 ± 23	313 ± 15	261 ± 15	<LOD	<LOD
PR-13	1/7/13	30.80	178 ± 6	513 ± 10	196 ± 6	476 ± 34	<LOD	<LOD
PR-8	1/11/13	35.30	175 ± 3	384 ± 5	168 ± 8	355 ± 34	<LOD	<LOD
PR-10	1/22/13	43.60	196 ± 2	852 ± 12	411 ± 8	842 ± 14	<LOD	<LOD
PR-14	4/25/13	128.50	183 ± 9	718 ± 4	157 ± 0	575 ± 7	<LOD	<LOD
LOD [ng/L]			25	5	10	25	10	25

* Average concentration ± standard deviation [n=3]

LOD = Limit of detection

Table A.3a continued.

Sample	Date	Travel time [d]	DEET [ng/L]	Dilantin [ng/L]	TDCP [ng/L]	Atrazine [ng/L]	Triclocarban [ng/L]	Meprobamate [ng/L]
Influent	12/10/12	n.a.	147 ± 3	151 ± 6	1087 ± 73	5 ± 0	88 ± 1	249 ± 6
Influent	12/11/12	n.a.	146 ± 5	151 ± 6	898 ± 18	<LOD	102 ± 3	264 ± 4
Influent	12/12/12	n.a.	66 ± 18	147 ± 9	663 ± 79	<LOD	74 ± 7	226 ± 15
Influent	12/17/12	n.a.	139 ± 10	152 ± 8	958 ± 101	<LOD	89 ± 6	271 ± 5
WPZ	12/10/12	0.45	162 ± 7	141 ± 6	665 ± 85	5 ± 0	<LOD	251 ± 7
WPZ	12/11/12	0.45	118 ± 7	156 ± 9	174 ± 19	6 ± 1	<LOD	264 ± 14
MLS-9	12/11/12	0.41	57 ± 4	98 ± 5	362 ± 42	5 ± 0	10 ± 2	30 ± 0
MLS-14	12/10/12	0.75	91 ± 6	129 ± 16	142 ± 53	6 ± 0	<LOD	69 ± 3
MLS-14	12/11/12	0.75	65 ± 2	144 ± 11	175 ± 24	6 ± 0	10 ± 3	75 ± 2
MLS-20	12/11/12	1.79	70 ± 4	154 ± 3	204 ± 41	6 ± 0	<LOD	21 ± 1
PR-9	12/12/12	3.50	90 ± 5	145 ± 12	156 ± 24	6 ± 0	<LOD	169 ± 8
PR-11	12/12/12	3.50	66 ± 5	142 ± 9	137 ± 28	6 ± 0	<LOD	222 ± 3
PR-19	12/17/12	8.30	76 ± 4	167 ± 6	130 ± 8	6 ± 0	<LOD	217 ± 11
PR-13	1/7/13	30.80	160 ± 47	130 ± 5	165 ± 14	<LOD	<LOD	78 ± 2
PR-8	1/11/13	35.30	57 ± 29	94 ± 1	126 ± 3	<LOD	<LOD	78 ± 2
PR-10	1/22/13	43.60	67 ± 8	206 ± 3	251 ± 8	6 ± 0	<LOD	237 ± 6
PR-14	4/25/13	128.50	35 ± 2	115 ± 3	232 ± 9	<LOD	<LOD	n.a.
LOD [ng/L]			25	25	50	5	10	10

* Average concentration ± standard deviation [n=3]

LOD = Limit of detection

Table A.3b. Average concentrations (ng/L; n = 2) and respective standard deviations of indicator compounds in the test basin and subsurface sampling locations at San Gabriel Spreading Grounds, CA during the April 2013 sampling campaign.

