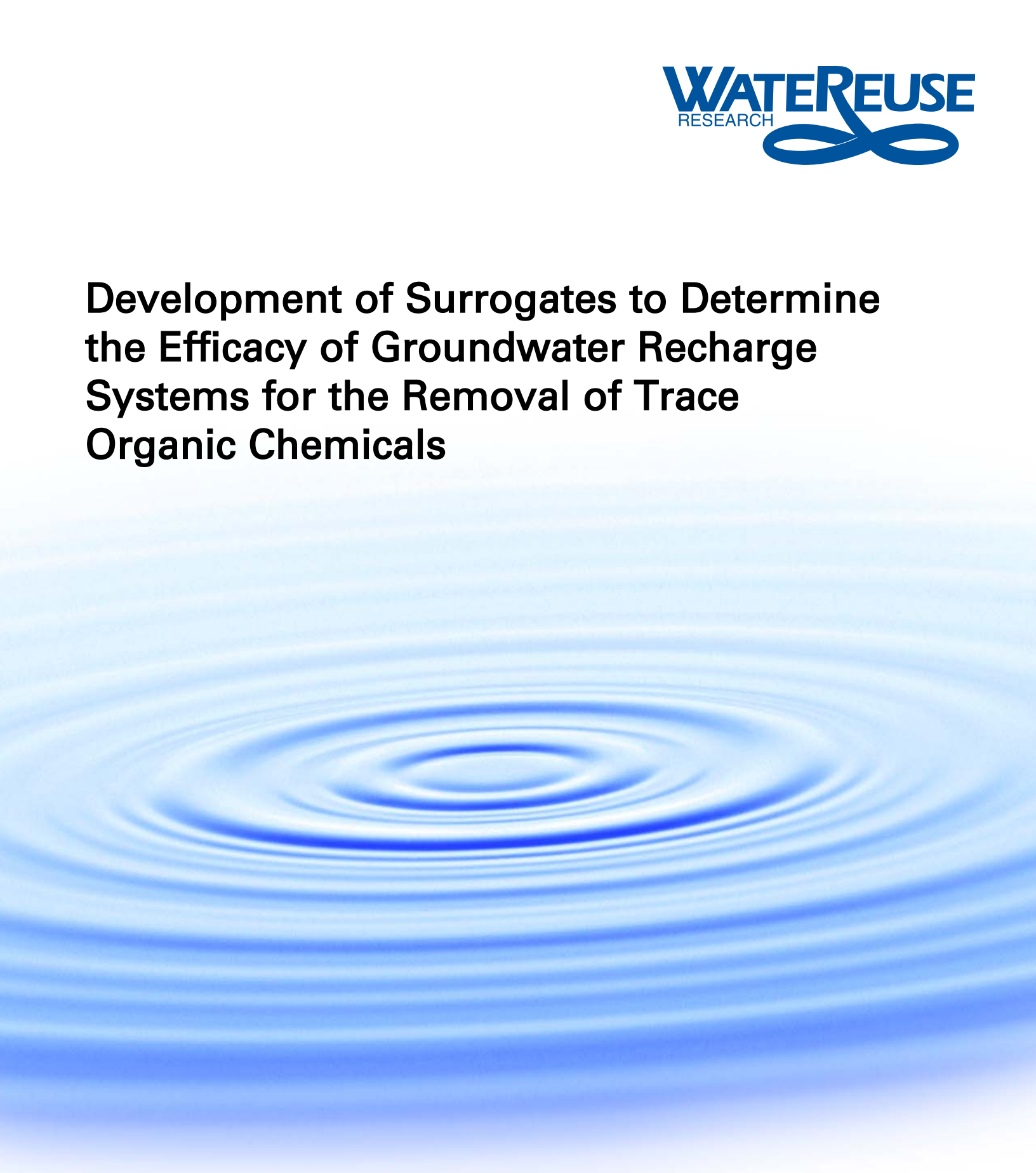
Development of Surrogates to Determine the Efficacy of Groundwater Recharge Systems for the Removal of Trace Organic Chemicals



WateReuse Research Foundation

Development of Surrogates to Determine the Efficacy of Groundwater Recharge Systems for the Removal of Trace Organic Chemicals

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 desalination and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

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

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

Development of Surrogates to Determine the Efficacy of Groundwater Recharge Systems for the Removal of Trace Organic Chemicals

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Inland Empire Utilities Agency
Southwest Florida Water Management District
California State Water Resources Control Board
Bureau of Reclamation

WateReuse Research Foundation
Alexandria, VA

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This report was sponsored by the WateReuse Research Foundation and cosponsored by the Sanitation Districts of Los Angeles County, the Inland Empire Utilities Agency, the Southwest Florida Water Management District, the California State Water Resources Control Board, and the Bureau of Reclamation. 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.

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WateReuse Research Foundation Project Number: WRF-05-004
WateReuse Research Foundation Product Number: 05-004-1

ISBN: 978-1-934183-44-1
Library of Congress Control Number: 2011926157

Printed in the United States of America

Printed on Recycled Paper

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ACRONYMS

AHTN	7-Acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene
ALK	Alkalinity
AOC	Assimilable organic carbon
AOI	Adsorbable organic iodine
AOP	Advanced oxidation process
AOX	Adsorbable organic halides
AWPF	Advanced Water Purification Facility
BAC	Biological activated carbon
BDOC	Biodegradable dissolved organic carbon
BHA	Butylated hydroxyanisole
BOD	Biochemical oxygen demand
BPA	Bisphenol A
CAP	Central Arizona Project
CBWCD	Chino Basin Water Conservation District
CDPH	California Department of Public Health
COD	Chemical oxygen demand
COL	Color
COND	Conductivity
CSDLAC	County Sanitation Districts of Los Angeles County
CSM	Colorado School of Mines
DEET	*N*,*N*-Diethyl-meta-toluamide
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DBPs	Disinfection by-products
DR	Detection ratio
E1	Estrone
E2	17β-Estradiol
E3	Estriol
EAT	Estrogens, androgens, thyroids
EDC	Endocrine disrupting compounds
EDTA	Ethylenediaminetetraacetic acid
EE2	17α-Ethynylestradiol
EEM	Excitation-emission matrix
EfOM	Effluent organic matter
EPA	Environmental Protection Agency

ESI	Electrospray ionization
FDA	Food and Drug Administration
FI	Fluorescence index
GAC	Granular activated carbon
GC/MS	Gas chromatography with mass spectroscopy
GC/MS-MS	Gas chromatography with tandem mass spectroscopy
Gfd	Gallons per square foot and day
GWRS	Groundwater Replenishment System
HAAs	Haloacetic acids
HHCB	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta[g][2]benzopyran
HLB	Hydrophilic–lipophilic balance
HPLC	High-performance liquid chromatography
IEUA	Inland Empire Utilities Agency
IMS	Integrated membrane system
IR	Infrared
LACDPW	Los Angeles County Department of Public Works
LC/MS-MS	Liquid chromatography with tandem mass spectroscopy
LMH	Liters per square meter and hour
LOD	Limit of detection
LOQ	Limit of quantification
LPRO	Ultra-low-pressure RO
MBR	Membrane bioreactor
MDL	Method detection limit
MF	Microfiltration
MFSG	Montebello Forebay Spreading Ground
MTBSTFA	*N*-(*t*-Butyldimethylsilyl)-*N*-methyl-trifluoroacetamide
MW	Molecular weight
MWCO	Molecular weight cut off
NDMA	*N*-Nitrosodimethylamine
NF	Nanofiltration
NOM	Natural organic matter
OCWD	Orange County Water District
OTNE	(1-[1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthalenyl]ethanone)
PAC	Powder-activated carbon
POC	Particulate organic carbon
PPCPs	Pharmaceuticals and personal care products
PFFBBr	Pentafluorobenzyl bromide
PhAC	Pharmaceutically active compounds
QA/QC	Quality assurance/quality control

RBF	Riverbank filtration
RIB	Rapid Infiltration Basin
RL	Reporting level
RO	Reverse osmosis
RSD	Relative standard deviation
RWC	Recycled water contribution
SAP	Science advisory panel
SAT	Soil aquifer treatment
SBCFCD	San Bernardino County Flood Control District
SCADA	Supervisory control and data acquisition
SEC	Size exclusion chromatography
SFLUOR	Specific fluorescence
SGCB	San Gabriel Coastal Basin Spreading Grounds
SM	Standard methods
SMPs	Soluble microbial products
SNWA	Southern Nevada Water Authority
SPE	Solid-phase extraction
SUVA	Specific UV absorbance
SWRF	Sweetwater Underground Storage and Recovery Facility
TCEP	Tris(2-chloroethyl)phosphate
TCPP	Tris(1,3-dichloroisopropyl)phosphate
TDCPP	Tris(1,3-dichloro-2-propyl)phosphate
TDS	Total dissolved solids
THMs	Trihalomethanes
TOC	Total organic carbon
TOI	Total organic iodide
TOX	Total organic halides
TURB	Turbidity
UF	Ultrafiltration
USGS	United States Geological Survey
UV	Ultraviolet light
UVA	Ultraviolet light absorbance
WRD	Water Replenishment District of Southern California
WRF	WateReuse Research Foundation

FOREWORD

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

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

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

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

The objectives of this project were (a) to identify potential surrogates and indicators for the removal of trace organic chemicals in groundwater recharge projects employing soil-aquifer treatment and high-pressure membrane treatment, (b) to validate the ability of chosen surrogates and indicators to predict the removal of trace organic chemicals in groundwater recharge projects, and (c) to develop recommendations and guidance for the water industry regarding suitable surrogates for groundwater recharge systems using reclaimed water. The project consisted of three major phases and was conducted over a four-year time period. The second phase of the project consisted of validating the use of surrogates and indicators at pilot- and full-scale SAT and high-pressure membrane systems. In the final phase of the project, recommendations were developed for monitoring programs for groundwater recharge applications using reclaimed water.

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ACKNOWLEDGMENTS

This project was funded by the WateReuse Research Foundation in cooperation with the Bureau of Reclamation, California State Water Resources Control Board, Southwest Florida Water Management District, Inland Empire Utilities Agency (CA), and the Sanitation Districts of Los Angeles County (CA).

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 PAC members (as identified below); the WateReuse Research Foundation's project managers, Taylor Mauck and Julie Minton; many key individuals at the participating utilities and related organizations; and the outstanding staff at the Advanced Water Technology Center (AQWATEC) at the Colorado School of Mines (including Mike Pamplin and JoJo Li).

The research team would like to thank the WateReuse Research Foundation for funding this applied research project, as well as the following organizations for their in-kind contributions: Inland Empire Utilities Agency (CA), Sanitation Districts of Los Angeles County (CA), Orange County Water District (CA), Southwest Florida Water Management District, the Water Replenishment District of Southern California, and Tucson Water (AZ).

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EXECUTIVE SUMMARY

PROJECT BACKGROUND

This research was performed by a team of faculty, scientists, and graduate students from the Colorado School of Mines and the Southern Nevada Water Authority. It was funded by the WateReuse Research Foundation, Bureau of Reclamation, California State Water Resources Control Board, Southwest Florida Water Management District, Sanitation Districts of Los Angeles County, and the Inland Empire Utilities Agency.

An increasing number of water utilities are using drinking water sources influenced by wastewater discharge and others are planning for or implementing indirect potable reuse via groundwater recharge systems. The use of water sources influenced by wastewater has raised public concerns because of the presence of trace organic contaminants. Trace organic compounds are often present at extremely low concentrations and no standardized analytical methods are available to test for them. For the majority of the compounds, it is difficult to assess human health or ecological risks associated with potable reuse because chemical and toxicological data for the hundreds of compounds potentially present in reclaimed water are lacking and because epidemiological methods are usually not sensitive enough to detect relatively small increases in the frequency of adverse health outcomes. Therefore, a conservative approach for monitoring potable reuse systems has evolved that assumes that certain bulk measurements of a limited list of wastewater-derived organic contaminants can be used to assess the removal of all of the wastewater-derived organic contaminants of concern in groundwater recharge systems.

PROJECT OBJECTIVES

The objectives of this project were (a) to identify potential surrogates and indicators for the removal of wastewater-derived chemical contaminants in groundwater recharge projects employing soil-aquifer treatment after surface spreading and membrane treatment ahead of direct injection projects, (b) to validate the ability of chosen surrogates and indicators to predict the removal of wastewater-derived contaminants in groundwater recharge projects, and (c) to develop recommendations for the water industry regarding suitable surrogates for groundwater recharge systems using reclaimed water.

The research study consisted of three major phases. The project was initiated with a comprehensive literature review to summarize available surrogates and indicators. The second phase of the project addressed the development and validation of analytical methods for surrogates and indicators. Testing of the predictive abilities of the surrogates and indicators was conducted at pilot- and full-scale units/facilities located in different geographical regions in the United States where indirect potable reuse is practiced. In the final phase of the project, recommendations were developed for monitoring programs for specific applications in which the presence of wastewater-derived contaminants in reclaimed water is an issue of concern.

STUDY FINDINGS

The approach for monitoring trace organic chemicals for groundwater recharge operations developed in this study utilizes a combination of surrogate parameters and indicator chemicals. In the context of this study, an indicator chemical is an individual chemical occurring at a quantifiable level, which represents certain physicochemical and biodegradable characteristics of a family of trace constituents that are relevant to fate and transport during treatment, and thus provides a conservative assessment of removal. A surrogate parameter is a quantifiable change of a bulk parameter that can serve as a measure of individual unit processes or operations' performance in removing trace compounds. This approach utilizes only a limited set of analytes for the evaluation of proper performance of soil-aquifer treatment and high-pressure membrane treatment systems and may be a reasonable way to circumvent the significant costs associated with analysis of a wide range of chemicals of concern, provided that the analytes monitored are good predictors of the contaminants of concern. The approach proposed to select feasible indicator chemicals is driven foremost by treatment performance and less so by toxicological relevance. Physicochemical properties (e.g., molecular size, pK_a, log K_{ow}, volatility, and dipole moment) often determine the fate and transport of a chemical in various treatment processes. Thus, selecting multiple indicators representing a broad range of properties will allow accounting for chemicals currently not identified ("unknowns") and new chemicals synthesized and entering the environment in the future (i.e., new pharmaceuticals), provided they fall within the range of properties covered. The underlying concept is that absence or removal of an indicator chemical during a treatment process would also ensure absence or removal of unidentified chemicals with similar properties. Proper removal is ensured as long as the treatment process of interest is operating according to its technical specifications. It is therefore necessary to define the operating conditions under which proper removal is to be expected for each treatment process. Predetermined changes of surrogate parameters can be utilized to define normal operating conditions according to a specification for a given treatment process.

For the surrogate/indicator framework, potential indicator chemicals are classified into four removal categories: "good removal (>90%)", two groups of "intermediate removal ($90\% < x < 50\%$ and $50\% < x < 25\%$)," and "poor removal (<25%)." This rating of indicators into removal categories of individual unit processes is dependent on the physicochemical and biodegradable properties of the chemicals. Whether the proposed degree of removal is achieved will depend on operational conditions of the treatment process. To assess the performance of a specific treatment process, the most sensitive compounds will be those that are partially removed under normal operating conditions. Thus, a system failure will be indicated by poor removal of indicator chemicals classified in the categories "good removal (>90%)" and "intermediate removal ($90\% < x < 50\%$)," whereas normal operating conditions will be indicated by partial or complete indicator chemical removal.

The proposed framework is a conservative approach designed to ensure proper removal of identified and unidentified trace organic contaminants and to detect failures in system performance.

Soil Aquifer Treatment (SAT) Operations

For SAT operations, several surrogate parameters were identified as differential measures (i.e., BDOC; ΔDOC; ΔUVA; ΔTOX; Δammonia; Δnitrate; fluorescence) that were considered suitable for performance assessment of this treatment process.

Based on findings derived from conducting field monitoring efforts at five different field sites, redox conditions and feed water types did not seem to affect the removal of indicator chemicals during SAT. The results indicate that removals for biodegradable indicator chemicals are similar across sites for similar travel times despite differences in the extent of vadose zones, which supports the robustness and reliability of SAT operations regarding the removal of biodegradable trace organic chemicals. Considering the travel times across different field sites, the results suggest that removal of DEET, diclofenac, ibuprofen, and meprobamate were characterized by slower kinetics and for these chemicals a travel time of more than 1 week is required to achieve a removal in excess of 90%. The chlorinated flame retardant compounds (i.e., TCEP, TCPP, TDCPP) were not well removed after 6 days under oxic or anoxic conditions and for various feed water types. This is in general agreement with observations from full-scale monitoring efforts, where these compounds were not well attenuated and persist for travel times exceeding many months. The antiepileptic compounds (i.e., primidone, dilantin, carbamazepine), sulfamethoxazole, and atrazine were not well removed after 5 days under either oxic or anoxic conditions, which also agrees with observations from full-scale monitoring. Indicator chemicals that exhibit persistent behavior (removal category of less than 25%) can serve as conservative tracers in SAT operations (e.g., primidone, carbamazepine) and can be used to assess the degree of dilution with native groundwater that is not influenced by wastewater recharge.

A more expanded suite of indicator compounds was examined using feed water with low organic carbon (~0.2 mg/L) and inorganic nitrogen concentrations. Under these feed water conditions, most of the biodegradable indicator chemicals were removed by more than 90% after 5 days of travel time under both oxic and anoxic conditions. This is an agreement with full-scale observations, where all of these compounds were removed in excess of 90% with travel times greater than 1 week.

Removal of indicator chemicals was correlated with removal of surrogate parameters, such as total organic carbon (TOC), total organic halides (TOX), and ultraviolet light absorbance (UVA). In general, select indicator chemicals, with the exception of benzophenone, exhibited a significant correlation (p-value < 0.05) with both TOC and TOX. These results demonstrate that changes in TOC and TOX do correlate with changes of indicator chemicals in the subsurface. However, based on laboratory soil-column experiments using feed water with a low carbon concentration (~0.2 mg/L), the same indicator compounds exhibited similar substantial reductions despite no changes in TOC concentrations being observed. This suggests that for sites using feed water qualities that are characterized by a low TOC concentration (< 2 mg/L), TOC monitoring would not be a sufficient surrogate parameter to assess the removal of trace organic chemicals during spreading-basin operation.

High-Pressure Membrane Operations

As demonstrated in previous studies, the vast majority of indicator chemicals are efficiently rejected by reverse osmosis (RO) membranes, achieving a removal percentage in excess of 90%. Chemicals that are nonionic (neutral) and small can exhibit a partial removal, as observed for nitrosamines, such as NDMA, or 1,4-dioxane. Indicator compounds that are small but exhibit hydrophobic properties can adsorb to the polymeric structure of thin-film composite membranes and partition through the active layer of the membrane into the permeate (e.g., chloroform). The highly efficient rejection of wastewater-derived contaminants by RO membranes limits the number of available indicator chemicals

representing intermediate removal to a few. None of the indicator chemicals considered in this study exhibited poor removal (<25%).

The findings of monitoring studies at a full-scale RO facility revealed that some indicator compounds occurred in the permeate at very low concentrations (less than 110 ng/L), whereas most of the compounds were either not detected or were less than 5 ng/L. The majority of the indicator compounds were removed greater than 99% during all sampling campaigns.

To assess proper operation of high-pressure membrane applications using surrogate parameters, electrical conductivity and boron are proposed.

FUTURE RESEARCH NEEDS

- Future research should evaluate the use and precision of appropriate analytical methods to quantify indicator chemicals in these water reuse applications. These methods should be validated through round-robin efforts.
- To increase the use of surrogate parameters rather than favoring the measurement of individual chemicals, additional or suggested surrogate parameters should be explored that can be measured in real time.
- A better relationship should be developed between removal of indicator chemicals and travel time during SAT operations, preferably resulting in rate constants for biotransformation. These rate constants could be used for contaminant transport models that can assist in design and operation of managed aquifer recharge facilities.
- A better understanding of pathways of biotransformation can also assist in a better classification of indicator compounds that are not solely based on observed removal efficiencies but rather on molecular fragments that are subject to a biological attack. The relationships can guide the development of quantitative structure property relationship models that, coupled with contaminant transport models, could provide an *a priori* assessment of emerging chemicals that have not been studied or monitored before.
- Methods to quantify suggested surrogate parameters, such as BDOC or fluorescence, should be standardized.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

With an increasing water demand and lack of alternative sources in semi-arid and arid regions, utilities are attracted to reuse treated municipal wastewater effluent to augment drinking water supplies. In the United States, intentional potable water reuse usually involves the indirect reuse of wastewater effluent after discharge to an environmental buffer, such as surface water reservoirs, infiltration through the vadose zone, or direct injection into potable aquifers (Drewes and Khan, 2010). Indirect potable reuse projects that employ vadose zone infiltration, which is also known as soil aquifer treatment (SAT), normally apply secondary or tertiary wastewater treatment prior to infiltration, whereas groundwater injection projects usually employ secondary or tertiary treatment followed by an integrated membrane system consisting of microfiltration (MF) and reverse osmosis (RO), and in some cases advanced oxidation processes (Drewes and Khan, 2010). The process of surface spreading has the added benefit of additional constituent removal that is due to transformation in the basin via volatilization and photodecomposition and during subsequent percolation, in the form of physical filtration, adsorption to soil particles, microbial biotransformation, and dilution with native groundwater (Rodriguez et al. 2009). Natural attenuation is an attractive option because it requires no chemical inputs and does not create a waste stream. The recent detection of a variety of chemicals in municipal wastewater effluents in water produced by indirect potable reuse systems has raised concern about the potential presence of trace organic chemicals and the associated adverse health effects (Focazio et al., 2008; La Farré et al., 2008; Mompleat et al.; 2009; Wells et al., 2009).

Prior to the late 1990s, concerns related to public health threats posed by indirect potable water reuse were directed mainly at the potential presence of pathogens in wastewater effluent (USEPA, 1992; NRC, 1998). However, chemical contaminants were also a concern. The potential presence of chemical contaminants was cited by the U.S. National Research Council's (NRC) panel on Indirect Potable Reuse as a reason to be cautious about water reuse, even though none of the priority pollutants or other compounds of concern had been detected at existing water reuse projects (NRC 1998). At that time, it was difficult to assess human health or environmental risks associated with indirect potable reuse because chemical and toxicological data for the hundreds of compounds potentially present in reclaimed water were lacking and epidemiological methods are usually not sensitive enough to detect relatively small increases in the frequency of adverse health outcomes (Sloss et al., 1996, 1999). The continuous creation of new synthetic organic chemicals precludes comprehensive testing for all potentially toxic compounds and creates an ever-present element of uncertainty for all indirect potable reuse projects. Therefore, a conservative approach for designing indirect potable reuse systems has evolved that employs multiple-barriers of treatment processes with a demonstrated ability to remove contaminants. These systems often are subjected to intensive water quality monitoring programs designed to detect failures in system performance. However, it is unknown whether the monitoring programs in place are adequate to demonstrate proper removal of chemicals of emerging concern.

By 2010, regulators and water utilities were looking for new approaches for monitoring conventional and advanced water treatment processes to respond to concerns associated with

trace organic chemicals. Because the list of individual chemicals that are potentially present in reclaimed water has likely grown more during the last 20 years, recent research studies and regulatory efforts provided needed guidance to identify benchmarks for a short list of trace organic chemicals regarding their human health relevance that frequently occur in reclaimed water (Schwab et al., 2005; EPHSC, 2008; Snyder et al., 2008; Schriks et al., 2009; Nellor et al., 2009). Other recent efforts were directed to identify certain trace organic chemicals that can be used to measure the effectiveness of a process for a family or group of compounds in a treatment process of interest (Drewes et al., 2008a). The selection of these indicator compounds is primarily driven by their physicochemical properties and treatment performance and less so by toxicological relevance. Thus, selecting multiple indicators representing a broad range of properties will allow accounting for compounds currently not identified ("unknowns") and new compounds synthesized and entering the environment in the future (i.e., new pharmaceuticals) provided they fall within the range of properties covered. The underlying concept is that absence or removal of an indicator compound during a treatment process would also ensure absence or removal of unidentified (or identified) compounds with similar properties.

Recent efforts have identified useful combinations of surrogate parameters and indicator compounds to monitor the removal efficiency of various advanced processes employed by treatment plants engaged in indirect potable water reuse programs (Drewes et al., 2008a; Dickenson et al., 2009). In this context, a surrogate is a quantifiable parameter that can serve as a performance measure of treatment processes that relates to the removal of specific contaminants. Surrogate parameters provide a means of assessing water quality characteristics of treatment processes without conducting difficult trace contaminant analysis.

1.2 REGULATORY FRAMEWORK FOR TRACE ORGANIC CHEMICALS OF EMERGING CONCERNS

To date, there are no federal regulations in the United States that specifically address monitoring requirements for trace organic chemicals in potable reuse and groundwater recharge projects. Nevertheless, the U.S. Environmental Protection Agency (EPA) has published a guidance document on water reuse that has no regulatory authority (USEPA, 2004). In the late 1980s, the California Department of Public Health (CDPH) developed draft criteria for the use of reclaimed municipal wastewater to recharge groundwater basins that are sources of domestic water supply (Crook et al., 2000). The CDPH criteria, which set forth the agency's approach to writing permits for indirect potable reuse systems, have been updated several times but as of 2010 have not been approved or finalized. In formulating the proposed criteria, CDPH considered both acute health effects from microbial pathogens and potential long-term health effects associated with chemical constituents, particularly trace organic compounds (Geselbracht and Crook, 2000). After receiving the final report prepared by a science advisory panel (SAP) submitted to the state in 1987, CDPH selected total organic carbon (TOC) limits in wastewater effluent prior to recharge as a means of ensuring the lowest possible concentration of unregulated wastewater-derived organic contaminants (Robeck, 1987). In its summary report, the SAP concluded that the concentration of organic carbon should be removed to "below 1 mg/L by reverse osmosis and essentially all identifiable trace organic compounds of significance should be absent in detectable concentrations."

The current draft criteria (CDPH, 2008) couple an even more stringent TOC limit with the fraction of the drinking water supply that is derived from wastewater effluent as a factor in determining system performance requirements (quantified as TOC). This fraction is referred

to as the "recycled water contribution" (RWC) and is calculated at a 60-month average. The current draft regulations require that groundwater recharge projects meet a TOC concentration of equal to or less than 0.5 mg/L divided by the approved RWC. Subsurface injection projects are required to treat 100% of the reclaimed water by RO to provide sufficient removal of organic chemicals and must meet a TOC limit of 0.5 mg/L or less prior to injection. For projects practicing direct injection into a potable aquifer, also advanced oxidation processes (AOPs) using UV/AOP must be employed following RO treatment. For surface spreading operations, TOC must be equal to or less than 0.5 mg/L divided by the RWC at the point where the reclaimed water meets the groundwater. Therefore, surface spreading projects can receive credit for TOC removal that occurs within the vadose zone. In recognition of the possible shortcomings of using TOC as a surrogate for trace organic chemicals, CDPH also included additional monitoring requirements in the 2003 draft criteria (CDPH, 2003). The new criteria require regular monitoring of specific trace organic chemicals including chemicals with a State Notification Level and a suite of endocrine disrupting compounds, pharmaceuticals, and personal care products for which action levels have not been established. At the time, the list of compounds was based on expert judgment, public perception, and available occurrence data. In the fall of 2009, the California State Water Resources Control Board convened a science advisory panel to provide recommendations for the development of a monitoring program of trace organic chemicals in reclaimed water for groundwater recharge projects. This effort was completed in November of 2010 and resulted in a short-list of indicator compounds that have human health relevance and can serve as indicator compounds for treatment performance assessments in groundwater recharge projects leading to drinking water augmentation.

The approach of using a surrogate measure such as TOC and a limited list of trace organic chemicals may be a reasonable way to circumvent the significant costs associated with the analysis of all the possible chemicals of concern if the analytes monitored are good predictors of the contaminants of concern. This project is the first study to test this proposition. Soil-aquifer treatment and membrane technologies that are commonly employed in surface and subsurface spreading operations differ in their dominant removal mechanisms: physical adsorption and biotransformation versus physical separation. It has been demonstrated in previous research that fate and transport of trace organic chemicals are correlated with the type of unit operation employed and depend on both physicochemical properties and biodegradability of the contaminant (Snyder et al., 2003; Bellona et al., 2004, 2008). Therefore, one unique set of analytes for any reuse application may not be appropriate to evaluate the absence or presence as well as fate of trace organic chemicals in both soil-aquifer treatment and membrane processes.

Although the use of surrogates is often problematic, it is possible that these shortcomings could be circumvented by adaptation of more appropriate bulk water quality parameters or use of a combination of bulk parameters. For example, the use of biodegradable dissolved organic carbon (BDOC) in conjunction with dissolved organic carbon (DOC) could serve as an indicator of the presence of organic compounds in SAT operations that are not derived from humic substances. Conversely, integrity measurements for membrane applications, such as conductivity and turbidity, could serve as a surrogate for system performance and integrity. The main advantage of bulk chemical parameters is that they are more easily measured than chemical contaminants and in some cases could be included in online monitoring programs.

1.3 FATE OF TRACE ORGANIC CHEMICALS IN SURFACE SPREADING OPRATIONS AND HIGH-PRESSURE MEMBRANE APPLICATIONS

Although TOC itself is an appropriate parameter for quantifying the bulk of organic matter in municipal wastewater effluents, its composition is controlled mainly by contributions from (a) natural organic matter (NOM) derived from drinking water sources, (b) BOD and organic chemicals of anthropogenic origin, and (c) soluble microbial products (SMPs) generated during biological wastewater treatment by the decomposition of organic matter (Drewes and Fox, 2000). These contributions can vary locally and seasonally (Drewes et al., 2001). Different approaches have been proposed to distinguish between naturally and wastewater derived organic carbon by using differences in functional groups, structural properties, molecular size distribution, aromaticity, reactivity, or acid/base solubility (Drewes and Fox, 1999; Leenheer et al., 2001; Imai et al., 2002; Müller and Frimmel, 2002; Her et al., 2003; Drewes et al., 2006b; Henderson et al., 2009). Although these methods are promising and provide more insight into the origin of organic matter, they are often semi-quantitative and require a significant degree of expertise for proper assessment.

Several previous studies have characterized the transformation and removal of bulk organic components and trace organic chemicals via SAT at full-scale field sites (Drewes et al., 2003a, 2003b; Montgomery-Brown et al., 2003; Quanrud et al., 2003; Mansell and Drewes, 2004; Grünheid et al., 2005; Amy and Drewes, 2006; Drewes et al., 2006b; Massmann et al., 2006) and in laboratory soil column studies (Cordy et al., 2004; Scheytt et al., 2004, 2006; Chefetz et al., 2008; Rauch-Williams et al., 2009; Ying et al., 2008; Yu et al., 2009). Overall, SAT is considered a feasible (Ternes et al., 2007) and sustainable process for the removal of trace organic chemicals present in reclaimed water (Amy and Drewes, 2007). However, trace organic chemical concentrations can vary significantly based on water consumption and chemical usage patterns. In addition, removal can vary among sites based on environmental conditions and management (Quanrud at al., 2003b; Diaz-Cruz and Barceló, 2008; Ying et al., 2008; Massmann et al., 2006; Grünheid et al., 2005). These variations and the potential health effects that may arise from exposure to reclaimed water necessitate comprehensive monitoring programs aimed at quantifying the robustness of underlying removal processes and developing positive correlations between surrogate measures and trace organic chemicals in SAT operations.

High-pressure membrane treatment, such as reverse osmosis (RO) and nanofiltration (NF), has been demonstrated to be a feasible barrier for a wide variety of organic contaminants (Snyder et al., 2007; Bellona et al., 2008). However, past research has shown the incomplete rejection of certain trace organic contaminants by RO and NF during pilot- and full-scale membrane applications (Bellona et al., 2008; Drewes et al., 2008). Major solute and membrane characteristics that influence solute removal include solute size, charge and hydrophobicity, membrane surface charge, hydrophobicity, and pore size/molecular weight cut off (MWCO; Bellona et al., 2004; Nghiem et al., 2005). In addition, hydrodynamic and operational conditions, such as cross-flow velocity, recovery, and concentration polarization, also influence the efficiency of solute removal (Ng and Elimelech, 2004). Whereas the influence of these factors on organic contaminant removal has been studied in depth on different membranes in their original virgin state, membranes exposed to organic matter during operation using reclaimed water accumulate material on the membrane surface (i.e., foulants), which modifies membrane characteristics and potentially rejection. Past studies have reported that membrane fouling can both increase and decrease solute rejection, depending on the solute, membrane, and foulant (Nghiem and Hawkes, 2007; Ng and

Elimelech, 2004; Agenson and Urase, 2007; Xu et al., 2006). A better understanding of operational conditions on rejection for problematic trace organic chemicals is needed as well as the identification of feasible and sensitive surrogate parameters that can provide an early indication of membrane systems deficiencies.

Ultimately, a monitoring system adopted for groundwater recharge projects using reclaimed water may include a combination of approaches discussed earlier that balances costs, reliability, and sample turnaround times. For example, a monitoring system might employ direct measurement of a broad suite of compounds during the initial start-up of a system followed by annual monitoring of indicators and weekly measurement of surrogates. The ultimate goal is monitoring by using a combination of indicator and surrogate parameters that will ensure the absence of unknown and potentially harmful contaminants, thus ensuring a product quality that is suitable for human consumption. Evaluation of the relative merits of these different monitoring approaches cannot be made without additional research. This project provides water utilities, regulators, and engineers with guidance on monitoring requirements for surrogates and a suitable list of indicators for groundwater recharge systems using reclaimed water.

1.4 OBJECTIVES

The objectives of this project were (a) to identify potential surrogates and indicators for the removal of trace organic chemicals in groundwater recharge projects employing soil-aquifer treatment and high-pressure membrane treatment, (b) to validate the ability of chosen surrogates and indicators to predict the removal of trace organic chemicals in groundwater recharge projects, and (c) to develop recommendations and guidance for the water industry regarding suitable surrogates for groundwater recharge systems using reclaimed water. The project consisted of three major phases and was conducted over a 4-year time period. The project was initiated with the identification of suitable surrogates and indicators to monitor the removal of trace organic chemicals in surface spreading and high-pressure membrane operations. The second phase of the project consisted of validating the use of surrogates and indicators at pilot- and full-scale SAT and high-pressure membrane systems. In the final phase of the project, recommendations were developed for monitoring programs for groundwater recharge applications using reclaimed water.

The study was conducted by a team of students, staff, faculty, and researchers of the Colorado School of Mines (CSM) and the Southern Nevada Water Authority (SNWA), with support by the staff of participating utilities.

CHAPTER 2

EXPERIMENTAL APPROACH

2.1 SURFACE-SPREADING OPERATIONS

For this study, four surface spreading facilities were selected, which are located in Arizona, California, and Florida. Table 2.1 summarizes the site locations for the full-scale surface spreading operations studied.

Table 2.1. Summary of Surface Spreading Operations

Facility/Basin	City/State	Feed Water	Vadose Zone Depth	Lysimeter/ Well Location ID	Lysimeter/ Well Depth
Montebello Forebay Spreading Grounds	Pico Rivera, CA	Tertiary-treated,	10'	#100914	15-40' screen
San Gabriel Coastal Basin		nitrified/denitrified,		#1620RR	50-80' screen
		chlorinated,		#1612T	60-80' screen
		dechlorinated effluent		#100090	100'
Montebello Forebay Spreading Grounds	Pico Rivera, CA	Tertiary-treated,	8'	PR 8	50'
USGS/WRD Test Basin		nitrified/denitrified,		PR 9	25'
		chlorinated,		PR 10	50'
		dechlorinated effluent		PR 11	25'
Chino Groundwater Basin		Tertiary treated,			
8th St. Basin	Ontario, CA	nitrified/denitrified,	450'	Lysimeters	5', 15', 25', 35'
		chlorinated effluent		Perimeter Monitoring Well	495-535' screen
Hickory Basin	Fontana, CA		385'	Lysimeters	5', 15', 25', 35'
				Perimeter Monitoring Well	365-405' screen
Brooks Basin	Montclair, CA		325'	Lysimeter	25'
Sweetwater Recharge Facility	Tucson, AZ	Secondary treated,	120'	MW#5	5'
Research Basin-1		non-nitrified,		WR-199A	130'
		chlorinated effluent			
Regional Rapid Infiltration Basin	Auburndale, FL	Secondary treated,	10'	MW#4	10-15' screen
		nitrified, UV treated effluent		MW#6	10-15' screen

These facilities receive reclaimed water that differs in the degree of above-ground treatment (i.e., secondary non-nitrified, secondary nitrified, and tertiary denitrified effluents). The spreading facilities are characterized by shallow (10 feet), moderate (120 feet), and extended (>300 feet) vadose zone depths. All sites were instrumented with downstream lysimeters and/or monitoring wells that allowed sampling reclaimed water after different travel times in the subsurface.

2.1.1 Montebello Forebay Spreading Grounds

The Montebello Forebay Spreading Ground (MFSG), located in Pico Rivera, California, is a valuable area for groundwater recharge because of its highly permeable soils, which allow deep percolation of surface waters. The Los Angeles County Department of Public Works (LACDPW) owns and operates the MFSG for storm water conservation and flood control. Since the late 1930s, they have been recharging the groundwater basins with storm water runoff. However, because storm water amounts are insufficient for the total groundwater replenishment needs, imported water was added in the 1950s and reclaimed water in the 1960s to supplement this natural source. The County Sanitation Districts of Los Angeles County (CSDLAC) and the Water Replenishment District of Southern California (WRD) help manage two of the most widely used groundwater basins in California within the Montebello Forebay. One of these basins is the San Gabriel Coastal Basin Spreading Grounds (SGCB) consisting of three spreading basins, totaling 128 acres in size with a capacity of 550 acre feet (af)[1] (Figures 2.1 and 2.2). The basins have an estimated percolation rate of 75 cfs. SGCB is located downstream of the Whittier Narrows Dam adjacent to the San Gabriel River channel. At the head works of the spreading grounds is an inflatable rubber dam, located on the river (Figure 2.3), which is used to divert flows to the grounds (Figure 2.4) or regulate releases downstream.

Figure 2.1. San Gabriel Coastal Spreading Grounds.

Figure 2.2. Dried recharge basin at SGCB.

[1] An acre-foot of water is equal to 325,900 gallons of water or equivalent to filling a 1-acre site that is 1 foot deep with water.

Figure 2.3. Rubber dam in the San Gabriel River.

Figure 2.4. Intake structure for the SGCB.

LACDPW has an extensive program of maintaining and grooming the spreading grounds to maximize groundwater recharge. During major storm events, the County works around the clock to ensure that as much runoff as possible is captured by diverting the flows to the various sub-basins instead of allowing the water to be lost to the ocean. During the times when the spreading grounds are not filled with storm water, WRD purchases imported and reclaimed water for artificial replenishment. Since Water Year 1962–63 (October–September), more than 6.3 million acre-feet of water has been recharged at the MFSG, including 2.6 million acre-feet (42%) of storm water, 1.5 million acre-feet (24%) of reclaimed water, and 1.6 million acre-feet (34%) of imported water (WRD, 2010). Over time, reclaimed water amounts increased while imported water amounts decreased. However, very recently imported water has not been available because of droughts and restrictions on imported water allocations. With this in mind, WRD has been looking into using storm and reclaimed waters to solely recharge the basins (WRD, 2008a).

The SGCB operation is characterized by spreading into a short vadose zone followed by saturated flow conditions. At this facility, synoptic sampling was attempted and samples were collected from the spreading basin and down-gradient monitoring wells representing travel times of approximately 2 weeks (Well #100914, 15-40' screen) and 1.4 months (Well #1620RR, 50-80' screen), 1.8 months (Well #1612T, 60-80' screen), and 7.4 months (Well #100090, 100' below ground surface) (Figure 2.5). Travel times were estimated based on peak arrival times observed for a sulfur hexafluoride tracer experiment study performed on the basins in 2003 (Clark et al. 2005). Four sampling events were completed at the SGCB operation. The four sampling campaigns were initiated in March (2007), June (2007), November (2007), and February (2008), respectively. Samples were collected at all locations with the exception of well #1612T, which was only sampled during the first three campaigns, whereas Well # 100090 was only sampled during the fourth sampling campaign. During the sampling periods, the recharge basin received a nitrified/denitrified tertiary-treated effluent (chlorinated followed by dechlorination).

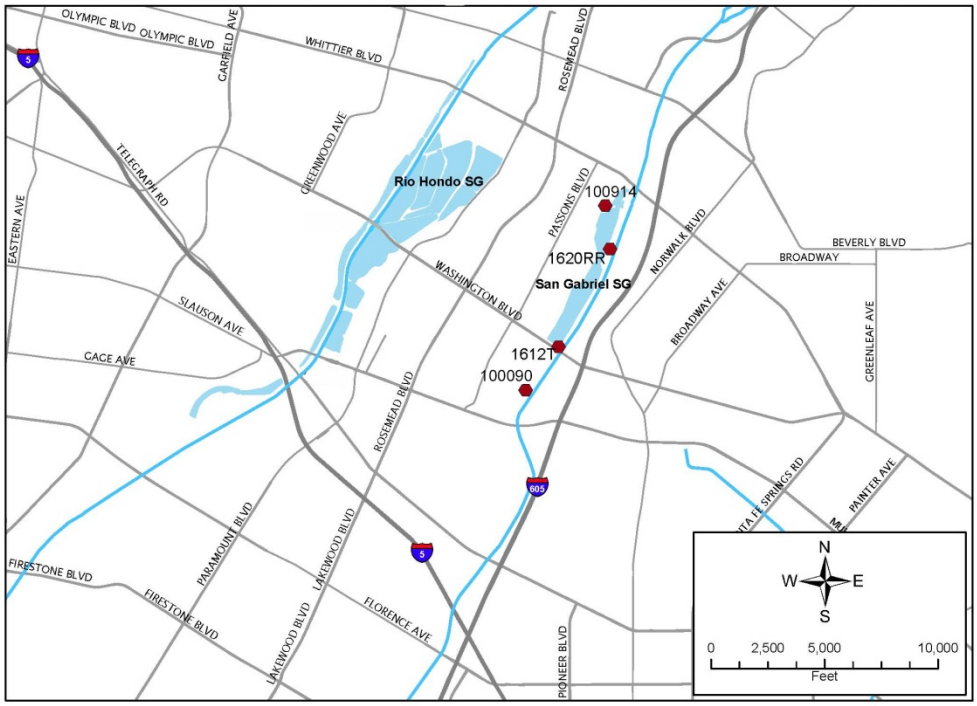


Figure 2.5. Field-scale sampling wells within or near the San Gabriel Spreading Grounds.

2.1.2 USGS/Water Replenishment District's Test Basin

During this study, one sampling campaign was carried out at a 0.5 acre pilot-scale test basin adjacent to the SGCB that was established by the U.S. Geological Survey (USGS) and WRD. The fully instrumented test basin was constructed specifically to capture reclaimed wastewater of the test basin (see Figure 2.6 for an aerial photograph of the grounds and test basin, Figure 2.7 for a close-up of the test basin, and Figure 2.8 for a schematic of the locations sampled in 2009). The underlying sandy aquifer is bisected by a clay-confining layer approximately 31 feet below the basin. The test basin and four subsurface locations are equipped with data loggers for monitoring temperature and electrical conductivity. During the 2009 study, eight locations were selected for sampling, beginning just below the water table, approximately 8 feet below the basin at the start of the synoptic sampling (Figure 2.8). Three points on a multilevel sampler (MLS 8, 14, and 20), two well points (WP Z and WPY), and four monitoring well points (PR 8, 9, 10, and 11) were utilized. The MLS allows for sample collection at 1-foot intervals from 3 to 20 feet below the basin. It was constructed using 18¼–inch Teflon tubes encased in a 2-inch PVC pipe, with holes drilled and tubes connected at the different depths below the basin. The underground ends of the tubes are covered with a Teflon mesh. Samples were collected from MLS 8, 14, and 20, at 8, 14, and 20 feet below the basin, respectively. WP Z and WP Y, located approximately 10 and 12 feet below the bottom of the basin (respectively), are 2-inch wells with 2.5 foot screens. The monitoring wells (PR 8, 9, 10, and 11) are 2-inch wells with 5-foot screens. PR 9 and 11 are approximately 25 feet below the bottom of the basin above a clay-confining layer, with PR 9 directly below the basin and PR 11 adjacent to the basin, beneath the berm. PR 8 and 10 are approximately 50 feet below the basin under the clay-confining layer, again, with PR 8 directly below the basin and PR 10 beneath the berm (Schroeder, 2003).

Figure 2.6. Location of the USGS/WRD test basin at the San Gabriel Spreading Grounds.

Figure 2.7. Close-up of USGS/WRD test basin, catwalk access to sampling points. Arrow indicates location of reclaimed water inlet.

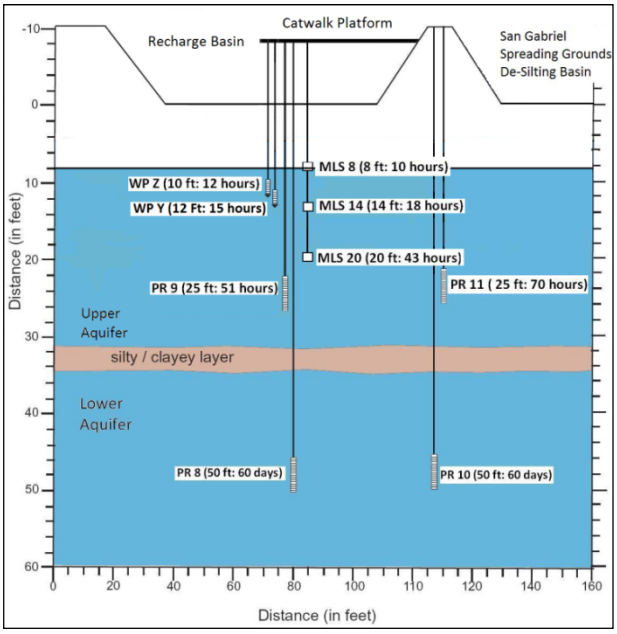


Figure 2.8. Schematic of equipment utilized during sampling at USGS/WRD test basin. Numbers in parentheses are distance below research basin floor and travel time. Water table is approximately 8 feet below basin at the beginning of synoptic sampling.

The research basin was continuously filled with tertiary-treated effluent, from April 15, 2009, to July 20, 2009. The wastewater treatment process included primary clarification, activated sludge treatment with nitrification and denitrification, secondary clarification, tertiary dual media filtration (anthracite and sand), chlorine disinfection, followed by dechlorination with

sulfur dioxide. Filling began a month prior to sample collection (which began May 20) to allow acclimation of the underlying microbial populations. The basin was considered acclimated when TOC concentrations in the subsurface locations remained constant, which occurred by May 13, 2009, in the upper aquifer and by June 25, 2009, in the lower aquifer (Figure 2.9). During the acclimation period TOC samples were collected bi-weekly on four different dates from the basin and six of the subsurface locations described earlier.

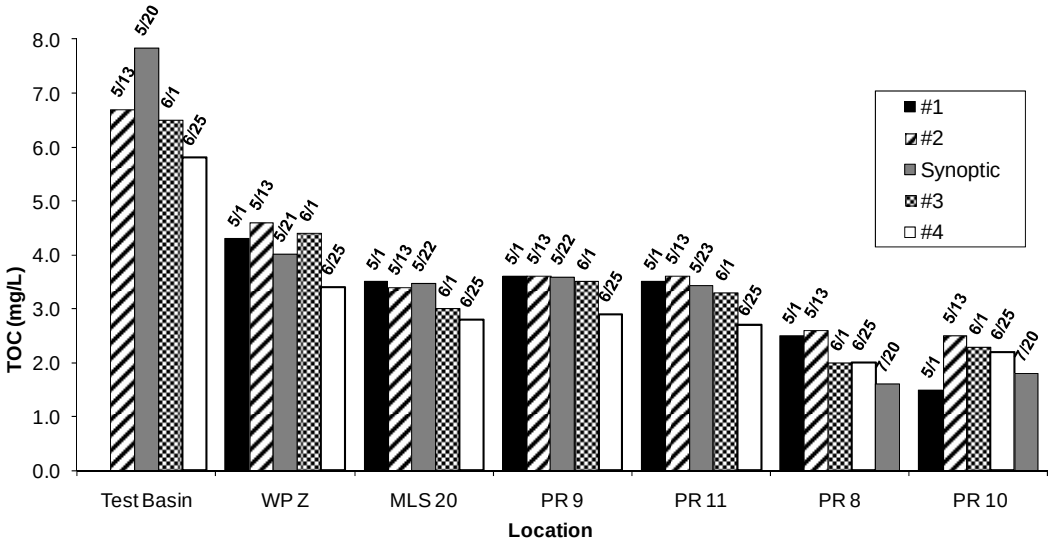


Figure 2.9. TOC concentration in lysimeters during USGS/WRD test basin acclimation. Note: The synoptic sampling took place over a 2-month period, whereas the other four samplings were carried out in a day. The numbers above the columns indicate the dates samples were collected.