Sample	Date	Travel time [d]	Atrazine [ng/L]	Atenolol [ng/L]	Caffeine [ng/L]	Carbamazepine [ng/L]	DEET [ng/L]	Dilantin [ng/L]	Diclofenac [ng/L]
Influent	4/25/13	n.a.	7 ± 0 *	301 ± 31	<LOD	269 ± 19	209	243 ± 41	13 ± 3
Influent	4/26/13	n.a.	7 ± 1	264 ± 0	<LOD	443 ± 18	189 ± 13	200 ± 5	33 ± 1
Influent	5/1/13	n.a.	8 ± 0	50 ± 2	<LOD	252 ± 22	107 ± 5	201 ± 11	68 ± 3
WPZ	4/24/13	0.45	7 ± 0	25 ± 0	14 ± 1	261 ± 5	112 ± 1	219 ± 9	43 ± 0
WPZ	4/25/13	0.45	6 ± 0	50 ± 2	10 ± 0	270 ± 11	140 ± 5	205 ± 5	41 ± 11
MLS-10	4/24/13	0.50	7 ± 1	16 ± 0	12 ± 0	271 ± 8	45 ± 1	80 ± 5	27 ± 4
MLS-10	4/25/13	0.50	8 ± 1	14 ± 2	13 ± 3	324 ± 57	79 ± 7	108 ± 21	33 ± 1
MLS-14	4/24/13	0.75	8 ± 1	23 ± 4	15 ± 1	305 ± 41	67	93	17 ± 2
MLS-14	4/25/13	0.75	7 ± 1	15 ± 1	15 ± 1	282 ± 1	118	185 ± 6	46 ± 1
MLS-20	4/24/13	1.79	7 ± 0	16 ± 2	14 ± 1	255 ± 16	144 ± 9	177 ± 3	62 ± 3
MLS-20	4/25/13	1.79	7 ± 0	16 ± 0	11 ± 1	272 ± 7	89 ± 11	188 ± 1	39 ± 3
PR-9	4/26/13	3.50	8 ± 0	16 ± 1	<LOD	287 ± 15	103 ± 15	195 ± 16	92 ± 23
PR-11	4/26/13	3.50	7 ± 0	59 ± 0	<LOD	304 ± 5	106 ± 0	172 ± 6	25 ± 2
PR-19	5/1/13	8.30	8 ± 0	<LOD	<LOD	372 ± 9	78 ± 12	187 ± 12	35 ± 2
PR-13	4/24/13	30.80	7 ± 0	<LOD	<LOD	345 ± 1	62	154 ± 1	24 ± 2
PR-8	5/29/13	35.30	6 ± 0	<LOD	<LOD	325 ± 7	50	159 ± 1	19 ± 3
PR-10	6/5/13	43.60	6 ± 0	<LOD	<LOD	324 ± 1	104 ± 1	159 ± 5	23 ± 1
LOD [ng/L]			5	10	10	25	25	25	10

* Average concentration ± standard deviation [n=2]

LOD = Limit of detection

Table A.3b continued.

Sample	Date	Travel time [d]	Fluoxetine [ng/L]	Gemfibrozil [ng/L]	Iopromide [ng/L]	Primidone [ng/L]	Sucralose [ng/L]	Sulfamethoxazole [ng/L]
Influent	4/25/13	n.a.	42 ± 1	153 ± 3	2483 ± 117	216 ± 20	2578 ± 25	91 ± 9
Influent	4/26/13	n.a.	46 ± 2	282 ± 0	698 ± 96	193 ± 5	4660 ± 297	137 ± 6
Influent	5/1/13	n.a.	58 ± 3	34 ± 1	169 ± 5	212 ± 3	4888 ± 74	633 ± 60
WPZ	4/24/13	0.45	<LOD	37 ± 1	60 ± 3	215 ± 8	3303 ± 230	489 ± 23
WPZ	4/25/13	0.45	<LOD	174 ± 0	703 ± 18	196 ± 6	5275 ± 177	152 ± 2
MLS-10	4/24/13	0.50	<LOD	<LOD	<LOD	203 ± 5	3190 ± 721	247 ± 6
MLS-10	4/25/13	0.50	<LOD	<LOD	30 ± 3	238 ± 37	5125 ± 106	179 ± 36
MLS-14	4/24/13	0.75	<LOD	<LOD	<LOD	249 ± 38	3278 ± 293	223 ± 29
MLS-14	4/25/13	0.75	<LOD	55 ± 1	203 ± 1	226 ± 18	5275 ± 248	124 ± 7
MLS-20	4/24/13	1.79	<LOD	85 ± 1	82 ± 22	180 ± 17	3035 ± 460	500 ± 28
MLS-20	4/25/13	1.79	<LOD	<LOD	<LOD	228 ± 0	4565 ± 438	520 ± 7
PR-9	4/26/13	3.50	<LOD	17 ± 0	39 ± 2	254 ± 18	4395 ± 64	963 ± 18
PR-11	4/26/13	3.50	<LOD	<LOD	44 ± 5	226 ± 3	3718 ± 74	140 ± 5
PR-19	5/1/13	8.30	<LOD	37 ± 1	77 ± 3	235 ± 9	5035 ± 163	660 ± 14
PR-13	4/24/13	30.80	<LOD	<LOD	<LOD	184 ± 7	n.a.	828 ± 4
PR-8	5/29/13	35.30	<LOD	<LOD	44 ± 4	168 ± 1	n.a.	810 ± 35
PR-10	6/5/13	43.60	<LOD	<LOD	47 ± 1	174 ± 4	n.a.	725 ± 28
LOD [ng/L]			5	10	25	25	250	5