Estimating the time it takes a slug of water to move from the test basin to sampling locations was essential to the success of this experiment. During a previous experiment at the test basin, it was determined that diurnal temperature changes that occur in the basin are an excellent indicator of breakthrough at the aquifer wells and could be used to estimate the percentage of reclaimed water at each well (Figure 2.10). During basin filling, temperature was monitored in the basin and in three groundwater wells (WP Y, 12' directly below basin, PR 9, 25' directly below basin, and PR 11, 25' below basin, off to the side). During the day the basin temperature peaks near midday and bottoms out near midnight. These temperature oscillations can later be seen in the groundwater wells, and the time delay in peak and valley observation between the basin and individual wells for 4 different peaks (representative of 4 days of infiltration) was averaged to determine travel times. This monitoring yielded travel times of 15, 51, and 70 hours, respectively, for WP Y (12' directly below basin), PR 9, and PR 11. The average travel times to these three locations were used to estimate travel times to the remainder of the synoptic sampling locations. Water moves quickly through the vadose zone and slows as it enters the saturated zone. In light of this, the velocity between the basin and WP Y (0.77 ft/hr) was only used to estimate travel times to wells less than 12 feet below the basin (i.e. MLS 8, WP Z). For the remainder of the wells (MLS 14, MLS 20, PR 9, and PR 11), the time to 12 feet below the basin was assumed to be 15 hours and the remainder of the distance was multiplied by the velocity to PR 9 (0.31 ft/hr) to determine the additional travel time. These six locations are in the upper aquifer and had travel times ranging from 18 to 70 hours. Travel time to the deeper wells in the lower aquifer (PR 8 and 10), also based on

peak temperature arrival, was estimated at 60 days. The clay-confining layer greatly slows the movement of groundwater into the deeper wells. Figure 2.11 provides a summary of locations and estimated travel times.

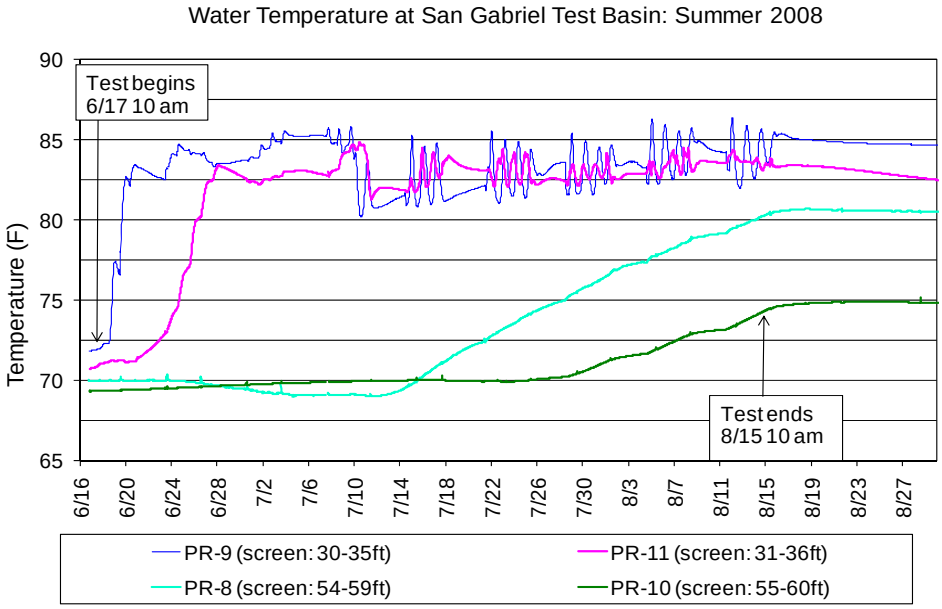


Figure 2.10. Water temperature trends in the saturated zone beneath the USGS/WRD test basin during a previous study (summer 2008).

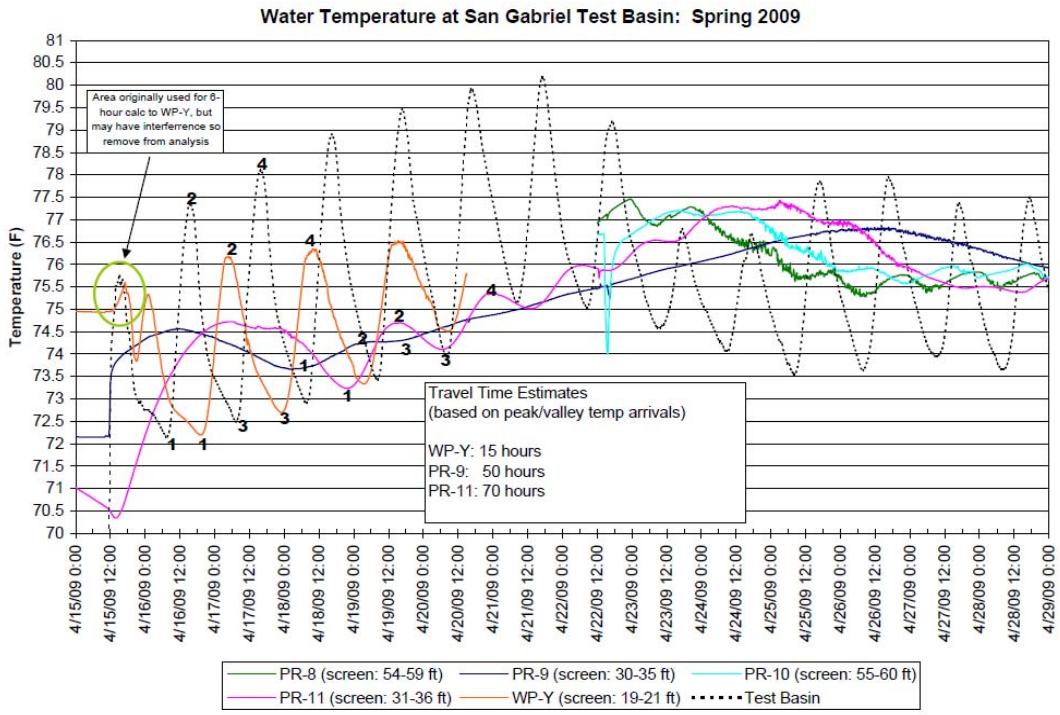


Figure 2.11. Water temperature trends at the USGS/WRD test basin and underlying groundwater wells. At the outset, data loggers were in WP Y, WP Z (not shown on graph), PR 9, and PR 11. Loggers were moved from WP Y and Z to PR 8 and 10 on April 22. Screen depths are feet below ground level (basin approximately 10 feet deep).

Synoptic sampling of the test basin and eight subsurface locations for surrogate parameters and indicator compounds was carried out in May and July of 2009 according to estimated travel times. Samples from the basin were collected using an ISCO composite sampler over a period of 10 minutes during basin acclimation or 3 hours for the synoptic sample after purging with approximately 10 L of sample. Samples from beneath the basin were collected with a peristaltic pump using dedicated silicone tubing to prevent cross contamination. The multilevel sampler locations were purged for 15 minutes and the wells were purged with at least three casing volumes prior to sample collection. Amber glassware were used for bulk analysis samples, 3.78 L plastic bottles were used for BDOC, and 1 L amber glass bottles (methanol rinsed) containing 50 mg of sodium azide and 0.5 mg of acetic acid were used for trace organic chemicals. Temperature and pH were recorded in the field and ranged from 20.3° to 34.4°C and 6.8 to 7.7, respectively. Samples were put on ice immediately and remained cooled during subsequent shipping and storage at 4°C.

As mentioned previously, synoptic sampling is essential in determining actual constituent removal. Analysis and comparison of the major cations and anions in water samples can be used to determine if the samples collected from beneath the basin were from the same slug of water (Figures 2.12 and 2.13). Piper diagrams create a graphical representation of the relationship between the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}, CO_3^{2-}, and HCO_3^{-}. Water of the same origin or similar chemical composition is clustered. Based on the Piper diagram and the comparison between sulfate and chloride concentrations, it appears that all of the samples were of the same origin; although it is likely that the deeper wells (PR 8 and 10)

were affected by dilution from native groundwater. Dilution was estimated using both temperature levels and the concentrations of the intrinsic tracer primidone (a persistent anti-epileptic drug residue) in the test basin and PR 10 during sampling. It is noteworthy that this sampling technique is suitable for polar, well water soluble trace organic chemicals, which tend to travel with the slug of water, but more hydrophobic chemicals can be retarded resulting in delayed travel in the subsurface.

- The background temperature (T_b, prior to the application of reclaimed water) at PR 10 was 20.1°C, and the temperature of the reclaimed water (T_r) in the test basin during sampling was 28°C. During synoptic sampling, the temperature at PR 10 was 24.8°C (T_s). The percentage of reclaimed water was calculated as:

$$\frac{T_s - T_b}{T_r - T_b} * 100$$

- The background concentration of primidone (C_b) was assumed to be zero. The concentration in the reclaimed water applied to the test basin (C_r) and PR 10 (C) was 155 and 90 ng/L, respectively. The percentage of reclaimed water was calculated with the following equation:

$$\frac{C - C_b}{C_r - C_b} * 100$$

Although these estimations are an oversimplification, the temperature data indicates that the samples collected from PR 8 and 10 consisted of approximately 62% reclaimed and 38% native groundwater, whereas the primidone data estimates that 58% of the water present was of wastewater origin.

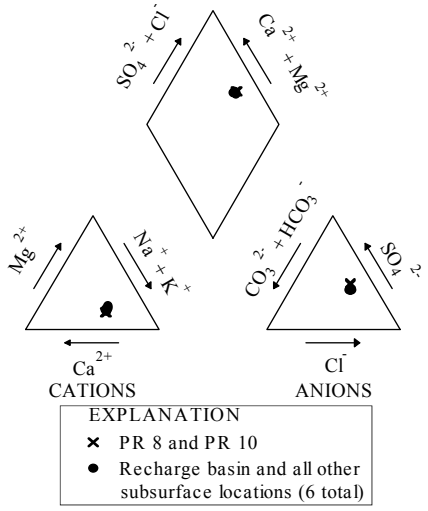


Figure 2.12. Piper diagram displaying the inorganic chemical matrix of the USGS/WRD test basin and subsurface sampling locations.

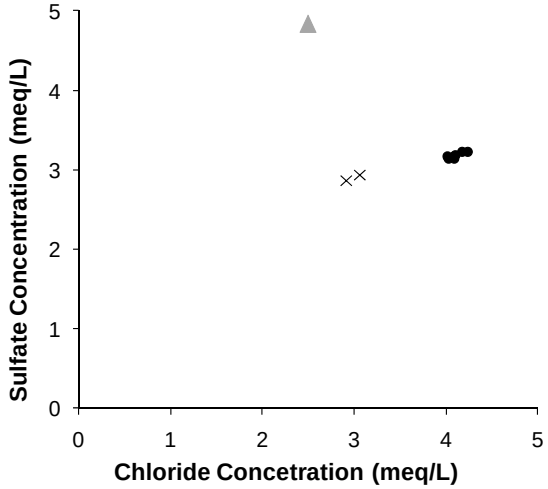


Figure 2.13. Comparison of sulfate and chloride concentrations in USGS/WRD test basin, subsurface sampling locations, and background well (7J1, Schroeder, 2003).

2.1.3 Tucson Water's Sweetwater Recharge Facility

Water reuse is a critical part of regional water supply planning for the city of Tucson, Arizona. The full utilization of the Tucson regional allotment of Central Arizona Project (CAP) water will not satisfy the regional water requirements. Thus, approximately 6,500 af of reclaimed water is infiltrated, stored (6–12 months), and recovered to be reused for landscape irrigation each year at the Sweetwater Underground Storage and Recovery Facility (SWRF). SWRF is located in Tucson along the east and west banks of the Santa Cruz River (Figure 2.14). The facility is operated by the city of Tucson, but receives chlorinated non-nitrified secondary effluent from Pima County's 41-mgd Roger Road Wastewater Treatment Plant. This plant uses trickling filters as secondary treatment. The SWRF consists of eight infiltration basins (28 acres) and has been in operation since 1989. The basin soils have been classified as sandy loam with porosity of 0.39 and cation exchange capacity of 5.7 meq/100g (Quanrud et al., 1996). The infiltration basins operate in cycles that consist of wet and dry periods. The lengths of wet and dry cycles are selected to maximize the amount of water recharged. Infiltration rates decrease during a wet period because of the gradual formation of a biologically active layer (schmutzdecke) on the basin surface. The subsequent drying period must be of sufficient duration to allow desiccation of the schmutzdecke and restore hydraulic capacity of the basin (typically 4 days). Wet/dry periods of equal duration (3 days wet, 3 or 4 days dry) are currently utilized. Basin maintenance is undertaken annually, usually in late summer. This procedure includes removal of plant growth and disking of the upper soil zone (6-12 inches). For this study, operation of only RB-1 research basin was examined (Figure 2.15). Average cycle infiltration rates in recharge basin RB-1 are approximately 1 ft/day (0.3 m/day). RB-1 is 3.3 acres in size.

Figure 2.14. Tucson Water's SWRF.

Figure 2.15. Aerial photo of Tucson Water's SWRF.

The SWRF aquifer recharge operation is characterized by a moderate vadose zone of approximately 120 feet (37 m) in depth. Samples were collected from the spreading basin, a piezometer (MW#5, 5 feet or 1.5 m below ground surface), and a shallow monitoring well (Well # WR-199A, 130 feet or 40 m below ground surface) representing the underlying groundwater quality (Figure 2.16). Synoptic grab sampling was attempted, where travel times to the piezometer (MW#5) and groundwater monitoring well (WR-199A) were estimated during previous studies (Fox et al., 2001) at 2 to 3 days and 2 weeks, respectively, The four sampling campaigns were initiated in January (2007), July (2007), December (2007), and April (2008), respectively. The MW#5 location was sampled in the following manner: (a) depth was recorded in the piezometer using a standard water level measuring device and

(a) sample was collected using a HDPE, 1 liter, ball-valve bailer. The casing for MW#5 is 2" of Schedule 40 PVC. This well was not purged for bailer samples. The WR-199A location was sampled in the following manner: (a) depth was recorded using a standard water level measuring device, (b) then the well was purged for five well volumes prior to sampling, and (c) a final sample was collected from a sample port (hose bib) at the well head. The casing at WR-199A is 6" of low carbon steel, and the column pipe is galvanized steel.

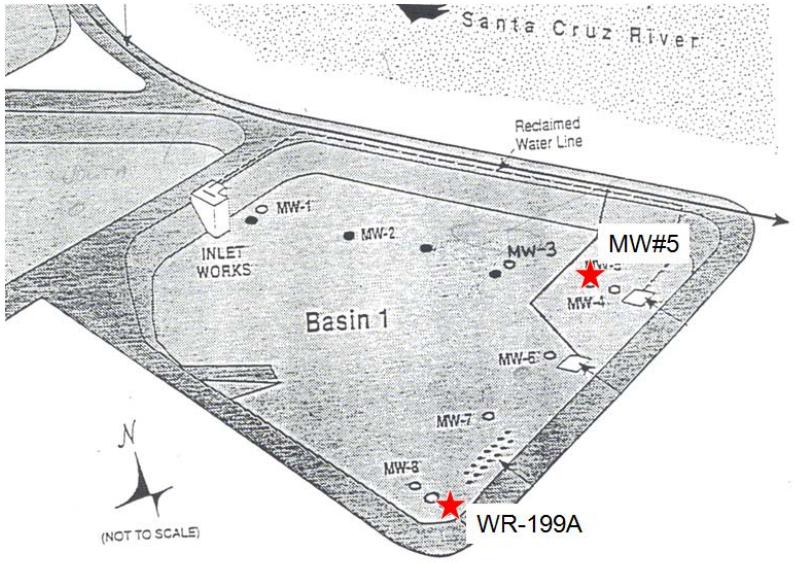


Figure 2.16. Field-scale sampling locations within Tucson's RB-1 basin.

2.1.4 Chino Basin Recharge Operations

The Chino Basin Recycled Water Groundwater Recharge Program's primary goals are reducing dependence on imported water that may not be available in the future, providing a local, drought-proof supply of new water, and improving groundwater quality in the Chino Groundwater Basin, California. This project is jointly sponsored by the Inland Empire Utilities Agency (IEUA), Chino Basin Water Conservation District (CBWCD), and the San Bernardino County Flood Control District (SBCFCD). This recharge operation consists of 19 recharge sites where most consist of multiple recharge basins. These recharge basins are located throughout the IEUA service area (approximately 245 square miles) and are designed to hold the water so that it can percolate into the ground and replenish the alluvial aquifers and groundwater supply (Figure 2.17). IEUA's goal is to recharge between 40,000 and 50,000 acre-feet of imported water from northern California, between 15,000 and 25,000 acre-feet of storm water, and 20,000 acre-feet of reclaimed water. Recharge operations are supplied with reclaimed water from two IEUA water reclamation facilities: Regional Plant No. 1 (RP-1, 60 mgd) and Regional Plant No. 4 (RP-4, 42 mgd). These plants consist of primary treatment, secondary treatment (nitrification/denitrification) and tertiary treatment processes (filtration and chlorine disinfection). This study focused on three of the recharge basin operations: 8th St., Hickory, and Brooks Basins. Conductivity was used to indicate breakthrough of the reclaimed water at lysimeter locations within the basins, which were used to determine the approximate travel time and sampling dates. However, conductivity breakthrough was never observed at the basin perimeter wells, so travel times were based on previously estimated infiltration rates.

The water-bearing sediments of Chino Basin are comprised of primarily unconsolidated sedimentary deposits of interbedded and discontinuous layers of gravel, sand, silt, and clay. The water-bearing sediments are grouped into three hydrostratigraphic layers. Layer 1 consists of the upper 200 to 300 feet of sediments. Layer 1 sediments are typically coarse-grained (sand and gravel layers) and, where saturated, transmit large quantities of groundwater to wells because of high hydraulic conductivities. On the west side of Chino Basin, such as at Brooks Basin, Layer 1 sediments are comprised of a greater fraction of finer-grained sediments (silt and clay layers), especially in the uppermost 100 feet. Layer 2 consists of 200 to 500 feet of sediments underlying Layer 1. On the west side of Chino Basin, such as at Brooks Basin, Layer 2 sediments are primarily fine-grained (silt and clay layers) with few interbedded sand and gravel layers. Layer 3 consists of 100 to 500 feet of sediments underlying Layer 2. Layer 3 sediments are typically coarse-grained (sand and gravel layers), but because of their greater age, consolidation, and state of weathering, these sediments have lower permeability than the coarse-grained sediments of Layer 1.

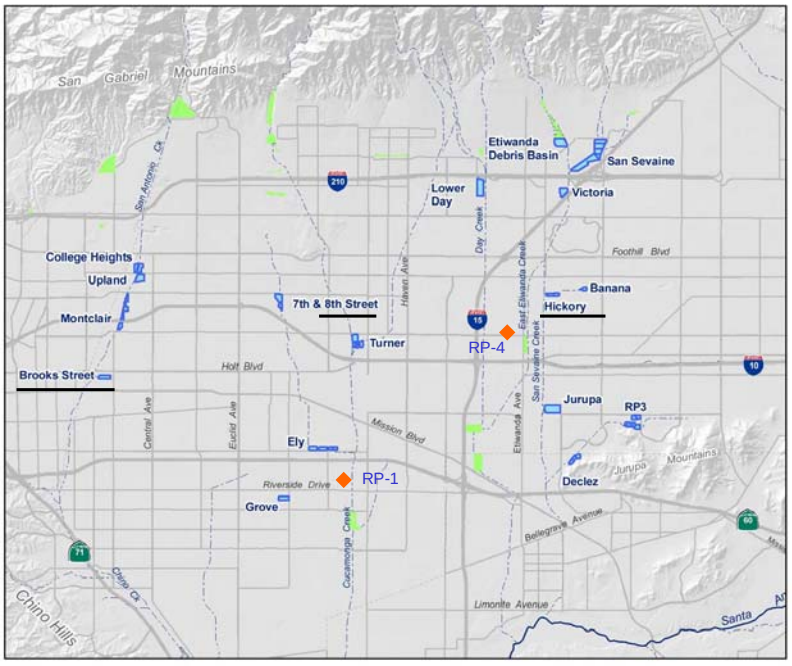


Figure 2.17. Chino Basin recharge basin and reclamation facility locations.

2.1.4.1 8th Street Basin

8th St. Basin is located on the border of the city of Ontario and the city of Upland and is owned by SBCFCD. It consists of two adjacent flowthrough basins (Figures 2.18 and 2.19). The two basins are essentially one large basin, separated by a street, yet connected by a gated box culvert under the road. The application of reclaimed water to 8th Street Basin was initiated in September 2007. The 8th St. basin recharge operation is characterized by an extensive vadose zone of approximately 450 feet. It has an effective recharge area of 14.5 acres and an estimated percolation rate of 0.5 ft/d. Samples were collected from the spreading basin, shallow lysimeters (5–25 feet; Figure 2.20) and a perimeter monitoring well (495–535' screen; 150' down-gradient) (Figure 2.21). Lysimeters samples were collected by applying a

positive pressure until all water stopped exiting the lysimeter tubing. Negative pressure was then applied to pull in a sample over the next 24 hours. The sample was then collected by again applying positive pressure. None of the sample was discarded. In order to get sufficient total sample volume for all the water quality analyses to be performed, the lysimeter samples were combined into one composite sample, representing samples from different lysimeter sampling locations (5', 10', 15', 25', and 35'). Synoptic sampling was attempted and samples were collected after 1 to 3 days for the lysimeter sample locations and ~3 weeks for the perimeter monitoring well. Three sampling campaigns were initiated in September (2007, start-up), March (2008), and May (2008), respectively.

Figure 2.18. Aerial photo of IEUA's 8th St. Basin's surface spreading operation.

Figure 2.19. View of IEUA's 8th St. Basin's surface spreading operation.

Figure 2.20. 8th St. Basin's lysimeter sampling ports.

Figure 2.21. 8th St. Basin's perimeter monitoring well.

2.1.4.2 Hickory Basin

Hickory Basin is located in the city of Fontana and is owned by SBCFCD (Figures 2.22 and 2.23). It is a multiple purpose basin used for flood control and groundwater recharge. The subsurface is characterized by an extensive vadose zone of approximately 385 feet. It has an effective recharge area of 8 acres and an estimated percolation rate of 0.7 ft/d. The application of reclaimed water to Hickory Basin was initiated in September 2005. Samples were collected from the spreading basin, shallow lysimeter sample locations (5–25 feet), and a perimeter monitoring well (365–405' screen; 340' downgradient). Synoptic sampling was

attempted and samples were collected after approximately 1 to 3 days from the shallow lysimeter sample locations and ~3 weeks from the perimeter monitoring well. One sampling campaign was initiated in March (2008).

Figure 2.22. Aerial photo of IEUA's Hickory surface spreading operation.

Figure 2.23. IEUA's Hickory surface spreading operation.

2.1.4.3 Brooks Basin

Brooks Basin is located in the city of Montclair and is owned by CBWCD (Figure 2.24). It is a conservation basin, which is operated to maximize the recharge of reclaimed water. The subsurface is characterized by an extensive vadose zone of approximately 325 feet. It has an effective recharge area of 7.7 acres and an estimated percolation rate of 1 ft/d.

Figure 2.24. Aerial photo of IEUA's Brooks Basin surface spreading operation.

The application of reclaimed water to Brooks Basin was initiated in September 2008. Two full-scale sampling events occurred at Brooks Basin. Samples were collected from the spreading basin and a shallow lysimeter sample location (25 feet). A perimeter well was not sampled at Brook Basin. Synoptic sampling was attempted and samples were collected after approximately 1 to 3 days for the shallow lysimeter sample locations. The two sampling campaigns were initiated in September (2008, start-up) and October (2008).

2.1.5 City of Auburndale's Rapid Infiltration Basins

The city of Auburndale, FL, operates the Regional Rapid Infiltration Basin (RIB; Figure 2.25) located within Polk County and the Peace River watershed. The operation consists of two basins totaling 27.5 acres with an application rate of 2.8 inches per week and a permitted flow of 0.28 MGD. The RIB received a secondary (nitrified) and UV treated effluent from the 4 mgd Regional Wastewater Treatment Facility[2]. The City of Auburndale's RIB recharge operation is characterized by a short vadose zone of approximately ~10 feet. The RIB feeds an unconfined surficial aquifer where the soil type is classified as high infiltration soil. The surficial aquifer, the unconfined and uppermost aquifer, ranges in thickness from a thin veneer of sand to greater than 50 feet. It is comprised of undifferentiated sands, clay, and shell. The quartz sand, which is generally uniform throughout the unit, grades to clay with depth as the surficial aquifer system approaches the intermediate aquifer system's upper confining unit. The depth to the water is about 5 to 10 feet below the surface. The confinement between the surficial and intermediate aquifers is well established. Samples were collected from the RIB influent and shallow (~10–15 feet) up-gradient (MW#4) and down-gradient (MW#6) wells (Figure 2.25). The up-gradient well was collected because there exists an up-gradient hay field spray field that sprays reclaimed water. This provides a background level of organic compounds that potentially contribute to the down-gradient RIB operation. The down-gradient well was located approximately 600 feet down-gradient of the RIB. The travel time to the down-gradient well was unknown, so synoptic sampling was not performed at this site. One sampling event occurred at this facility in March 2008.

Figure 2.25. Aerial photo of City of Auburndale's Regional RIB operation.

[2] Impact from pesticide application at the adjacent citrus grove is unknown. The information was requested but not received prior to completion of the final project report.

2.1.6 Laboratory-Scale Soil Column Set-ups

Soil-aquifer treatment was simulated at CSM using existing and well-established soil column set-ups. Soil column systems consisted of three independent laboratory-scale soil-column systems: PC_{anoxic}, $C1_{anoxic}$, and $C2_{oxic}$. The column configurations and operational parameters are summarized in Table 2.2. The PC_{anoxic} and $C1_{anoxic}$ systems consisted of four 4-foot acrylic glass columns in series (inner diameter 6 inches), which were operated under anoxic and saturated conditions (Figures 2.26 and 2.27).

Table 2.2. Column Configuration and Operational Parameters for PC, C1, and C2 Columns

	Column PC_{anoxic}	Column $C1_{anoxic}$	Column $C2_{oxic}$
Conditions	Biodegradation under saturated anoxic flow conditions	Biodegradation under saturated anoxic flow conditions	Biodegradation under unsaturated oxic flow conditions
Media	Native alluvial material	Native alluvial material	Native alluvial material
Design	Four 4-ft acrylic columns in series	Four 4-ft acrylic columns in series	One 4-ft acrylic column
Sampling Ports	After 4', 8', 12', and 16'	After 1', 2', 3', 4', 8', 12', and 16'	Four intermediate sampling ports

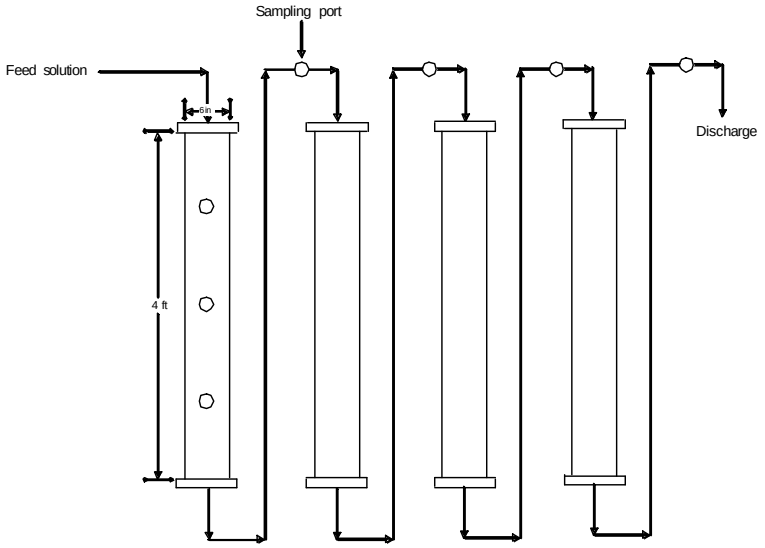


Figure 2.26. Column configuration for PC_{anoxic} and $C1_{anoxic}$ column systems.

The influent water was purged with nitrogen gas to remove any dissolved oxygen (DO) present in the influent water. The PC_{anoxic} feed was stored in a 55-gallon blue plastic barrel at room temperature, whereas $C1_{anoxic}$ feed was stored in a 5-gallon covered glass container at room temperature. The $C2_{oxic}$ system consisted of one 4-foot column segment, which was operated under unsaturated flow conditions (continuously wetted; Figure 2.28). Depending on

the measured DO in the influent water, it was purged with air to raise the DO to a saturated level (around 8 mg/L). The $C2_{oxic}$ feed was stored in a 5-gallon covered glass container at room temperature.

Figure 2.27. Experimental set-up of the PC_{anoxic} column system.

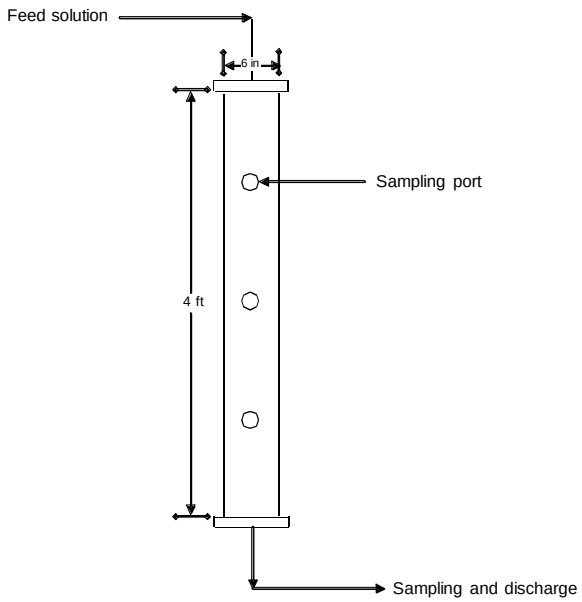


Figure 2.28. Column configuration for the C2-oxic column.

An abiotic 4-foot control column was used to account for removal of organic contaminants through adsorption processes. This column was operated under saturated and anoxic conditions. To keep the conditions abiotic, sodium azide was fed at a concentration of 2 mmol/L to the influent water. The feed water to all column systems was applied at a rate of approximately 1 mL/min or a loading rate of 0.08 m/day. All column systems were filled with native alluvial material from a local groundwater recharge site where gravel larger than 2 mm were sieved out.

The systems were fed water over a period of several months. Feed water was continuously spiked with selected target indicator compounds. The spiking solution was stored at 4°C and was continuously spiked directly into the system by the feed line (10% of the total influent flow is from the spiking solution). Feed samples were collected and time-composite samples (~12 hours) for treated soil-column water were collected for designated travel times (i.e., 7, 14, 21, and 28 days). Table 2.3 provides a summary of the soil-column experiments performed for this project.

Table 2.3. Soil-Column Experiments Simulating Surface Spreading Operations

Type of Water	TOC (mg/L)	Ammonia-N (mg/L)	Nitrate-N (mg/L)
Anoxic Conditions			
Nitrified wastewater[1]	5-7	<1	9-10
Nitrified/denitrified wastewater[2]	5.8	1.6	3.3
Biologically filtered nitrified/denitrified wastewater[3]	3.0	<0.6	~2.7
Drinking water[4]	1.8	<1	5.6*
Ultra-pure water	~0.2	<1	<0.1
Oxic Conditions			
Nitrified wastewater[1]	6.1	<1	9.3
Ultra-pure water	~0.2	<1	<0.1

* Spiked with nitrate
1 – South Platte River dominated by wastewater effluent; downstream of Denver Metro's Wastewater Reclamation Plant, Colorado
2 – CSDLAC's San Jose Creek East's wastewater effluent
3 – Riverbank filtered water; South Platte River, Brighton, Colorado
4 – City of Golden, Colorado, tap water

2.2 HIGH-PRESSURE MEMBRANE OPERATIONS

2.2.1 OCWD's Groundwater Replenishment System

The Orange County Water District (OCWD), CA Groundwater Replenishment System (GWRS) Advanced Water Purification Facility (AWPF) utilized reclaimed water after primary and secondary treatment. Primary wastewater treatment consists of coagulant addition and sedimentation. Following primary clarification, the primary effluent flow stream was split and oxidized using two secondary treatment processes, activated sludge and trickling filters. Secondary clarifiers at the activated sludge system and tricking filters produced fully oxidized and clarified secondary effluent. Subsequently, the effluent was pumped to the GWRS AWPF where it was treated with microfiltration, reverse osmosis (RO), and UV-peroxide advanced oxidation processes. The secondary treated wastewater was first chloraminated prior to microfiltration. The water was then treated by microfiltration using Siemens/Memcor submerged hollow fiber membranes with a maximum nominal pore size of 0.2 micron. The water was then diverted to the reverse osmosis (ESPA-2 membranes, Hydranautics, Oceanside, CA) system (Figures 2.29 and 2.30). Upstream of the RO process, the flow was pretreated by adding sulfuric acid for pH adjustment and scaling inhibitor to prevent precipitation of sparingly soluble salts, and by 10-micron cartridge filtration. The system was designed to operate at pH 6.8, an 85% recovery rate, and a permeate flux of 12

gfd (gallons per square foot per day). Four quarterly sampling campaigns were completed at the RO operation within the GWRS in April 2008, July 2008, October 2008, and January 2009. Note, the GWRS became operational in January 2008.

Figure 2.29. OCWD's RO membrane gallery.

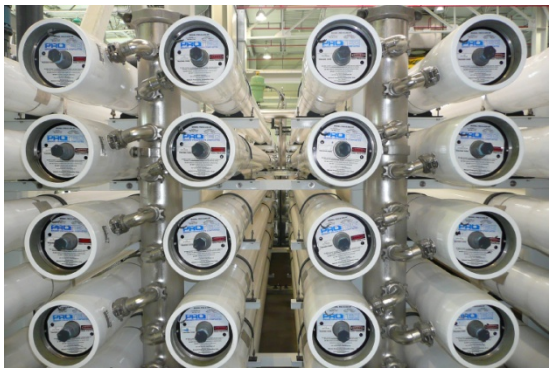


Figure 2.30. OCWD's RO membrane elements within pressure vessels.

2.2.2 CSDLAC's Pilot-Scale Reverse Osmosis System

County Sanitation Districts of Los Angeles County (CSDLAC), CA, pilot-scale RO system consists of two stages and was operated at pH 6.2–6.5 at a recovery of 82–83% using a conventional RO membranes. The RO system was fed membrane bioreactor (MBR) permeate. The 25 gpm MBR system treated domestic primary effluent provided from Whittier Narrows Water Reclamation Plant. The MBR pilot plant was designed to treat a nominal flow of 30 gpm or a membrane flux of approximately 9 gfd. The MBR consisted of nitrification/denitrification processes and a Zenon hollow-fiber ZeeWeed™ 500c membrane system. One sampling campaign occurred at this facility in May 2008.

2.2.3 CSM's Pilot-Scale Nanofiltration System

A pilot-scale nanofiltration/reverse osmosis system at CSM was used for controlled spiking studies in tap water to study the rejection of select nitrosamines by nanofiltration membranes. The pilot-scale system is a 2-stage membrane unit that was designed to mimic a 2-stage full-scale treatment system. The unit was built in a 4-stage array configuration to minimize space and consists of six pressure vessels, four in the first stage and two in the second stage. The pilot-scale unit requires 21 4040-spiral wound elements, with 14 elements in the first stage and 7 elements in second stage. The system is equipped with a supervisory control and data acquisition (SCADA) system, has a variable speed feed pump, and can be operated at different recoveries, feed flow rates, and permeate flux rates. Based on the system's configuration, it requires a feed flow rate between 15 and 25 gpm and therefore was operated in recycle mode, where permeate and concentrate streams were returned to the feed water tank. The system is fed water from two 500-gallon feed tanks that are temperature controlled using an in-house chilled process water stream. The pilot-scale system has multiple sampling locations that allows for samples to be collected from the feed, permeate from each pressure vessel, combined permeate from 1st stage, combined permeate from 2nd stage, total combined permeate, concentrate from pressure vessels, 1st stage combined concentrate, and total combined concentrate. A schematic and picture of the pilot-scale unit with sampling locations is presented in Figures 2.31 and 2.32, respectively.

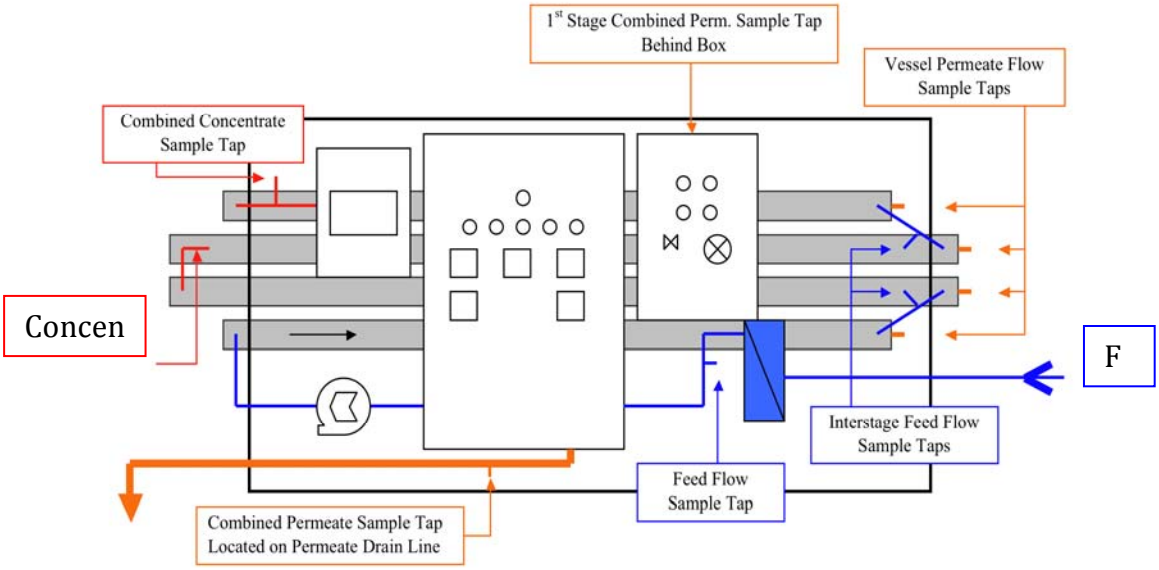


Figure 2.31. Schematic of pilot-scale membrane unit and sampling locations.

Figure 2.32. CSM's pilot-scale membrane skid.

2.2.4 CSM's Laboratory-Scale Nanofiltration System

Laboratory-scale experiments were performed to assess the removal of a suite of trace organic compounds. CSM's system consisted of 2 stages (1:1). The system was operated at a pH of 6.1–7.0 using NF 4040 (Dow/Filmtec) membranes (operated in recycle mode). The NF feed consisted of microfiltered/non-nitrified secondary effluent from Denver Metro Wastewater Reclamation District spiked with nitrate. The NF system was operated in recycle mode and at two constant permeate fluxes: 10 and 16 gfd. At each flux, the system was

operated at three different recoveries: 12, 48, and 75% (at 10 gfd) and 22, 48, and 80% (at 16 gfd). A suite of trace organic compounds was spiked in the feed, where feed concentrations for individual compounds ranged from a couple of ng/L to 3,000 ng/L. These experiments were performed in August 2008.

2.3 ANALYTICAL METHODS

2.3.1 BDOC Tests

Biodegradable dissolved organic carbon (BDOC) quantifies the dissolved biodegradable organic matter (BOM) using indigenous bacterial populations. BOM consists of organic compounds that undergo microbial biotransformation and mineralization to form biomass. The use of BDOC in conjunction with DOC serves as a surrogate of the presence of organic compounds that are not derived from humic substances. BDOC has been proposed as an effective surrogate measurement for assessing the performance of soil aquifer treatment systems (Drewes and Fox 1999; Drewes and Jekel 1998; Fox et al. 2001; Drewes and Fox 2000), and BDOC measurements have been strongly correlated with the distribution of biomass in surface spreading operations (Rauch-Williams and Drewes 2006). BDOC is an operationally defined parameter that depends upon the measurement protocol and experimental conditions (particularly, contact time, biomass, redox conditions).

Figure 2.33. CSM laboratory-scale membrane system.

Different methods of quantifying biodegradable dissolved organic carbon (BDOC) were evaluated. Batch and column BDOC tests were performed on CSDLAC's San Jose Creek tertiary-treated effluent.

Triplication was performed and 0.1 mg-C/L was the associated analytical error associated with these measurements. The average BDOC values were 2.3 and 2.2 mg/L for batch and column experiments, respectively, where these values fall within analytical error, and, thus, they were presumed similar. The batch BDOC method was recommended (described in the following) as this method proved more practical to employ. The minimum detection limit for the batch method was determined to be 0.1 mg-C/L.

BDOC was analyzed using 1 L amber glass aerobic batch reactors containing approximately 200 g of sand previously acid- and base-washed before continuous acclimation with samples from spreading-basin operations. The reactors were kept on a shaker table to ensure aerobic conditions. Each reactor was rinsed three times and filled with sample and acclimation of the microbial populations to the sample was allowed to occur for 10 days. At the end of the 10 days, each batch reactor was again rinsed and filled with 600 mL of sample. Samples were

collected (at various intervals, up to 40 days after the start of the test) from the reactors using a syringe and neoprene tubing for DOC analysis.

2.3.2 pH and Conductivity

pH was determined using a Beckman 260 portable pH meter with combination of a gel-filled electrode (Beckman, Fullerton, CA) (Standard Method 4500-H^+) (APHA 1998). Conductivity was determined using an YSI model 85 multi-meter (YSI Incorporated, Yellow Springs, OH) (Standard Method 2510).

2.3.3 Alkalinity

Alkalinity was measured using the Hach Alkalinity Kit. 100 mL sample was titrated with 1.6N sulfuric acid to a pH of 4.3 using the Hach digital titrator model 16900 (Hach, Loveland, CO).

2.3.4 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-NH3 B & C (APHA 1998). Metals were determined using a Perkin Elmer Elan 6100 inductively coupled plasma mass spectrometry system (Standard Method 3125 B) (APHA 1998). This method measured a suite of metals. These metals included Sc, Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn, and U.

2.3.5 TOC/DOC

TOC/DOC was quantified using a Sievers 5310 TOC analyzer with autosampler (Ionics Instruments, Boulder, CO) according to Standard Method 5310 B (APHA 1998). The samples were placed into 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 through a 0.45um filter.

2.3.6 UV Absorbance and SUVA

UV absorbance was analyzed using a Beckman UV/VIS spectrophotometer with a 1-cm quartz cell (Standard Method 5910 B) (APHA 1998). Samples were measured at wavelengths of 200 to 400 nm. The specific UV absorbance (SUVA) is defined as the ratio between UVA (254 nm) and DOC.

2.3.7 Fluorescence Spectroscopy

Fluorescence spectrometry expressed as excitation-emission matrices (EEMs) were developed using a Fluoromax 4 spectrofluorometer (HORIBA Jobin Yvon) blanked with Ultrapure Milli-Q water across an excitation spectrum of 240–450 nm and emission spectrum of 290–580 nm. Samples were brought to room temperature prior to analysis. The blank was subtracted and final matrices were further corrected with data from a full spectrum UVA scan. EEMs were corrected and graphed using MatLab software. Fluorescence spectrometry

can be used to distinguish humic-like organic matter from protein-like organic matter (Figure 2.34). The fluorescence of NOM is due to the presence of fluorophores that absorb photons, followed by the excitation to a higher electronic energy state. The absorbed energy is released to the environment at a longer wavelength. McKnight et al. (2001) derived a simple fluorescence index (FI) ratio to determine whether organic matter in aqueous systems is terrestrial or microbially derived. FI is the ratio of emission intensity at a wavelength of 450 nm to that at 500 nm, obtained with an excitation of 370 nm. In addition, the fluorescence intensity for protein-like organic matter can be quantified at an emission wavelength of 330 nm and an excitation wavelength of 270 nm. Also, humic- and fulvic acid-like intensities can be quantified at emission wavelengths of 420 and 440 nm and at excitation wavelengths of 330 and 240 nm, respectively. The specific fluorescence (SFLUOR) intensity is defined as the protein or humic fluorescence intensities (see earlier wavelengths) divided by DOC. Last, differential EEM spectra can be used to assess the performance treatment processes.

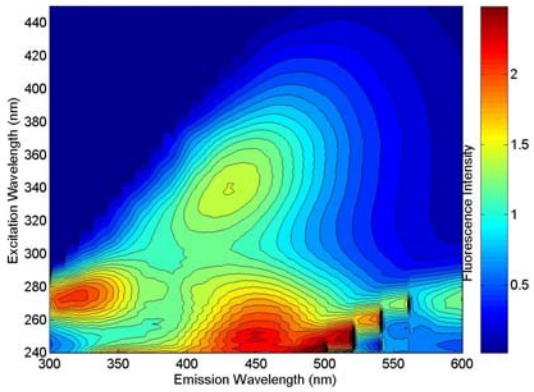


Figure 2.34. Fluorescence excitation-emission matrix for a treated wastewater sample.

2.3.8 Size Exclusion Chromatography

Size exclusion chromatography (SEC) was carried out using paired 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. Initially, samples were filtered, acidified with phosphoric acid (pH < 3), sparged with nitrogen gas for 2 minutes, and pH readjusted with sodium hydroxide (pH~7) prior to analysis to remove interfering inorganic carbon fraction. SEC measures the molecular weight distribution for a heterogeneous NOM mixture (Figure 2.35). This system uses UV and DOC detection (Her et al. 2002). The NOM present can differ in its molecular weight (MW) and can range from a few hundred to a high of several thousands. SEC-DOC is used to reveal transformation/removal patterns of the entire NOM, which consists of the following main fractions: polysaccharides, humic substances, and low MW acids.

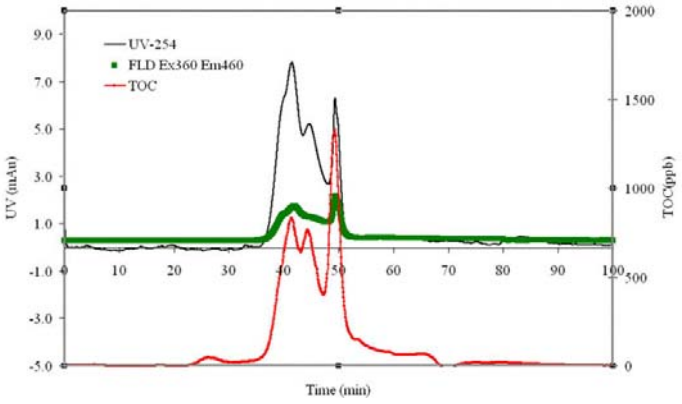


Figure 2.35. Distribution of organic compounds measured via size exclusion chromatography.

2.3.9 Trace Organic Compound Analysis—GC/MS

Pharmaceuticals, pesticides and chlorinated flame retardants were extracted using C-18 solid-phase extraction material followed by derivatization and gas chromatography with mass spectroscopy (GC/MS) as described by Reddersen and Heberer (2003). Samples were acidified to pH 2 using reagent grade HCl. For the surrogate standards, 100 ng of 10,11-dihydrocarbamazepine and 100 ng of 2-(m-chlorophenoxy) propionic acid in methanol (100 mL of a 1 ng/µL solution in methanol) were spiked into the filtered samples. Methanol was added to the samples (1% methanol per sample) as a modifier for solid phase extraction. Analytes were then pressure-extracted via a vacuum from the filtrate (5–8 mL/min) using 1 g of preconditioned RP-C-18 solid-phase extraction material. The C-18 cartridges were then dried overnight with a gentle stream of medical-grade nitrogen.

2.3.9.1 PFBBr Method

The analytes were eluted from the cartridges three times with 1 mL of acetone directly into sampler vials. Afterward, the eluent was dried with medical-grade nitrogen again, resuspended in 100 µL solution of pentafluorobenzyl bromide (PFBBr; 2% in toluene), derivatized with 4 µL of triethylamine and placed in a 100°C drying cabinet for 1 hour. The residue was resuspended again in toluene (100 µL) and transferred into 200 µL glass inserts.

2.3.9.2 MTBSTFA Method

The analytes were eluted from the cartridges three times with 1.5 mL of methanol through another cartridge filled with sodium sulfate into sampler vials (the eluent was dried in between with medical-grade nitrogen). Afterward, the eluent was dried with medical-grade nitrogen again, resuspended in 50 µL of acetonitrile, derivatized with 50 µL of N-(t-butyldimethylsilyl)-N-methyl-trifluoraacetamide (MTBSTFA) and placed in an 80°C drying cabinet for 1 hour. The remaining solution was transferred into 200 µL glass inserts.