* Average concentration ± standard deviation [n=2]

LOD = Limit of detection

Table A3.b continued.

Sample	Date	Travel time [d]	TCEP [ng/L]	TCPP [ng/L]	TDCP [ng/L]	Triclocarban [ng/L]	Trimethoprim [ng/L]	Diphenhydramine [ng/L]
Influent	4/25/13	n.a.	540 ± 35	2468 ± 152	1178 ± 67	181 ± 14	18 ± 1	82 ± 7
Influent	4/26/13	n.a.	464 ± 25	2355 ± 212	1023 ± 53	192 ± 19	30 ± 2	98 ± 4
Influent	5/1/13	n.a.	535 ± 35	2320 ± 177	1200 ± 78	152 ± 12	26 ± 2	98 ± 8
WPZ	4/24/13	0.45	440 ± 32	685 ± 78	196 ± 29	37 ± 0	42 ± 1	<LOD
WPZ	4/25/13	0.45	457 ± 5	818 ± 4	375 ± 8	22 ± 5	45 ± 0	<LOD
MLS-10	4/24/13	0.50	291 ± 0	395 ± 24	120 ± 12	19 ±4	23 ± 1	<LOD
MLS-10	4/25/13	0.50	338 ± 58	309 ± 61	76 ± 15	27	29 ± 6	<LOD
MLS-14	4/24/13	0.75	378 ± 68	244 ± 64	138 ± 27	20	42 ± 5	<LOD
MLS-14	4/25/13	0.75	381 ± 11	373 ± 2	160 ± 9	<LOD	35 ± 0	<LOD
MLS-20	4/24/13	1.79	445 ± 35	570 ± 50	273 ± 21	<LOD	13 ± 2	<LOD
MLS-20	4/25/13	1.79	362 ± 1	354 ± 0	244 ± 3	<LOD	15 ± 0	<LOD
PR-9	4/26/13	3.50	334 ± 28	408 ± 57	272 ± 36	<LOD	40 ± 3	<LOD
PR-11	4/26/13	3.50	1023 ± 53	233 ± 6	103 ± 1	<LOD	46 ± 3	<LOD
PR-19	5/1/13	8.30	424 ± 20	481 ± 77	224 ± 31	<LOD	<LOD	<LOD
PR-13	4/24/13	30.80	408 ± 6	650 ± 0	307 ± 14	<LOD	<LOD	<LOD
PR-8	5/29/13	35.30	319 ± 2	563 ± 4	271 ± 1	<LOD	<LOD	<LOD
PR-10	6/5/13	43.60	248 ± 0	700 ± 14	287 ± 0	<LOD	<LOD	<LOD
LOD [ng/L]			10	25	50	10	10	25

* Average concentration ± standard deviation [n=2]

LOD = Limit of detection

Table A.4. Selected field parameter readings of groundwater and recharge basin samples at Prairie Waters Project, Colorado.

Well ID		Conductivity		Temperature		pH	
	n	[µS/cm]	STD	[˚C]	STD		STD
Recharge basin influent	3	1123	17	16.9	1.29	7.1	0.1
RW-A1	3	1161	16	18.5	0.5	7.2	0.15
RW-A2	3	1147	8	16.8	1.1	7.2	0.16
RW-A22	3	1116	14	17.0	1.4	7.2	0.05
MW-A17A	3	1087	9	17.9	0.38	7.1	0.01
MW-A20 (background)	1	1394	n.a.	13.6	n.a.	6.8	n.a.
MW-A25A	3	1077	38	16.5	4.17	7.6	0.16
MW-A27A	1	1091	n.a.	18.4	n.a.	7.9	n.a.
MW-A28A	3	1105	14	17.3	2.57	7.6	0.07

n.a. = Data not available

Table A.5. Selected bulk water quality parameter of groundwater and recharge basin samples at Prairie Waters Project, Colorado.

Well ID		Manganese		Nitrate		Sulfate		Chloride		TOC		UV_{254nm}	
	n	[mg/L]	STD	[mg/L]	STD	[mg/L]	STD	[mg/L]	STD	[mg/L]	STD	[1/m]	STD
Recharge basin influent	3	0.80	0.06	3.31	0.35	218.70	11.59	124.75	3.48	3.03	0.32	6.13	0.51
RW-A1	3	0.02	0.01	3.11	0.56	226.99	9.36	127.08	3.07	2.30	0.14	4.38	n.a.
RW-A2	3	0.03	0.00	2.48	0.31	229.97	7.73	127.46	2.31	2.17	0.00	3.77	n.a.
RW-A22	3	0.03	0.02	2.81	0.27	229.39	11.81	126.52	3.92	2.16	0.24	3.27	0.14
MW-A17A	3	0.05	0.02	2.67	0.17	229.14	10.52	127.63	3.81	2.29	0.28	3.62	n.a.
MW-A20 (background)	1	<0.0001	n.a.	4.90	n.a.	335.12	n.a.	128.38	n.a.	1.71	n.a.	2.54	n.a.
MW-A25A	3	0.04	0.02	2.56	0.19	222.33	7.13	126.80	3.86	2.54	0.10	4.56	0.82
MW-A27A	1	0.03	n.a.	1.83	n.a.	234.60	n.a.	133.02	n.a.	2.40	n.a.	4.55	n.a.
MW-A28A	3	0.05	0.03	2.78	0.22	220.72	11.44	125.56	4.58	2.70	0.22	4.87	n.a.

n.a. = Data not available

Table A.6. Average concentrations and respective standard deviations of selected indicator compounds in groundwater and recharge basin samples at Prairie Waters Project, Colorado.

Well ID		CBZ		Primidone		Dilantin		DEET		SMX		Diclofenac		Gemfibrozil		Naproxen	
	n	[ng/L]	STD	[ng/L]	STD	[ng/L]	STD	[ng/L]	STD	[ng/L]	STD	[ng/L]	STD	[ng/L]	STD	[ng/L]	STD
Recharge basin influent	5	177	17	69	5	71	8	206	142	337	32	16	4	75	9	14	2
RW-A1	3	134	41	55	17	<LOD	n.a.	56	74	40	21	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.
RW-A2	3	153	11	59	5	<LOD	n.a.	42	50	20	3	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.
RW-A22	4	149	13	60	6	33	4	124	77	68	4	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.
MW-A17A	4	143	10	61	6	35	7	47	19	84	22	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.
MW-A20 (background)	3	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.	60	36	56	18	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.
MW-A25A	4	167	16	67	5	56	8	40	32	45	4	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.
MW-A27A	1	167	n.a.	<LOD	n.a.	27	n.a.	53	n.a.	56	n.a.	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.
MW-A28A	4	167	12	65	5	<LOD	n.a.	53	37	42	5	<LOD	n.a.	<LOD	n.a.	<LOD	n.a.

n.a. = Data not available, <LOD = Below detection limit

CBZ = Carbamazepine; SMX = Sulfamethoxazole

Table A.7. Field parameter readings of groundwater sampling locations at the Sweetwater Recharge Facility, Arizona.

Sampling location	n	Conductivity		Temperature		pH		Turbidity	
		[µS/cm]	STD	[˚C]	STD		STD	[NTU]	STD
MW-5	4	1249.50	93.81	27.73	1.55	7.26	0.14	3.58	0.70
WR-069B	4	1238.25	20.61	25.68	0.67	6.87	0.11	6.53	3.52

n.a. = Data not available

Table A.8. Selected bulk water quality parameter of groundwater and recharge basin samples at Sweetwater Recharge Facility, Arizona.