2.3.10 Trace Organic Compound Analysis—LC/MS-MS

Trace organic compounds were measured by liquid chromatography with tandem mass spectroscopy (LC/MS-MS; Table 2.4) as described by Vanderford and Snyder (2006). This method analyzes pharmaceuticals and other trace organic compounds in water by isotope dilution liquid chromatography/tandem mass spectrometry. Analytes were extracted using solid-phase extraction (SPE) followed by LC/MS-MS as described by Vanderford et al. (2003). The surrogate standards [$^{13}C_3$]-caffeine, [$^{13}C_3$]-atrazine, [^{13}C]-sulfamethazine, carbamazepine-d10, [^{13}C]-ibuprofen, [^{13}C]-triclosan, and [$^{13}C_2$]-estradiol were spiked into the filtered samples at a concentration of 50 ng/L. Analytes were extracted in batches of six samples using preconditioned 500-mg hydrophilic-lipophilic balance (HLB) cartridges. All extractions were performed using an automated SPE system. The sample was then loaded (15 mL/min) on to the cartridges, after which the cartridges were rinsed with 5 mL of reagent water and then dried with a stream of nitrogen for 60 minutes. Next, the cartridges were eluted with 5 mL of 10/90 (v/v) methanol/MTBE followed by 5 mL of methanol into 15-mL calibrated centrifuge tubes.

Table 2.4 Trace Organic Compounds Measured by LC/MS-MS

Sulfamethoxazole	Atrazine	Bisphenol A
Atenolol	Diazepam	Diclofenac
Trimethoprim	Atorvastatin	Naproxen
Iopromide	Benzophenone	Triclosan
Caffeine	Primidone	Octyphenol
Fluoxetine	TCPP	BHA
Meprobamate	DEET	Musk Ketone
Dilantin	TCEP	Ibuprofen
Carbamazepine	Gemfibrozil	

The resulting extract was concentrated with a gentle stream of nitrogen to a volume of 50 μL. Then 20 μL of a 2.5 mg/L solution of internal standards (diazepam-d5 and testosterone-d3) was added, and the extract was brought to a final volume of 1 mL using methanol. The final concentrations of the internal standards were 50 μg/L.

2.3.10.1 Comparison of Indicator Analytical Methods

Observed concentrations for trace organic compounds measured using both analytical methods (data obtained from the first sampling campaigns in 2007 at both Tucson Water's Sweetwater Recharge Facility and CSDLAC's SAT sites) are summarized and compared in Table 2.5. These results indicate that the methods employed (GC-MS and LC-MS/MS) during this study are comparable. For another project funded by the Water Reuse Foundation (Drewes et al., 2008a), interlaboratory round-robin experiments were performed and field monitoring data were compared to assess the precision of differing methods (LC-MS/MS, GC-MS/MS, GC-MS). In summary, these findings demonstrated that the methods employed resulted in comparable results. The results were more dependent on the skill and level of

experience of each laboratory, where high variations in relative standard deviations (RSDs) for replicate samples were observed among laboratories that recently established methods for the compounds of interest. Findings also suggested that RSDs of less than 30% are achievable by an experienced laboratory. All methods that targeted for multi-component analysis exhibited high variations of recovery, indicating the degree of uncertainty that is still associated with reported low ng/L-level results. There are clear limitations to improve recovery by good laboratory practice, and it appeared that consistently high recoveries could only be assured by method modifications. Vanderford and Snyder (2006) proposed isotope dilution for each target analyte during multicomponent LC/MS-MS analysis to correct for matrix suppression, SPE losses, and instrument variability.

Table 2.5. Comparison of Observed Concentrations in ng/L for Compounds Measured Using Differing Methods

Analyte	Lab/Method	Tucson Recharge Basin	Tucson Piezometer	Tucson Monitoring Well/ #1	CSDLAC Recharge Basin	CSDLAC Shallow Monitoring Well #1	CSDLAC Shallow Monitoring Well #2	CSDLAC Shallow Monitoring Well #3
Carbamazepine	SNWA LC-MS/MS	440	380	530	98	96	110	110
Carbamazepine	CSM GC-MS-MTB	517	374	269	150	94	144	108
Diclofenac	SNWA LC-MS/MS	190	110	<0.25	0.72	<0.25	<0.25	<0.25
Diclofenac	CSM GC-MS-PFB	105	40	detect (<25)	n/a	n/a	n/a	n/a
Diclofenac	CSM GC-MS-MTB	n/a	n/a	n/a	n/a	n.d.	n.d.	n.d.
Gemfibrozil	SNWA LC-MS/MS	3500	2000	<0.25	740	<0.25	<0.25	<0.25
Gemfibrozil	CSM GC-MS-MTB	1509	668	n.d.	375	n.d.	n.d.	n.d.
Gemfibrozil	CSM GC-MS-PFB	1128	398	n.d.	64	n.d.	n.d.	n.d.
Naproxen	SNWA LC-MS/MS	1600	640	<0.50	13	<0.50	<0.50	<0.50
Naproxen	CSM GC-MS-MTB	801	250	n.d.	n/a	n/a	n/a	n/a
Naproxen	CSM GC-MS-PFB	787	222	n.d.	detect (<25)	n.d.	n.d.	detect (<10)
TCEP	SNWA GC-MS/MS	740	630	243	370	77	120	<50
TCEP	CSM GC-MS-PFB	500	361	320	177	25	37	detect (<25)
TCPP	SNWA GC-MS/MS	860	820	227	420	210	150	96
TCPP	CSM GC-MS-PFB	647	1065	710	438	165	106	73

Note. n/a = not analyzed; n.d. = non detected

2.3.10.2 Bisphenol A Contamination

Tables 2.6, 2.7, 2.8, and 2.9 illustrate bisphenol A contaminations in samples collected at Tucson's SWRF, City of Auburndale's RIB, and Chino Groundwater operations. These results indicate there is bisphenol A contamination associated with certain lysimeter and well samples. Note, the bisphenol A concentration in travel blanks were < 5.0 ng/L, indicating the contamination was not associated with handling of samples. The contamination is likely associated with the method used to collect the samples. The Tucson Water piezometer sample was collected using a HDPE, 1 liter, ball-valve bailer, where the casing for this piezometer was 2" of Schedule 40 PVC.

Table 2.6. Bisphenol A Concentrations (ng/L) at Tucson Water's SWRF Spreading Ground Operation

Sampling Period	Recharge Basin (ng/L)	Piezometer (ng/L)	Monitoring Well #1 (ng/L)
June 2006	<5	1,299	19
January 2007	13	3,100	<5
July 2007	<5	10,000	<5
April 2008	<5	2,900	<5

Table 2.7. Bisphenol A Concentrations (ng/L) at Montebello Forebay Spreading Grounds

Sampling Period	Recharge Basin (ng/L)	Shallow Monitoring Well #1 (ng/L)	Shallow Monitoring Well #2 (ng/L)	Shallow Monitoring Well #3 (ng/)
March–May 2007	<5	<5	<5	<5
June–August 2007	<5	<5	<5	<5
Nov.–Jan. 07-08	5.9	<5	<5	<5
Feb.–March 2008	34	<5	<5	Did not sample

Table 2.8. Bisphenol A Concentrations (ng/L) at a Chino Groundwater Basin Spreading Ground Operation

		Recharge Basin (ng/L)	Lysimeter (ng/L)	Monitoring Well (ng/L)
8th St. Basin	Sept.–Oct. 2007	27	1,400	<5.0
8th St. Basin	Mar.–April 2008	27	47.5	5.3
Hickory Basin	Mar.–April 2008	<5	6	<5.0
Brooks Basin	Sept.–Oct 2008	<5	140	Did not sample
Brooks Basin	Oct 2008	<5	68	Did not sample

Table 2.9 Bisphenol A Concentrations (ng/L) at City of Auburndale's RIB Operation

Sampling Period	Recharge Basin (ng/L)	Monitoring Well #1 (ng/L)	Monitoring Well #2 (ng/L)
March 2008	13	2200	2300

CHAPTER 3

IDENTIFICATION OF SURROGATES AND INDICATORS TO MONITOR THE REMOVAL OF TRACE ORGANIC COMPOUNDS IN SURFACE SPREADING OPERATIONS

3.1 IDENTIFICATION AND FATE OF INDICATOR COMPOUNDS

3.1.1 Montebello Forebay Spreading Grounds

The following sections present results for the removal of trace organic compounds from water samples taken at the Montebello Forebay Spreading Ground's San Gabriel Coastal Basin (SGCB) including the adjacent USGS/WRD Test Basin. The observed removal percentages of trace organic compounds quantified at this site over five sampling campaigns at SGCB and one campaign at the Test Basin are summarized in Table 3.1. In Table 3.1 the number in parentheses next to the compound name is the number of sampling campaigns in which the removal percentage of the particular compound was averaged. For some campaigns some compounds were not measured or not detected; thus, for these compounds, the number in parentheses was less than 6. Removal of compounds were categorized according to good (>90%), moderate (90–25%), and poor (<25%) removals relative to each other. This method follows an approach developed during a previous study (Drewes et al., 2008a). Results from one of the five sampling campaigns were adopted from a previous related project that was conducted at the same facility (Drewes et al., 2008a). To provide an idea of the magnitude observed, concentrations for selected compounds for samples collected from SGCB and the adjacent Test Basin are presented in Figures 3.1 and 3.2, respectively. Measured concentrations are tabulated in the Appendix (Table 7.4) for the SGCB sampling campaigns performed during this study.

In the short term (travel time <3 days), constituent removal at the Test Basin took place in the vadose zone: concentrations decreased within the first 8 feet (MLS 8 travel time = 10 hours) of SAT and remained relatively consistent up to 25 feet below the basin, (PR 11, travel time = 70 hours). Within the 3 days, atenolol, fluoxetine, gemfibrozil, and iopromide were well removed (>90%), whereas dilantin, diclofenac, ibuprofen, and naproxen were moderately removed. DEET, primidone, sulfamethoxazole, carbamazepine, tris(2-chloroethyl)phosphate (TCEP), tris(chloroisopropyl)phosphate (TCPP), and meprobamate were negligibly removed after 72 hours. With an increased travel time (2 months), the concentration of all trace organic contaminants detected in the basin decreased further, which was expected as subsurface travel time has been shown to a have a significant impact on removal (Drewes et al., 2003b; Grünheid et al., 2005; Amy and Drewes, 2006; Osenbruck et al., 2007). However, much of this attenuation is a result of dilution with native groundwater.

Table 3.1 Summary of the Removal of Indicator Compounds During CSDLAC's SAT Operation[a,b]

Good Removal	Intermediate Removal		Poor Removal
>90%	**90–50%**	**25–50%**	**<25%**
	San Gabriel Coastal USGS/WRD Test Basin		
	Travel Time = 0.5–3 days		
Atenolol (1)	Diclofenac (1)	Dilantin (1)	Carbamazepine (1)
Iopromide (1)	Naproxen (1)	Ibuprofen (1)	DEET (1)
Fluoxetine (1)			Meprobamate (1)
Gemfibrozil (1)			Primidone (1)
			Sulfamethoxazole (1)
			TCEP (1)
			TCPP (1)
	Travel Time = 2 months		
Atenolol (1) > 99%	Meprobamate (1)	Carbamazepine (1)	
Diclofenac (1)	TCEP (1)	Dilantin (1)	
Fluoxetine (1)	TCPP (1)	Primidone (1)	
Gemfibrozil (1)	Sulfamethoxazole (1)		
Iopromide (1)			
Trimethoprim (1)			
Ibuprofen (1)			
Naproxen (1)			
DEET (1)			
	San Gabriel Coastal Basin		
	Travel Time = 1.8 months		
Acetaminophen (1)	Sulfamethoxazole (4)	TDCPP (3)	Atrazine (4)
Atenolol (3) ***> 99%***	TCEP (3)	Primidone (1)	
Caffeine (2)	TCPP (3)	Dilantin (4)	
DEET (2)		Carbamazepine (4)	
Diclofenac (2) ***>99%***			
Erythromycin (1) ***>99%***			
Estrone (1)			
Gemfibrozil (5) ***>99%***			
Hydrocodone (1)			
Ibuprofen (1)			
Iopromide (1) ***>99%***			
Meprobamate (4)			
Naproxen (4) ***>99%***			
Salicyclic Acid (1)			
Triclosan (1)			
Trimethoprim (4) ***>99%***			
	7.4 months		
Atenolol (1) ***> 99%***	Sulfamethoxazole (1)	Primidone (1)	Atrazine (1)
Caffeine (1)	TCEP (1)	Carbamazepine (1)	Dilantin (1)
DEET (1)	TCPP (1)		
Diclofenac (1)			
Gemfibrozil (1) ***>99%***			
Ibuprofen (1)			
Iopromide (1)			
Meprobamate (1) ***>99%***			
Naproxen (1)			
Salicyclic Acid (1)			
Trimethoprim (1) ***>99%***			

[a] Recharge basin water quality: TOC = 4.6–7.8 mg/L; NH_3-N < 1 mg/L; NO_3-N = 1.7-3.9 mg/L.
[b] Number in parentheses indicates number of sampling campaigns.

Carbamazepine and primidone are especially recalcitrant molecules that have previously been used to determine the anthropogenic impact on water resources (Drewes et al., 2003b; Heberer et al., 2004; Godfrey et al., 2007; Strauch et al., 2008; Guo and Krasner, 2009). Neither compound is easily biodegraded or sorbs well to soil particles (Yu et al., 2009). However, the movement of carbamazepine through the vadose zone is retarded through soils and it is considered a slow-mobile chemical in subsurface environments (Scheytt et al., 2006; Chefetz et al., 2008).

It is interesting to note that the removal of trace organic compounds was similar for the San Gabriel Coastal Spreading Basin and the adjacent Test Basin for travel times of ~2 months (Table 3.1), which supports the robustness and reliability of SAT operations and the removal of trace organic chemicals. Meprobamate is one exception where less removal was observed at the Test Basin as compared to SGCB. The ~2 months removal data is similar to removals observed after a couple of weeks at Tucson Water's and the City of Auburndale's spreading operations, Tables 3.3 and 3.4, respectively. After 7.4 months of travel time at the SGCB , the degree of removal did not relatively change as compared to 1.8 months of travel time. This suggests that an additional 5 months of subsurface treatment did not result in further attenuation of these more recalcitrant compounds.

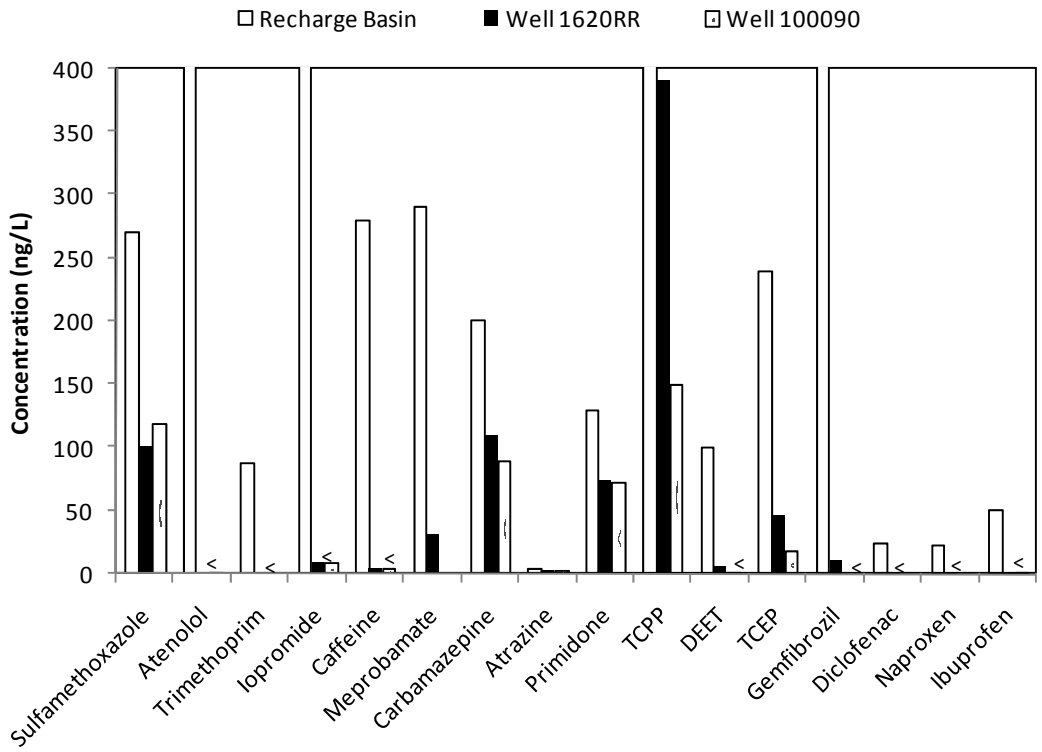


Figure 3.1. Concentrations of select indicator compounds for the fourth campaign at Montebello Forebay Spreading Ground's SGCB operation. Less than signs indicate concentration is less than the detection limit presented in the graph.

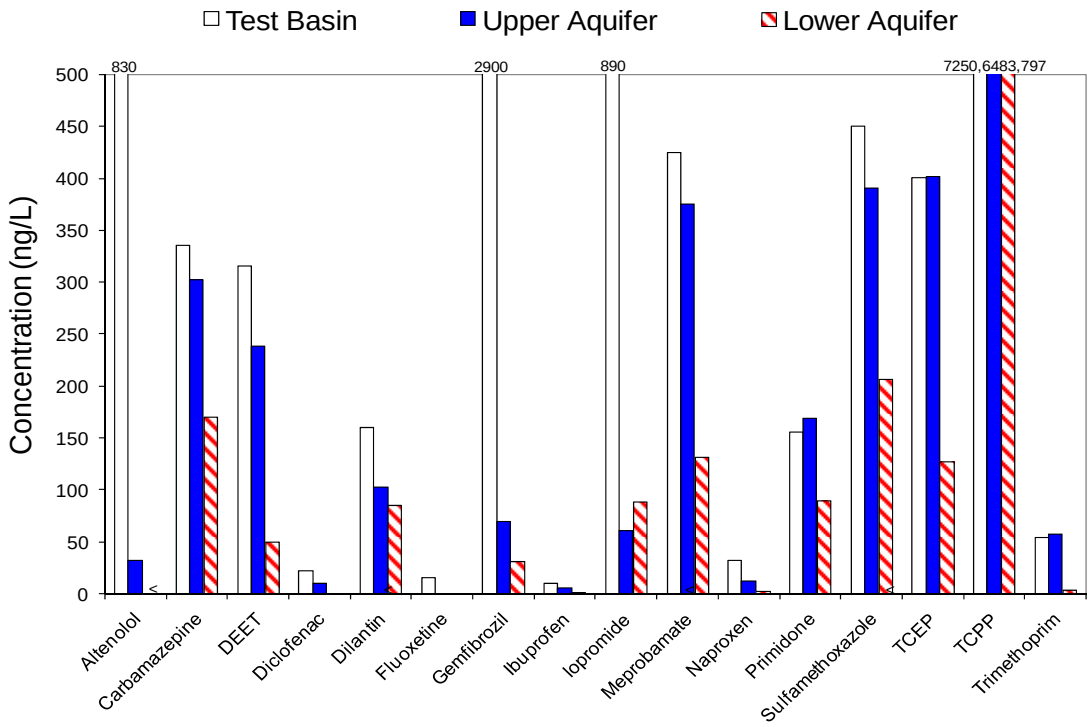


Figure 3.2. Concentrations of select indicator compounds for the USGS/WRD Test Basin at Montebello Forebay Spreading Ground. Less than signs indicate concentration is less than the detection limit presented in the graph.

3.1.2 Chino Groundwater Basin's Spreading Operations

The following sections present results for the removal of trace organic compounds at Inland Empire Utilities Agency's 8th Street, Hickory and Brooks spreading basins. The observed removal percentage ranges of trace organic compounds quantified at these sites are summarized in Table 3.2. To provide an idea of the magnitude observed, concentrations for selected compounds from samples collected during one sampling campaign at each site are presented in Figures 3.3, 3.4, and 3.5. Measured concentrations are tabulated in the Appendix (Tables 7.5 and 7.6) for the campaigns performed during this study.

The shallow lysimeter sample represents a composite of samples collected at various lysimeter locations between 5 feet and 35 feet at 8th St. and Hickory Basins. At Brooks Basin, the 25 feet lysimeter location was sampled. Similar to the results from Tucson Water's surface spreading operation (Table 3.3), atenolol, caffeine, and fluoxetine exhibited more than 90% removal at the lysimeter sampling locations, which represent travel times on the order of a couple of days. Also, similar to Tucson Water's spreading operation, carbamazepine, DEET, dilantin, ibuprofen, meprobamate, primidone, sulfamethoxazole, TCEP, and TCPP were partially or not removed after a couple days. In the perimeter monitoring well samples at the 8th St. and Hickory Basins, most of the organic compounds were not detected (Figures 3.3 and 3.4). Although samples are likely influenced by dilution (atrazine detection indicate impact from sources resulting from historical agricultural practices in the area), it is hypothesized that an unrepresentative slug of water was sampled and the travel time was miscalculated based on prediction rates, because conservative

recalcitrant compounds, such as carbamazepine and primidone, were not detected in this sample. Conductivity was examined to indicate breakthrough of the reclaimed water at lysimeter locations, which were used to determine the approximate travel time and sampling dates. However, conductivity break through was never observed at the perimeter wells. It is hypothesized that breakthrough was too small to be detected because of dilution and an extensive vadose zone at IEUA's 8th St. Basin (> 450') and Hickory Basin (> 385').

Table 3.2. Summary of the Removal of Indicator Compounds after 2–3 days of Travel Time During Spreading Basin Operations within the Chino Groundwater Basin[a,b]

Good Removal >90%	Intermediate Removal		Poor Removal < 25%
	90–50%	50–25%	
8th St. Basin			
Atenolol (2)	Triclosan (1)	Benzophenone (1)	Carbamazepine (2)
Caffeine (1)		Ibuprofen (1)	DEET (1)
Fluoxetine (1)		TCEP (2)	Dilantin (2)
		TCPP (1)	Meprobamate (1)
		TDCPP (2)	Primidone (1)
			Sulfamethoxazole (2)
Brooks Basin			
Atenolol (1)	Iopromide (1)	Benzophenone (2)	Carbamazepine (2)
Caffeine (1)		Ibuprofen (1)	DEET (2)
			Dilantin (2)
			Meprobamate (2)
			Primidone (2)
			Sulfamethoxazole (1)
			TCEP (2)
			TCPP (2)
Hickory Basin			
Atenolol (1)		Benzophenone (1)	Carbamazepine (1)
Fluoxetine (1)		TCEP (1)	DEET (1)
			Dilantin (1)
			Primidone (1)

[a] Recharge basin water quality: TOC = 5.6–12.8 mg/L; NH_3-N = <0.3 mg-N/L; NO_3 < 3 mg-N/L; subsurface conditions: travel time of 2 to 3 days; predominant redox conditions: oxic to anoxic.
[b] Number in parentheses indicates number of sampling campaigns.

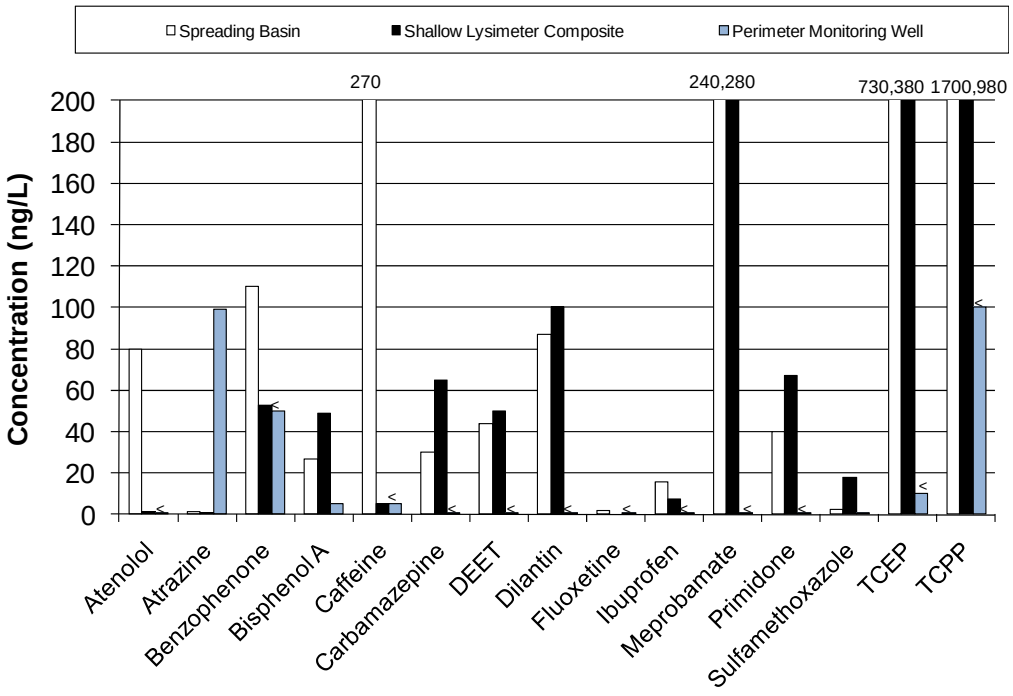


Figure 3.3. Concentrations of select indicator compounds for the second sampling campaign at IEUA's 8th St. Basin's surface spreading operation. Less than signs indicate concentration is less than the detection limit presented in the graph. The lysimeter sample is a composite of samples collected at 15' and 25' lysimeter locations.

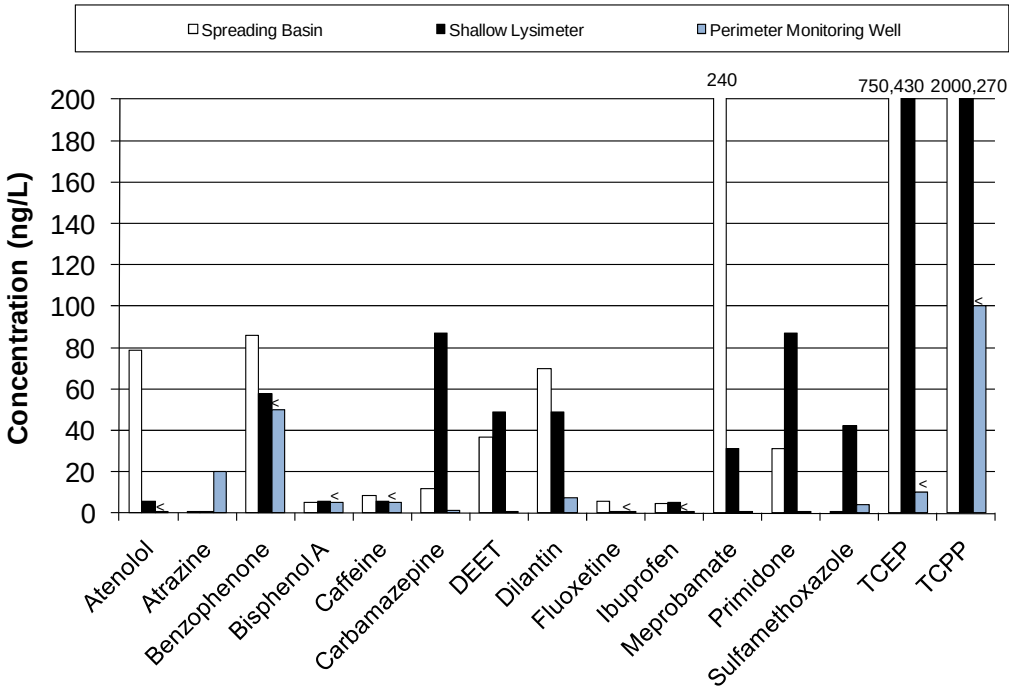


Figure 3.4. Concentrations of select indicator compounds at IEUA's Hickory surface spreading operation. Less than signs indicate concentration was less than the detection limit presented in the graph. The lysimeter sample is a composite of samples collected between 5' and 35' lysimeter locations.

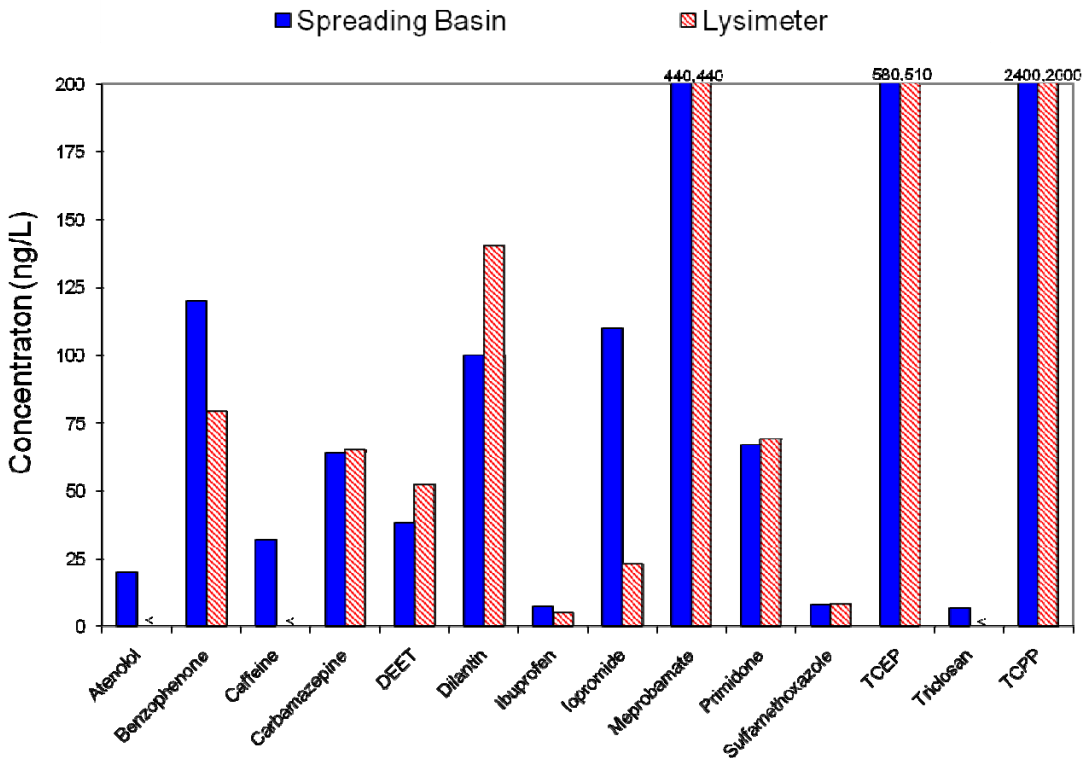


Figure 3.5. Concentrations of select indicator compounds at IEUA's Brooks Basin surface spreading operation. Less than signs indicate concentration was less than the detection limit presented in the graph. The lysimeter sample is a sample collected at the 25' lysimeter location.

3.1.3 Tucson Water's Sweetwater Recharge Facility

The following sections present results for the removal of potential indicator trace organic compounds from Tucson Water's Sweetwater Recharge Facility. The observed removal percentages of indicator compounds quantified at this site over six sampling campaigns are summarized in Table 3.3. Results from two of the six sampling campaigns were derived during a previously conducted WRF-funded project (WRF-03-014; Drewes et al., 2008a). To provide an idea of the magnitude observed, concentrations for selected compounds for samples collected during one sampling campaign are presented in Figure 3.6. Measured concentrations are tabulated in the Appendix (Table A.3) for all four campaigns performed during this study.

Several compounds classified as Good Removal (>90%) during SAT were already removed in the piezometer sample (MW#5), representing a travel time of 2 to 3 days. However, some compounds, such as diclofenac, gemfibrozil, ibuprofen, naproxen, meprobamate, and sulfamethoxazole, required a longer retention time (~2 weeks) to achieve a similar degree of removal. A delayed removal of meprobamate and sulfamethoxazole was observed, where removal was only observed after 2 to 3 days, suggesting that changes in redox conditions may be important for the removal of these compounds.

The more recalcitrant compounds, such as the antiepileptic drugs (i.e., carbamazepine, primidone, dilantin), chlorinated flame retardants (i.e., TCEP, TCPP, tri(2,3-dichloropropyl)phosphate (TDCPP)), and the herbicide atrazine were not removed or were

removed to a lesser degree (<50% removal) after 2 to 3 days of SAT. However, some of these compounds (i.e., TCPP, TCEP, and dilantin) shifted to higher removal categories after 2 weeks of retention in the subsurface. This shift could be due to a combination of biotransformation via denitrification, potential errors associated with the measurement of low ng/L-level concentrations, and an unrepresentative slug of water that was sampled after 2 weeks, although synoptic sampling was attempted. It is noteworthy that for a majority of target compounds, their concentrations decreased >90% after 2 weeks of travel time.

Table 3.3. Summary of the Removal of Indicator Compounds during Tucson Water's SWRF Operation[a,b]

Good Removal >90%	Intermediate Removal 90–50%	Intermediate Removal 50–25%	Poor Removal < 25%
	Travel Time: 2–3 days		
Atenolol (4)	Diclofenac (5)	DEET (3)	Atrazine (4)
Atorvastatin (2) ***>99%***	Benzophenone (3)	Dilantin (4)	Carbamazepine (4)
BHA (3)	Gemfibrozil (3)	Iopromide (1)	EDTA (1)
Caffeine (3) ***>99%***	Ibuprofen (5)	Primidone (1)	Meprobamate (4)
Dioctyl phthalate (1)	Naproxen (6)	TCEP (5)	Sulfamethoxazole (4)
Enalapril (1)	Octylphenol (1)	TDCPP (3)	TCPP (6)
Fluoxetine (4) ***>99%***	Tonalide (2)		
Galaxolide (2) ***>99%***			
Nonylphenol (1)			
Norfluoxetine (3)			
Salicyclic Acid (3)			
Simvastatin hydroxy acid (1)			
Triclosan (3)			
Trimethoprim (4)			
Travel Time: 2 weeks			
Atenolol (4) ***>99%***	Dilantin (4)	TDCPP (4)	Atrazine (4)
Atorvastatin (3) **>99%**	TCPP (5)		Carbamazepine (4)
Benzophenone (3)	TCEP (5)		Primidone (1)
BHA (3) ***>99%***			
Caffeine (3)			
DEET (3)			
Diclofenac (5) ***>99%***			
Dioctyl phthalate (1)			
EDTA (1)			
Enalapril (1)			
Fluoxetine (4) ***>99%***			
Galaxolide (2) ***>99%***			
Gemfibrozil (6) ***>99%***			
Ibuprofen (5)			
Iopromide (1)			
Meprobamate (4)			
Naproxen (6) ***>99%***			
Nonylphenol (1) ***>99%***			
Norfluoxetine (3)			
Octylphenol (1)			
Salicyclic Acid (3)			
Simvastatin hydroxy acid (1)			
Sulfamethoxazole (4)			
Tonalide (2)			
Triclosan (3)			
Trimethoprim (4) ***>99%***			

[a] Recharge basin water quality: TOC = 10–13 mg/L; NH_3-N = 10–30 mg/L; NO_3-N < 5 mg/L; subsurface conditions: travel time of 1 to 7 days; predominant redox conditions: oxic to anoxic.
[b] Number in parentheses indicates number of sampling campaigns.

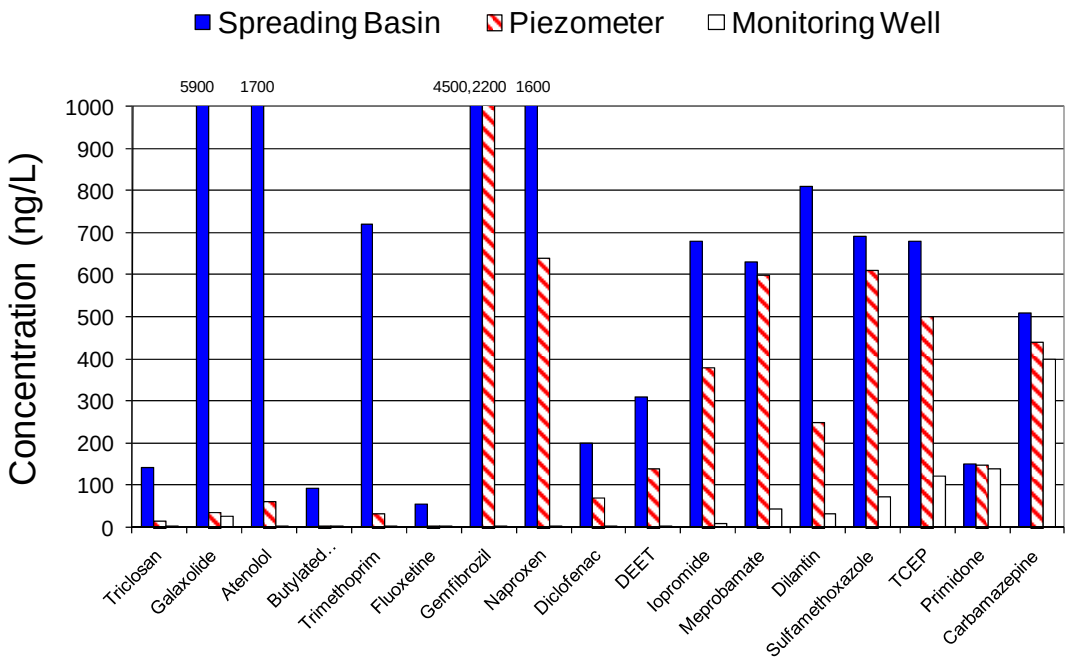


Figure 3.6. Concentrations of select indicator compounds for the fourth sampling campaign at Tucson Water's surface spreading operation.

3.1.4 City of Auburndale's Regional Rapid Infiltration Basin

The following sections present results for the removal of trace organic compounds at the City of Auburndale's regional rapid infiltration basin operation. The observed removal percentages of trace organic compounds quantified at this site are summarized in Table 3.4. To provide an idea of the magnitude observed, concentrations for selected compounds for samples collected are presented in Figure 3.7. Measured concentrations are tabulated in the Appendix (Table 7.7) for the campaign performed during this study.

As suspected, the up-gradient spray field contributes to background level for some organic compounds, such as carbamazepine, dilantin, gemfibrozil, meprobamate, primidone, sulfamethoxazole, and TCPP, which were detected in the up-gradient well (Figure 3.7). As compared to Tucson Water's SWRF operation (Table 3.3), the RIB operation achieved similar removals for the same compounds, for travel times greater than a week.

Table 3.4. Summary of the Removal of Indicator Compounds after a Week of Travel Time During the City of Auburndale's RIB Operation[a,b]

Good Removal >90%	Intermediate Removal 90–50%	Intermediate Removal 50–25%	Poor Removal < 25%
Atenolol (1)	Dilantin (1)	Primidone (1)	Carbamazepine (1)
BHA (1)	Sulfamethoxazole (1)		Atrazine (1)
Diclofenac (1)	TCPP (1)		
Fluoxetine (1)			
Gemfibrozil (1) ***>99%***			
Meprobamate (1) ***>99%***			
Naproxen (1)			
Triclosan (1)			
Trimethoprim (1)			

[a] Recharge basin water quality: TOC = 7.7 mg/L; NH_3-N = <5 mg-N/L; NO_3 = 0.2 mg-N/L; subsurface conditions: travel time > one week; predominant redox conditions: oxic to anoxic
[b] Number in parentheses indicates number of sampling campaigns.

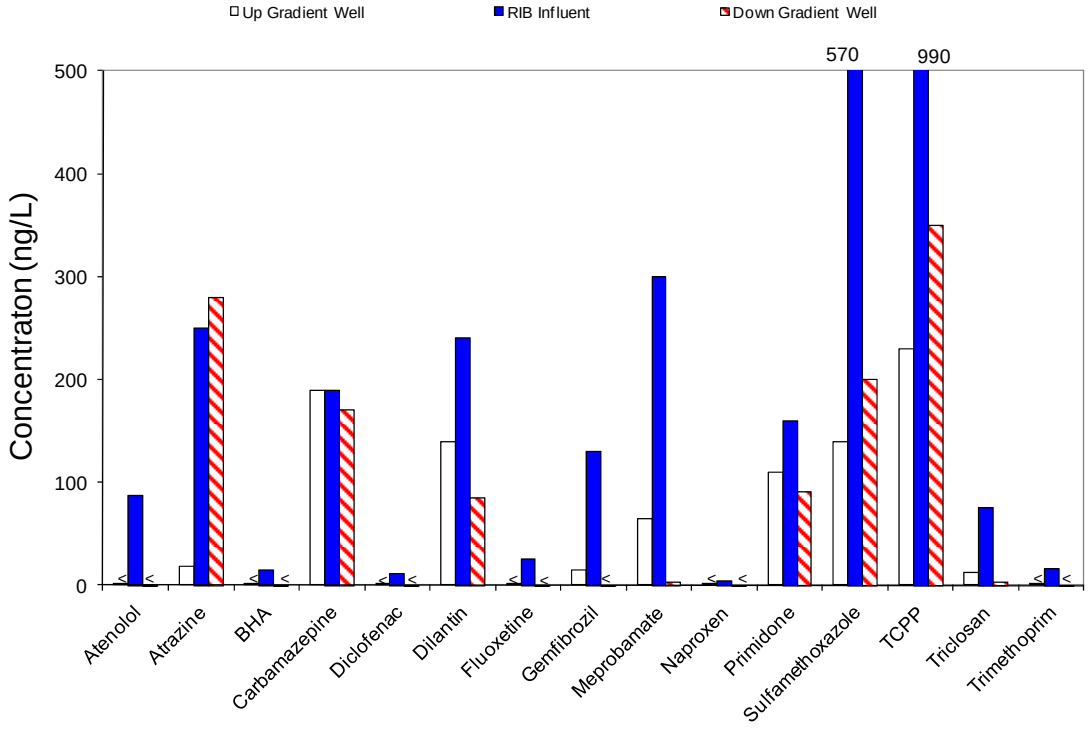


Figure 3.7. Concentrations of select indicator compounds for the City of Auburndale's RIB operation. Less than signs indicate concentration is less than the detection limit presented in the graph.

3.1.5 Laboratory-Scale Soil Column Experiments

The following sections present results for the removal of trace organic compounds during controlled soil column experiments. The observed removal percentages of indicator compounds quantified during the column experiments are summarized in Tables 3.5 and 3.6. The results are divided into prevalent redox conditions as well as the range of organic carbon and inorganic nitrogen (i.e., ammonia and nitrate) concentrations in the feed waters. All trace organic compounds were spiked into the feed waters at concentrations ranging from 50 to 500 ng/L.

Table 3.5. Summary of the Removal of Indicator Compounds after a Week of Travel Time Under Oxic Conditions[a]

Good Removal	Intermediate Removal		Poor Removal
>90%	**90–50%**	**50–25%**	**< 25%**
TOC = 6.1 mg/L	**NH_3 = <1 mg-N/L**		**NO_3 = 9.3 mg-N/L**
	Travel Time = 6 days		
Naproxen (1)		TCPP (1)	TCEP (1)
Gemfibrozil (1)		TDCPP (1)	
TOC = 0.2 mg/L	**NH_3 = <1 mg-N/L**		**NO_3 = <0.1 mg-N/L**
	Travel Time = 5 days		
Atenolol (1)	Meprobamate (1)	Diazepam (1)	Atrazine (1)
Atorvastatin (1)		Dilantin (1)	Carbamazepine (1)
Caffeine (1)		Primidone (1)	
DEET (1)		Sulfamethoxazole (1)	
Bisphenol A (1)		TCEP (1)	
Diclofenac (1)			
Ibuprofen (1)			
Iopromide (1)			
Naproxen (1)			

[a] Number in parentheses indicates number of replicate of experiments.

The pharmaceutical residues naproxen and ibuprofen were well attenuated after 6 days under both oxic and anoxic conditions as well as for various feed water types. The redox conditions and feed water types did not seem to have an impact on the removal of these compounds. A more expanded suite of indicator compounds was examined using feed water with low organic carbon (~0.2 mg/L) and inorganic nitrogen concentrations. Under these feed-water conditions, most of the compounds were removed by more than 90% after 5 days of travel time under both oxic and anoxic conditions. This is in agreement with full-scale observations, where all of these compounds were removed in excess of 90% with travel times greater than one week. It is interesting to note that meprobamate was better attenuated under anoxic than oxic conditions. The overall results suggest these indicator compounds can be attenuated even under low organic carbon and inorganic nitrogen levels.

The chlorinated flame retardant compounds (i.e., TCEP, TCPP, TDCPP) were not well removed after 6 days under oxic or anoxic conditions and for differing feed water types. This is in general agreement with observations from full-scale monitoring efforts, where these compounds were not well attenuated. The antiepileptic compounds (i.e., primidone, dilantin, carbamazepine), sulfamethoxazole, and atrazine were not well removed after 5 days under either oxic or anoxic conditions, which agrees with observations from full-scale monitoring.

Table 3.6. Summary of the Removal of Indicator Compounds after a Week of Travel Time Under Anoxic Conditions[a]

Good Removal >90%	90–50%	Intermediate Removal 25–50%	Poor Removal <25%
TOC = 2.2 mg/L	**NH_3 = 0.6 mg-N/L**		**NO_3 = 0.1 mg-N/L**
	Travel Time = 6 days		
Naproxen (1)			TCPP (1)
Ibuprofen (1)			TCEP (1)
Gemfibrozil (1)			TDCPP (1)
Caffeine (1)			
TOC = 1.8 mg/L	**NH_3 = <1 mg-N/L**		**NO_3 = 5.6 mg-N/L**
	Travel Time = 6 days		
Naproxen (1)	Diclofenac (1)	TCEP (1)	TCPP (1)
Ibuprofen (1)	Gemfibrozil (1)		TDCPP (1)
TOC = 5.7 mg/L	**NH_3 = <1 mg-N/L**		**NO_3 = 9.9 mg-N/L**
	Travel Time = 6 days		
Naproxen (2)	Diclofenac (1)		TCEP (3)
Gemfibrozil (2)			TCPP (3)
Ibuprofen (3)			TDCPP (2)
TOC = 5.7 mg/L	**NH_3 = <1 mg-N/L**		**NO_3 = 2.7 mg-N/L**
	Travel Time = 6 days		
Naproxen (1)	Gemfibrozil (1)		TCEP (1)
Ibuprofen (1)			TCPP (1)
Caffeine (1)			TDCPP (1)
TOC = 0.2 mg/L	**NH_3 = <1 mg-N/L**		**NO_3 = <0.1 mg-N/L**
	Travel Time = 5 days		
Atenolol (1)	TCEP (1)	Diazepam (1)	Carbamazepine (1)
BHA (1)			Primidone (1)
Bisphenol A (1)			Sulfamethoxazole (1)
Caffeine (1)			Dilantin (1)
DEET (1)			
Fluoxetine (1)			
Gemfibrozil (1)			
Ibuprofen (1)			
Mebrobamate (1)			
Naproxen (1)			
Trimethoprim (1)			

[a] Number in parentheses indicates number of replicate of experiments.

Removal kinetics of select indicator compounds are presented in Figure 3.8. As expected, caffeine and trimethoprim concentrations decreased rapidly. Similar rapid disappearances were observed for atenolol, atorvastatin, BHA, bisphenol A, and naproxen (data not shown). It is interesting that DEET, diclofenac, meprobamate, sulfamethoxazole, and iopromide had slower transformation kinetics, which is consistent with slow removal of these compounds based on field observations (Figure 3.7).

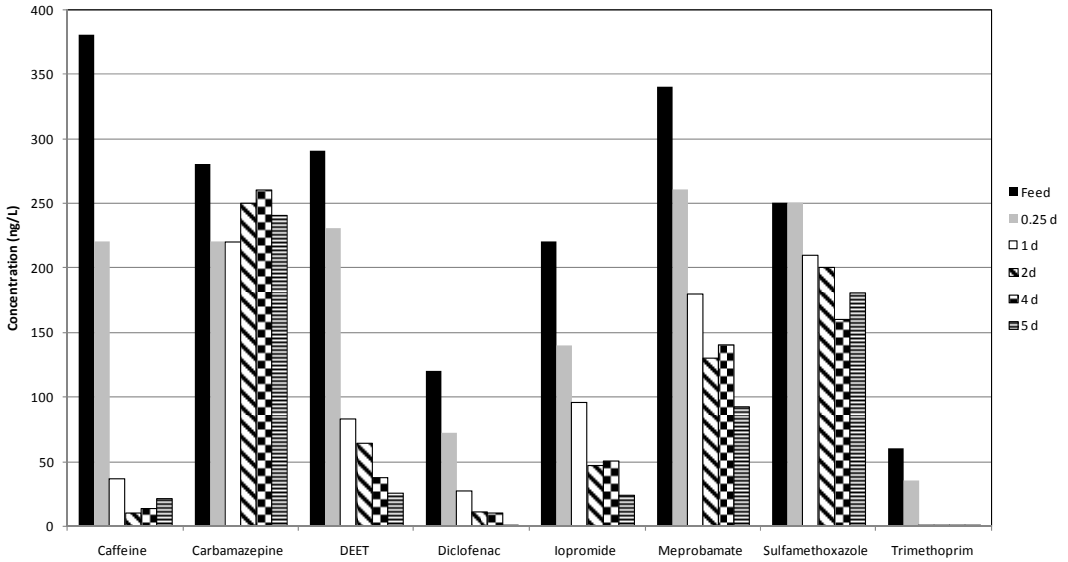


Figure 3.8. Removal kinetics of select indicator compounds during soil-column treatment under oxic conditions.