Sample	**Influent RB-1**	**Influent RB-1**	**Influent RB-1**	**MW-5**	**WR-69B**
Date	2/21/13	2/21/13	2/21/13	2/25/13	3/8/13
Time	8:00 AM	12:00 PM	4:00 PM	8:00 AM	8:00 AM
Chloride [mg/L]	124	126	127	125	164
Sulfate [mg/L]	93	94	94	91	161
N-nitrate [mg/L]	0.08	0.13	0.13	0.10	8.01
Phosphate [mg/L]	8.55	8.15	8.15	11.74	n.a.
Manganese [mg/L]	0.017	0.004	0.016	1.215	0.009
Iron [mg/L]	0.146	0.100	0.124	0.028	0.093
DOC [mg/L]	15.87	16.67	15.93	7.83	1.11

n.a. = Data not available

Table A.9. Average concentrations (ng/L, n = 3) and respective standard deviations of indicator compounds in groundwater and recharge basin influent samples at Sweetwater Recharge Facility, Arizona.

Sample	**Influent RB-1**	**Influent RB-1**	**Influent RB-1**	**MW-5**	**WR-69B**
Date	2/21/13	2/21/13	2/21/13	2/25/13	3/8/13
Time	8:00 AM	12:00 PM	4:00 PM	8:00 AM	8:00 AM
Concentration [ng/L]					
Acetaminophen	<LOD	12 ± 2	14 ± 1	<LOD	<LOD
Atrazine	6 ± 1	<LOD	<LOD	<LOD	<LOD
Caffeine	14383 ± 202	13367 ± 1049	13967 ± 592	833 ± 75	<LOD
Carbamazepine	535 ± 5	490 ± 9	533 ± 16	436 ± 12	540 ± 22
DEET	658 ± 3	635 ± 13	683 ± 30	625 ± 25	n.a.
Diazepam	6 ± 1	5 ± 1	5 ± 1	8 ± 1	5 ± 0
Dilantin	312 ± 37	264 ± 19	298 ± 9	297 ± 22	45 ± 1
Fluoxetine	177 ± 16	86 ± 4	157 ± 11	<LOD	<LOD
Primidone	253 ± 9	260 ± 12	267 ± 2	263 ± 25	181 ± 7
Sulfamethoxazole	2362 ± 119	2317 ± 28	2427 ± 86	5467 ± 440	43 ± 4
Trimethoprim	982 ± 33	963 ± 18	1018 ± 19	38 ± 2	<LOD
TCEP	410 ± 10	406 ± 14	424 ± 7	458 ± 9	162 ± 5
TCPP	1375 ± 64	1370 ± 28	1425 ± 84	1702 ± 56	83 ± 6
TDCP	1107 ± 63	1113 ± 34	1163 ± 34	1245 ± 28	202 ± 3
Amitriptyline	99 ± 2	78 ± 2	96 ± 2	<LOD	<LOD
Diphenhydramine	1497 ± 31	1362 ± 20	1480 ± 30	<LOD	<LOD
Iopromide	6567 ± 153	5667 ± 257	5360 ± 428	3698 ± 456	<LOD
Bisphenol A	97 ± 10	162 ± 51	185 ± 40	3993 ± 737	<LOD
Diclofenac	264 ± 44	n.a.	228 ± 13	102 ± 9	<LOD
Gemfibrozil	4568 ± 97	4105 ± 44	5583 ± 225	4772 ± 199	<LOD
Triclocarban	1340 ± 173	565 ± 79	1492 ± 146	26 ± 9	<LOD
Ibuprofen	433 ± 18	377 ± 24	490 ± 45	295 ± 15	<LOD
Naproxen	2533 ± 96	1512 ± 16	2285 ± 95	822 ± 60	<LOD
Propylparaben	<LOD	<LOD	<LOD	15 ± 0	<LOD
Sucralose	n.a.	n.a.	4730 ± 777	5710 ± 34	3548 ± 220

n.a. = Data not available; <LOD = Below detection limit




WATEREUSE

1199 North Fairfax Street, Suite 410
Alexandria, VA 22314 USA
703.548.0880
703,548.5085 (fax)
foundation@watereuse.org
www.WateReuse.org