3.1.6 Comparison of Field Spreading Basin Operations

The removal of select indicator compounds across various spreading basin operations are presented in Figure 3.9. Removal data in Figure 3.9 represent data from one sampling campaign at each site. Table 3.7 lists the details on the spreading basin operations for the data reported in Figure 3.9. The results indicate that removals for these indicator compounds are similar across sites for the given operational conditions, where removals at City of Auburndale's and Tucson Water's SWRF for travel times of more than 2 weeks are comparable to removals observed at MFSG operations at travel times of more than 2 months. In addition, removals are similar despite a deeper vadose zone at Tucson Water's SWRF and the use of reclaimed water types that differed in quality (Table 3.7). It is noteworthy that the removal of sulfamethoxazole was higher at Tucson Water's SWRF as compared to the other sites, even though removals at MFSG were determined for longer travel times.

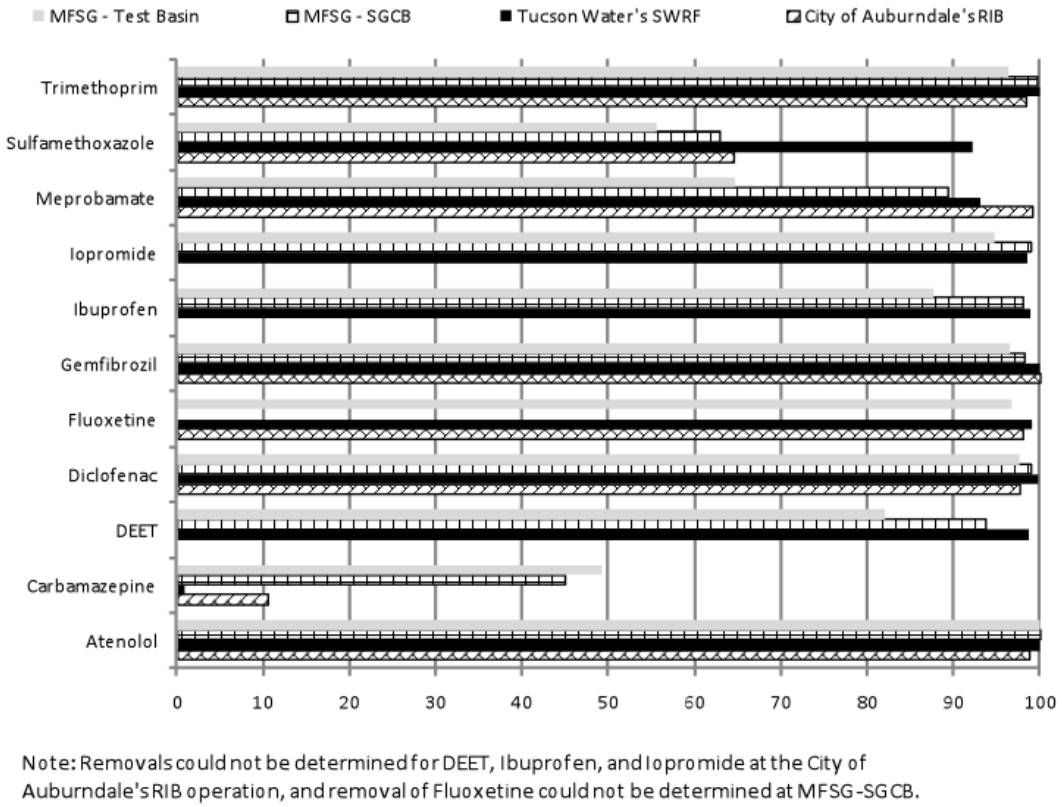


Figure 3.9. Removal of select indicator compounds across spreading basin operations. See Table 3.7 for details on well locations considered.

Table 3.7. Details on the Spreading Basin Operations for the Data Reported in Figure 3.9.

	MFSG – SGCB	MFSG – USGS/WRD Test Basin	Tucson Water's SWRF	City of Auburndale RIB
Vadose Zone Depth	10'	10'	120'	10'
Travel Time to Monitoring Well	1.4 months	2 months	2 weeks	> 1 week
Feed-Treated Wastewater Type	nitrified/ denitrified	nitrified/ denitrified	partially nitrified	nitrified

The average concentrations for sulfamethoxazole at Tucson Water's SWRF (four sampling campaigns) and San Gabriel Coastal Basin's (five sampling campaigns) recharge operations are presented in Figure 3.10. The average sulfamethoxazole removals at SWRF and SGCB were 93±3% and 66±29%, respectively. Tucson Water's SWRF is different than the SGCB

operation as it is characterized by a deeper vadose zone (i.e., 120 feet) as compared to 10 feet vadose zone for SGCB. In addition, partially nitrified treated secondary effluent is applied to SWRF as compared to a fully nitrified/denitrified tertiary effluent quality applied to SGSB. Sufficient anoxic conditions at SWRF may explain the further reduction of sulfamethoxazole. For travel times between 0.5 to 3 days and 2 months at SGCB (Table 3.4), the TOC and nitrate concentrations were low and varied little. However, for travel times of between 2 to 3 days and 2 weeks at Tucson Water's SAT site, there was sufficient removal of TOC (~Δ5 mg/L) and nitrate (~Δ9 mg-N/L) to suggest denitrification (anoxic) conditions were present.

The removal kinetics of select indicator compounds across spreading basin operations are presented in Figure 3.11. Considering the travel times across sites, the results indicate that slower kinetics were observed for DEET, diclofenac, ibuprofen, and meprobamate. Note, the average concentrations for these compounds across the basins were 191±143, 64±91, 40±40 and 416±139 ng/L, respectively. These results suggest that, for these compounds, a travel time of more than 1 week is required to observe a removal in excess of 90%. It is interesting that gemfibrozil had improved removal at MFSG Test Basin after 3 days as compared to at Tucson Water's SWRF after 3 days. Figure 3.12 reports the average concentrations for gemfibrozil at Tucson Water's SWRF (across three sampling campaigns) and MFSG Test Basin (across six sampling locations for one sampling campaign) recharge operations. Although the relative removal of gemfibrozil was lower at Tucson Water's SWRF, a greater mass reduction of gemfibrozil was observed at Tucson Water's SWRF as compared to MFSG Test Basin. Therefore, it is important to consider the initial concentration level when utilizing and interpreting percentage removal data. Similar to the previously mentioned compounds, travel time affects the removal of gemfibrozil when initial gemfibrozil levels are high, ~4,000 ng/L.

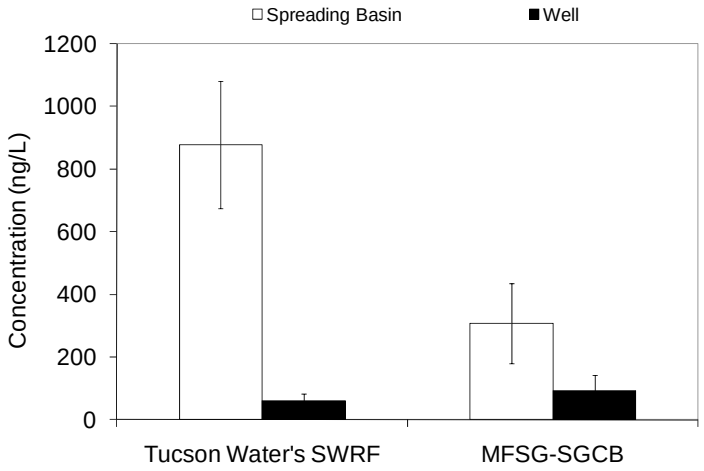


Figure 3.10. Average sulfamethoxazole concentrations at Tucson Water's SWRF and MFSG SGCB surface spreading operations.

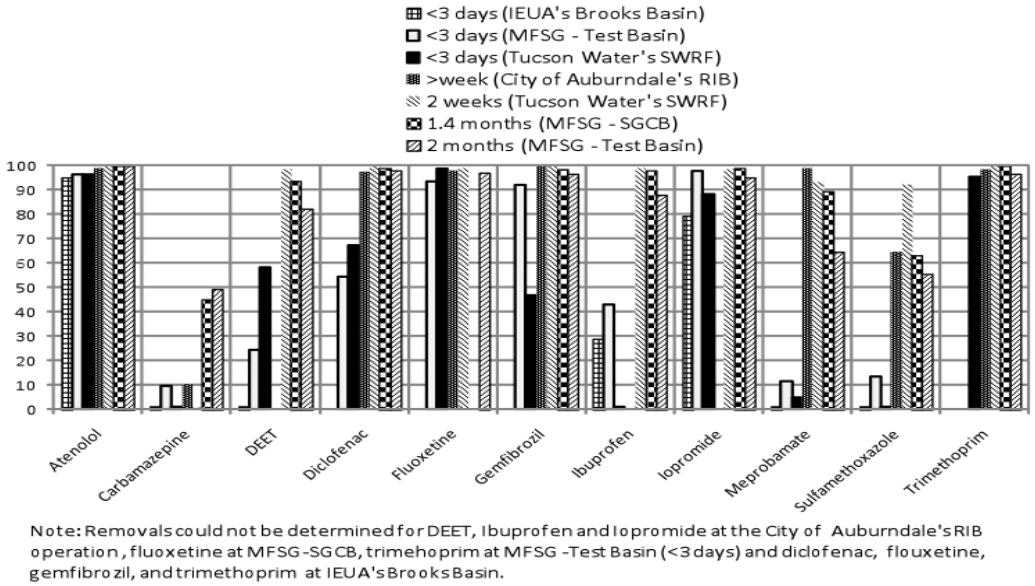


Figure 3.11. Kinetics of select indicator compounds as removal percentage across spreading basin operations.

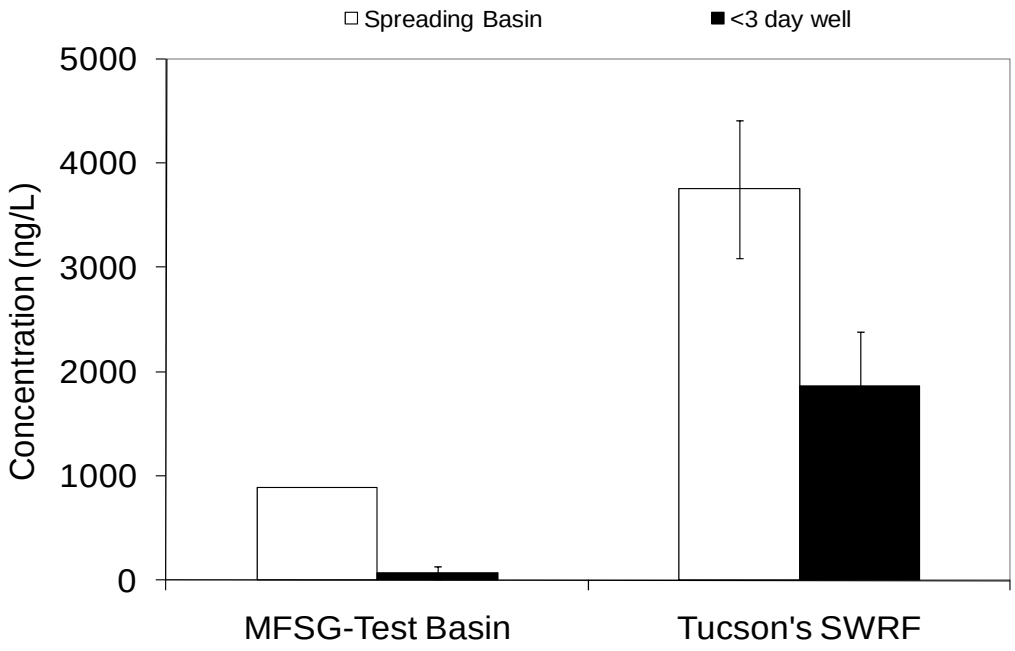


Figure 3.12. Average gemfibrozil concentrations at Tucson Water's SWRF (averaged across three sampling campaigns) and MFSG Test Basin (averaged across six sampling locations representing travel times between 10 h and 3 days).

3.2 IDENTIFICATION AND FATE OF SURROGATE PARAMETERS

3.2.1 Total Organic Carbon

Total organic carbon (TOC) has previously been proposed as a surrogate parameter to assess the performance of SAT operations. TOC profiles for Tucson Water's SWRF, MFSG's SGCB and Test Basin, City of Auburndale's RIB, and IEUA's recharge operations are presented in Figure 3.13. TOC concentrations were averaged across sampling campaigns, except for MFSB's Test Basin where TOC concentrations were averaged across upper and lower aquifer locations. As expected, the TOC concentrations from the basin to perimeter monitoring wells decreased for all the aquifer recharge operations. Previous studies revealed that TOC removal can vary from site to site and with effluent concentrations (Amy and Drewes, 2006; Drewes et al., 2003a; Quanrud et al., 2003; Grünheid et al., 2005; Lin et al., 2008). There is a portion of the TOC that is recalcitrant and not well removed. The amount of this persistent TOC can vary from site to site, depending on the background recalcitrant TOC that is present in the drinking water system that eventually feeds into the reclamation system. TOC can be used as a surrogate to assess SAT performance by observing a change of TOC in the system and subtracting out background recalcitrant TOC in down-gradient wells.

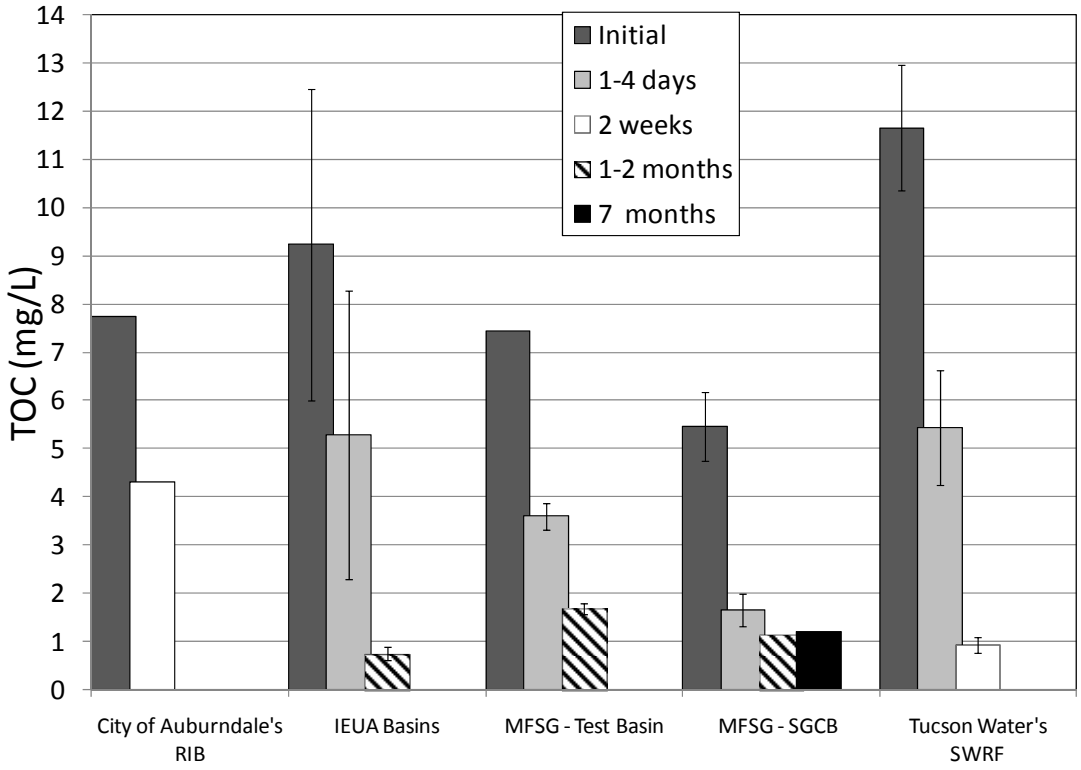


Figure 3.13. Average TOC concentrations for surface spreading operations.

3.2.2 Total Organic Halides

Total organic halides (TOX) was measured for samples from Tucson Water's SWRF and IEUA's 8th St. surface spreading operations. Chloramination and chlorination is applied at Tucson Water's and IEUA reclamation facilities, respectively. For both systems the reclaimed water is not dechlorinated before delivery to the spreading basins. The average TOX concentrations at Tucson Water's and IEUA's 8th St. surface spreading operations are presented in Figure 3.14. Concentrations are averaged across five and two sampling campaigns at Tucson Water's and IEUA's 8th St. surface spreading operations, respectively. The TOX concentrations from the basin to the perimeter monitoring wells decrease below detection levels for both aquifer recharge operations. TOX has the potential to be used as a surrogate to assess SAT performance and specifically the removal of unregulated halogenated organic compounds that are already present in reclaimed water or produced during chlorine and chloramine disinfection.

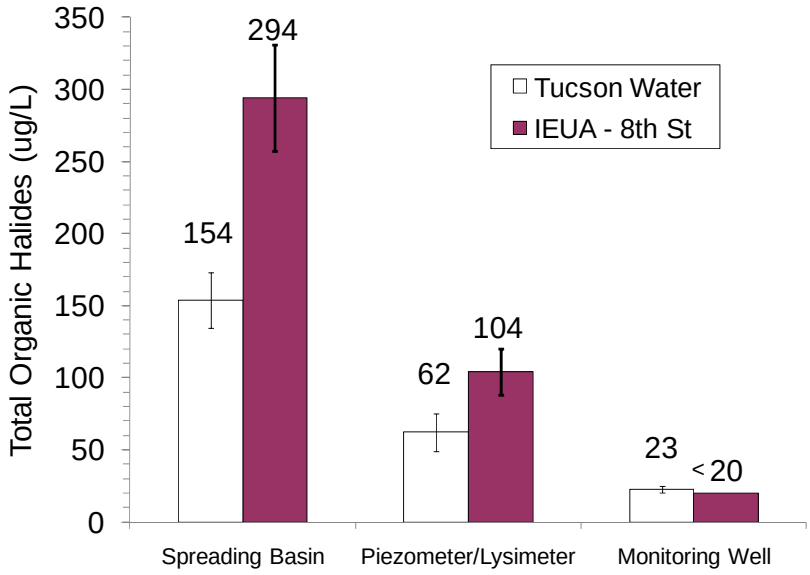


Figure 3.14. Average TOX concentrations at Tucson Water's and IEUA's 8th St. Basin's surface spreading operations.

3.2.3 Specific UV Absorbance

Specific UV absorbance (SUVA) is the normalization of UVA_{254} by DOC. SUVA represents the degree of aromaticity of the organic carbon present. At WRD's Test Basin, the SUVA increased from 1.34 to 2.3 L/mg-m (Figure 3.15). An increase in SUVA is indicative of a microbial-driven and preferential decrease in the non-aromatic portion of DOC, which includes aliphatic hydrophilic acids and biopolymers. SUVA increases are typical of short-term SAT and were observed in previous field and soil column studies (Drewes at al., 2003a, 2003b, 2006b;Quanrud et al., 2003; Grünheid et al., 2005; Lin et al., 2005; Xue et al., 2009).

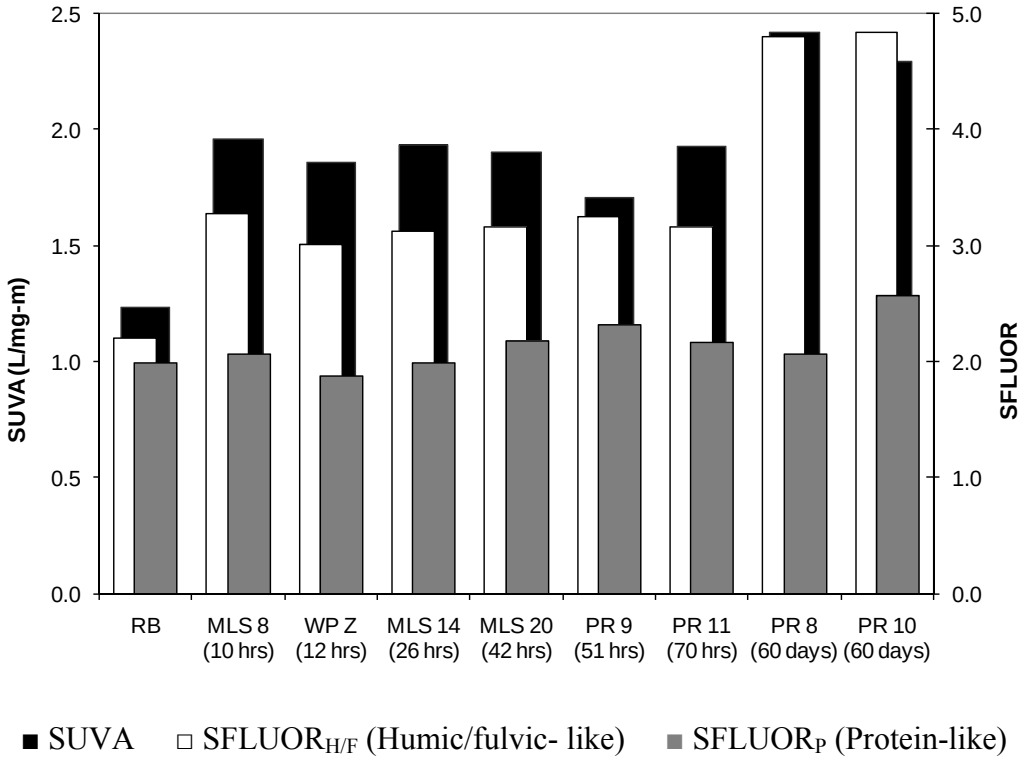


Figure 3.15. Specific UV absorbance (SUVA), specific fluorescence of humic/fulvic and protein-like organic matter in WRD's Test Basin and suburface sampling locations. Travel times are noted in parentheses.

3.2.4 Fluorescence Spectroscopy

Fluorescence provides a *sensitive* surrogate parameter that can help describe the biological activity and biological performance of a SAT process. The fluorescence of NOM is due to the presence of fluorophores that absorb photons, followed by the excitation to a higher electronic energy state. Then the absorbed energy is released to the environment at a greater wavelength where this intensity of the energy is recorded in a fluorescence excitation-emission matrix (EEM). Figure 3.16 presents graphically the fluorescence EEMs for samples from WRD's Test Basin. EEMs for samples from WRD's SGCB, Tucson Water's SWRF, and IEUA's surface spreading operations are presented in the Appendix. Similar EEMs have been reported in previous full-scale SAT studies (Drewes, 2009; Amy and Drewes, 2006).

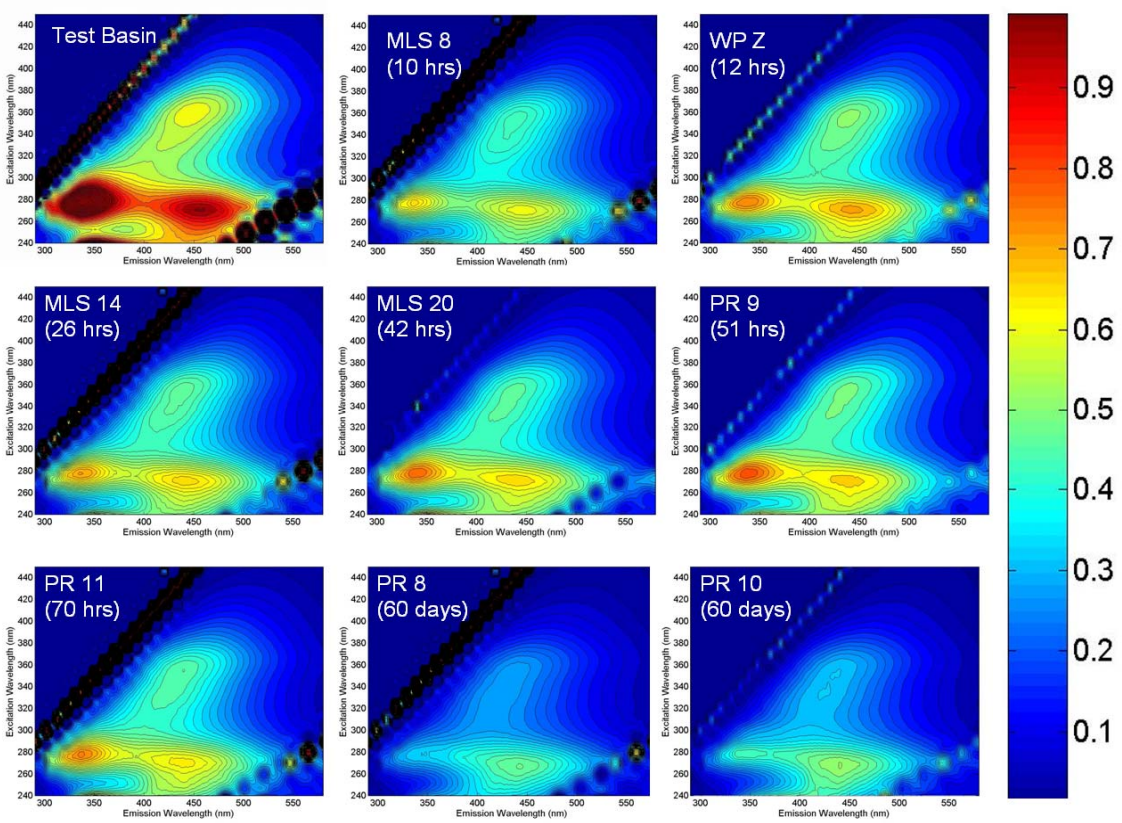


Figure 3.16. Flourescence EEMs highlighting organic matter composition for samples collected from MFSG's Test Basin (travel time noted in parentheses). Peak intensity scale is shown along the right-hand side. Peaks, going clockwise starting from lower left corner, represent protein-like, fulvic-like, and humic-like organic matter.

Fluorescence spectroscopy can be used to distinguish humic-like organic matter from protein-like organic matter. This is important because much of the protein-like organic matter in reclaimed water is a result of biological wastewater processes. The fluorescence peak for protein-like organic matter can be found at an excitation wavelength of 270 nm and an emission wavelength of 330 nm. Humic- and fulvic acid-like intensities were quantified at excitation wavelengths of 240 and 330 nm and at emission wavelengths of 440 and 420 nm, respectively. The intensities at humic- and protein-like peak regions decrease during SAT as shown in Figure 3.16. Although fluorescence measurements are limited to measuring fluorophores, the observed changes in the spectra give insight into the biologically driven transformations of organic matter during SAT. Also, the lack of a protein-like peak down-gradient of a surface spreading operation can indicate the reclaimed recharged water is of less wastewater character.

The fluorescence index (FI) was calculated by comparing the emission intensity at excitation wavelengths of 450 and 500 nm (Table 3.8). FI is an indication of whether organic matter is microbially or terrestrially derived (McKnight et al. 2001). The FI for the Test Basin was 1.38 in the basin and higher in the well samples, where the average FI in the wells was 1.45 ± 0.03 (Table 3.9). This is consistent with findings from a previous study using fluorescence to characterize and differentiate wastewater effluent from natural waters, suggesting that the organic matter is microbial in origin (Nam et al., 2007). However, this is contrary to the findings of McKnight et al. (2001) where water with terrestrial organic matter had an FI of 1.4.

Table 3.8. Summary of Specific Wavelengths for Fluorescence Peaks within EEMs for Samples from MFSG's Test Basin

Measurement	Excitation (nm)	Emission (nm)
Fluorescence Index	370	$\frac{\text{intensity@450}}{\text{intensity @ 500}}$
Protein-like fluorescence intensity (T1)	270	330
Fulvic-like fluorescence intensity (A)	240	440
Humic-like fluorescence intensity (C1)	330	420

Table 3.9. Fluorescence Index Values for Samples Collected at MFSG's Test Basin

Location	FI
Test Basin	1.38
MLS 8	1.44
WP Z	1.47
MLS 14	1.44
MLS 20	1.44
PR 9	1.47
PR 11	1.48
PR 8	1.45
PR 10	1.50

Table 3.10. SFLUOR Equations

Measurement	Equation
SFLUOR (protein-like)	$\frac{T1}{DOC * 10}$
SFLUOR (humic/fulvic-like)	$\frac{A + C1}{DOC * 10}$

The intensity at specific emission/excitation wavelengths also can be used to calculate specific protein and humic fluorescence (SFLUOR), where the fluorescence intensity of protein- and humic-like organic matter is normalized by DOC (Table 3.10).

The SFLUOR can be used to define the changes in organic matter composition that take place during SAT. The specific fluorescence presented in Figure 3.15 indicate the protein-like organic matter was not preferentially removed during long-term SAT (up to 60 days) because there is no change in protein-like SFLUOR in all wells. Results presented in Figure 3.15 also indicate that the humic fraction is increasing, given the rise in humic/fulvic-like SFLUOR. This corresponds with the increase in SUVA, which is also indicative of the relative increase in the humic fraction and with previous studies (Drewes et al., 2003b; Amy and Drewes, 2006).

3.2.5 Size Exclusion Chromatography

Size-exclusion chromatography (SEC) can be used to characterize the organic fraction of water samples, combining UV and DOC measurements to determine the size distribution of organic molecules. Samples from the WRD test basin and one of the corresponding deep wells (PR 8) was measured and the results show that biopolymers are completely removed via degradation and dilution with native groundwater, while humic-like compounds are also removed, but to a lesser extent (Figure 3.17). This observation is similar to results observed during field-scale studies (Amy and Drewes, 2006; Drewes et al., 2006b).

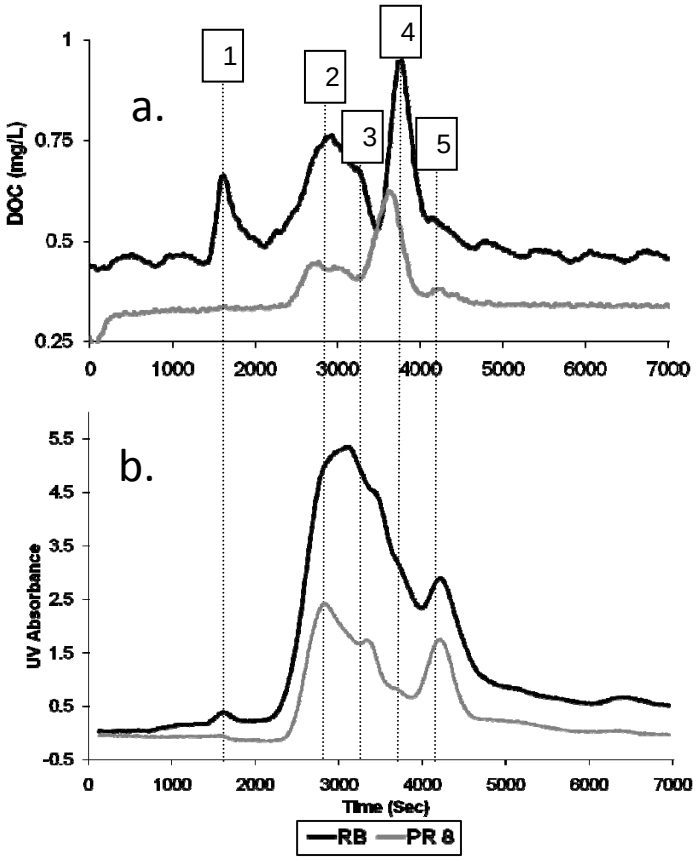


Figure 3.17. SEC data for dissolved organic carbon (a) and UV absorbance (b) in WRD's Test Basin (RB) and corresponding monitoring well (PR 8). There are five major peaks representing bipolymers (1), humic-like substances (2), polymer building blocks (3), acids and low molecular weight (LMW) humic-like substances (4), and LMW neutrals (5).

3.2.6 Biodegradable Dissolved Organic Carbon

Biodegradable dissolved organic carbon (BDOC) might also be a suitable surrogate to measure system performance of surface spreading operations. BDOC is an operationally defined parameter that quantifies the easily biodegradable dissolved organic matter using indigenous bacterial populations. The BDOC test consists of an oxic and continuously mixed batch system, which contains acclimated biologically active sand (low fraction of organic carbon) and sample where the DOC is monitored over time in the aqueous phase. Figure 3.18 presents BDOC data for basin, lysimeter, and monitoring well samples at City of Auburndale's RIB, MFSG's SGCB and WRD's Test Basin, IEUA's Basin, and Tucson

Water's SWRF surface spreading operations. BDOC was detected in samples representing travel times on the order of 1 to 4 days, which indicates that not all the BDOC was consumed within a couple of days during travel through these systems. In general, for wells that represent travel times greater than 2 weeks, BDOC was below or near the detection limit of 0.1 mg/L. This indicates that all the detectable BDOC (based on operational definition) can be removed during SAT. If BDOC was detected in one of these wells, this would indicate that the treatment system is not performing properly.

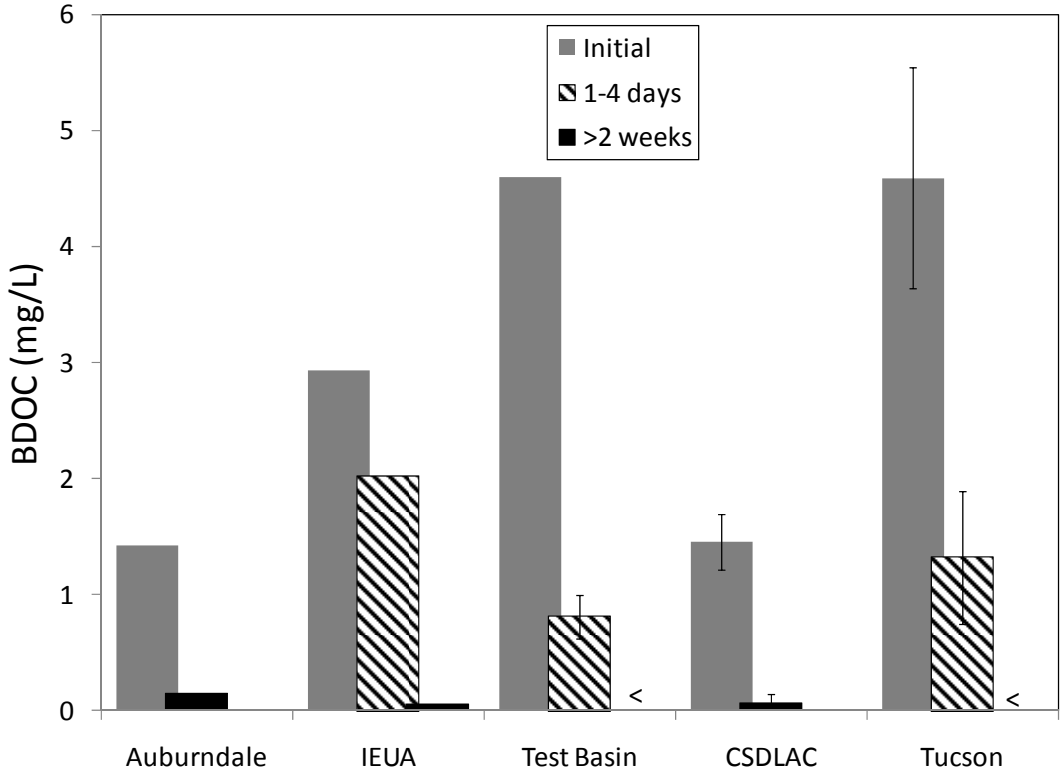


Figure 3.18. Average BDOC concentrations for surface spreading operations.

However, BDOC as an analytical measurement has its limitations and might represent a conservative measurement. In samples from the upper aquifer at WRD's Test Basin, DOC reached a plateau at approximately 2.8 mg/L during BDOC experiments using water from wells PR 9 or PR 11, which is higher than the actual 1.8 mg/L that was measured in the deeper wells (Table 3.11). Samples from the deeper wells, however, did not exhibit a measurable BDOC. This indicates that the field site achieved an additional DOC removal during subsequent travel, likely because of the specific microbial populations and because of the anoxic conditions. This finding revealed that the feed water DOC to the basin contains approximately 9 mg/L of which 7 mg/L are degraded during SAT and 2 mg/L remain as refractory DOC.

Table 3.11. BDOC Values from WRD's Test Basin

Location	BDOC (mg/L)	Final DOC (mg/L)
Test Basin	7.1	2.8
MLS 8	2.2	2.5
WP Z	2.2	2.9
MLS 14	2.5	2.8
MLS 20	1.4	2.8
PR 9	1.6	2.8
PR 11	1.8	2.8
PR 8	<0.1	1.8
PR 10	<0.1	1.9

3.3 CORRELATIONS BETWEEN SURROGATE PARAMETERS AND INDICATOR COMPOUNDS

The following sections present results for the removal of indicator compounds with respect to changes in surrogate parameters, such as TOC, TOX, and UVA. Data from Tucson Water's SWRF and MFSG's SGCB recharge operations were used to demonstrate the development of correlations between changes in surrogate parameters and the removal of select indicator compounds.

For Tucson Water's SWRF several positive correlations emerged from the data analysis (Figures 3.19–3.24). Table 3.12 also indicates the statistical significance of these correlations, where the Pearson's product moment correlation coefficient was calculated. The correlation coefficient has a domain of [-1,1], where a value 1 or -1 indicates perfect collinearity. The *p*-values (in parentheses in Table 3.12) test the hypothesis that there is no association between the variables ($r = 0$), so a low *p*-value is strong evidence that the two variables are correlated. In general, all the compounds in Table 3.12, except for benzophenone, show a significant correlation (*p*-value < 0.05) with both TOC and TOX. In the case of DEET and gemfibrozil, when the percentage removal of indicator compounds is plotted against the percentage removal of TOC (ΔTOC), the relationship appears linear (Figures 3.19 and 3.20). The removal of chlorinated flame retardants, TCEP and TDCPP, was positively correlated with the elimination of both TOC and TOX, although the relationship does not appear to be linear (Figures 3.25–3.28). The chlorinated flame retardants and dilantin are still detectable after 2 weeks of travel time.

However, monitoring ΔTOC or ΔTOX down-gradient of the monitoring well will not pick up further removal of these compounds. This is because at the monitoring well the TOC is 1 mg/L, and although it may undergo further chemical transformations, the total organic concentration will not likely change because the remaining organic carbon is not completed mineralized. The TOX is near the detection limit at the monitoring well; thus, further decreases in TOX will not be detected down-gradient. Similar to Tucson Water's SWRF, several positive correlations with changes in TOC emerged from the WRD Test Basin data (Figure 3.29).

These results demonstrate that changes in TOC and TOX do correlate with changes of indicator compounds in the subsurface. However, based on laboratory soil-column experiments using feed water with a low carbon concentration (~0.2 mg/L), the same indicator compounds exhibited similar substantial reductions despite no changes in TOC concentrations being observed. This suggests that for sites using feed water qualities that are

characterized by a low TOC concentration (< 2 mg/L), TOC monitoring would not be a sufficient surrogate parameter to assess the removal of trace organic chemicals during spreading-basin operation.

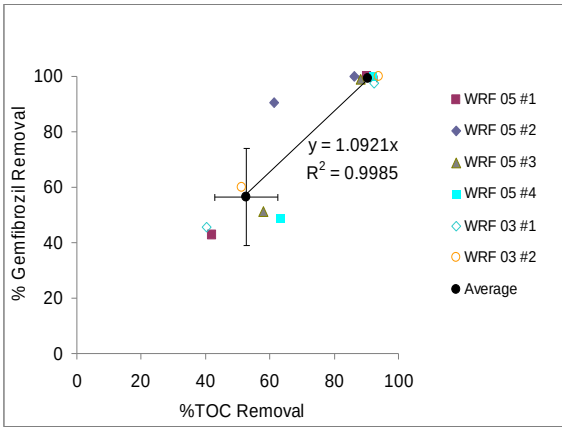


Figure 3.19. Gemfibrozil removal vs. TOC removal.

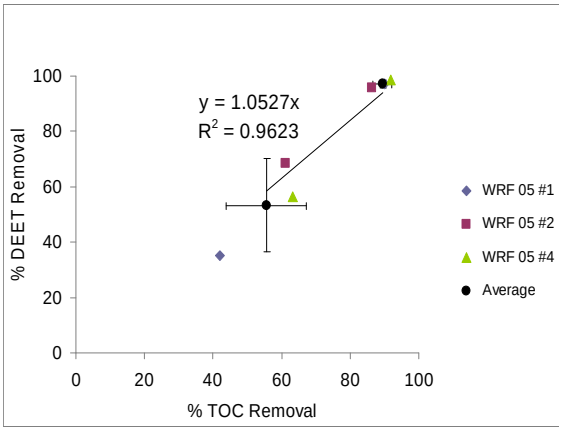


Figure 3.20. DEET removal vs. TOC removal.

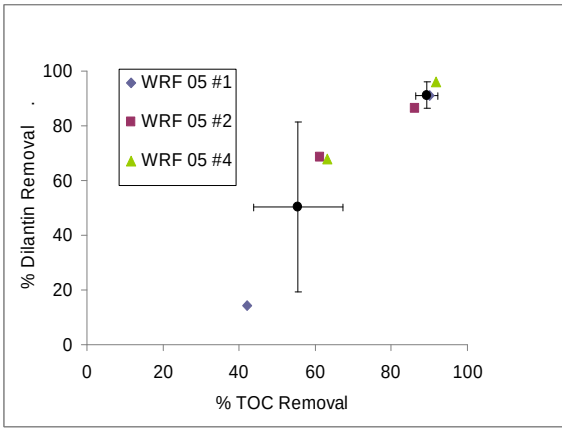


Figure 3.21. Dilantin removal vs. TOC removal.

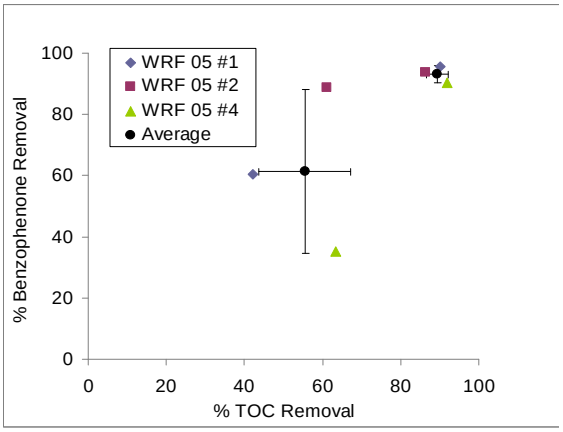


Figure 3.22. Benzophenone removal vs. TOC removal.

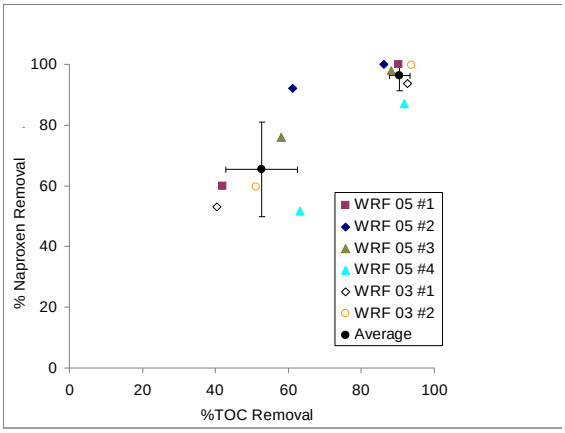


Figure 3.23. Naproxen removal vs. TOC removal.

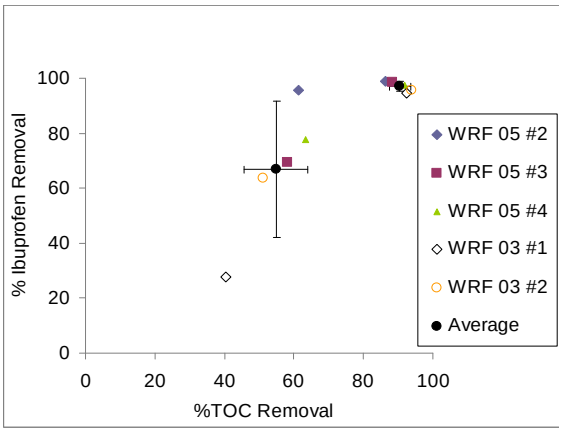


Figure 3.24. Ibuprofen removal vs. TOC removal.

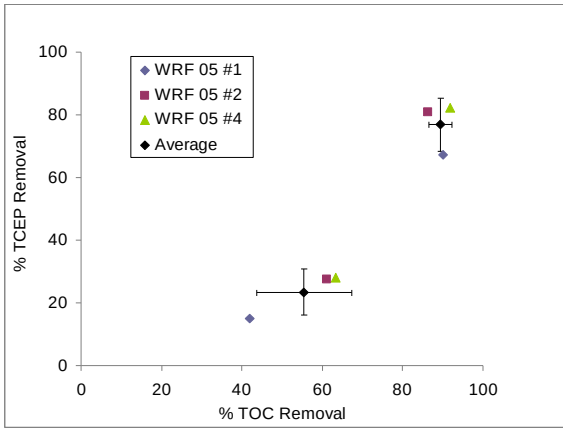


Figure 3.25. TCEP removal vs. TOC removal.

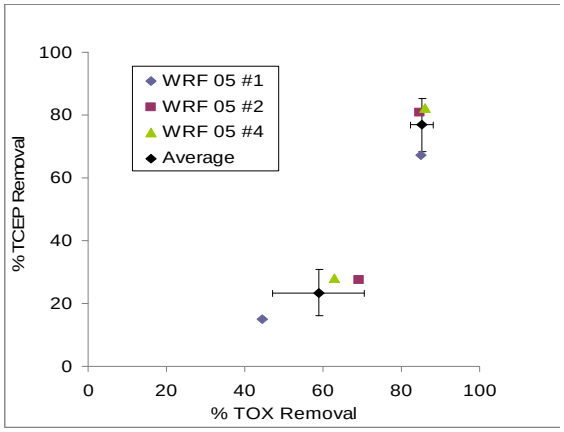


Figure 3.26. TCEP removal vs. TOX removal.

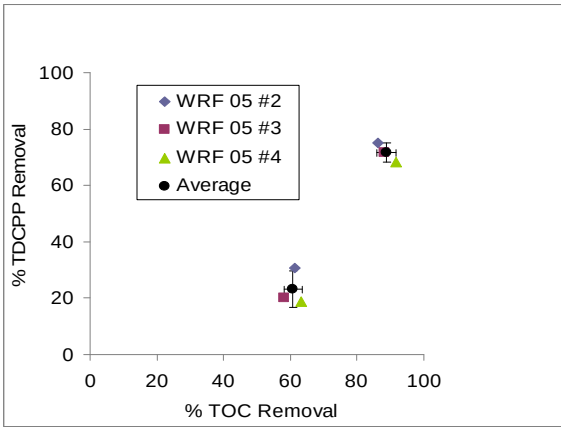


Figure 3.27. TDCPP removal vs. TOC removal.

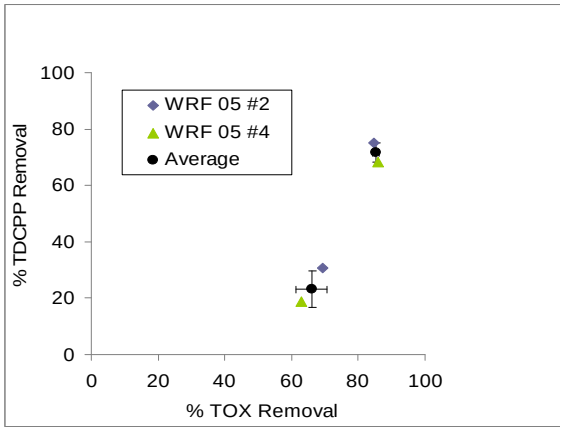


Figure 3.28. TDCPP removal vs. TOX removal.

Note: For Figures 3.19–3.28 the first data point represents a travel time of 2 days (MW #5) and the second a travel time of 2 weeks (WR-199A) at Tucson Water's SWRF. (WRF-05-004: current study; WRF-03-014: Drewes et al. 2008a).

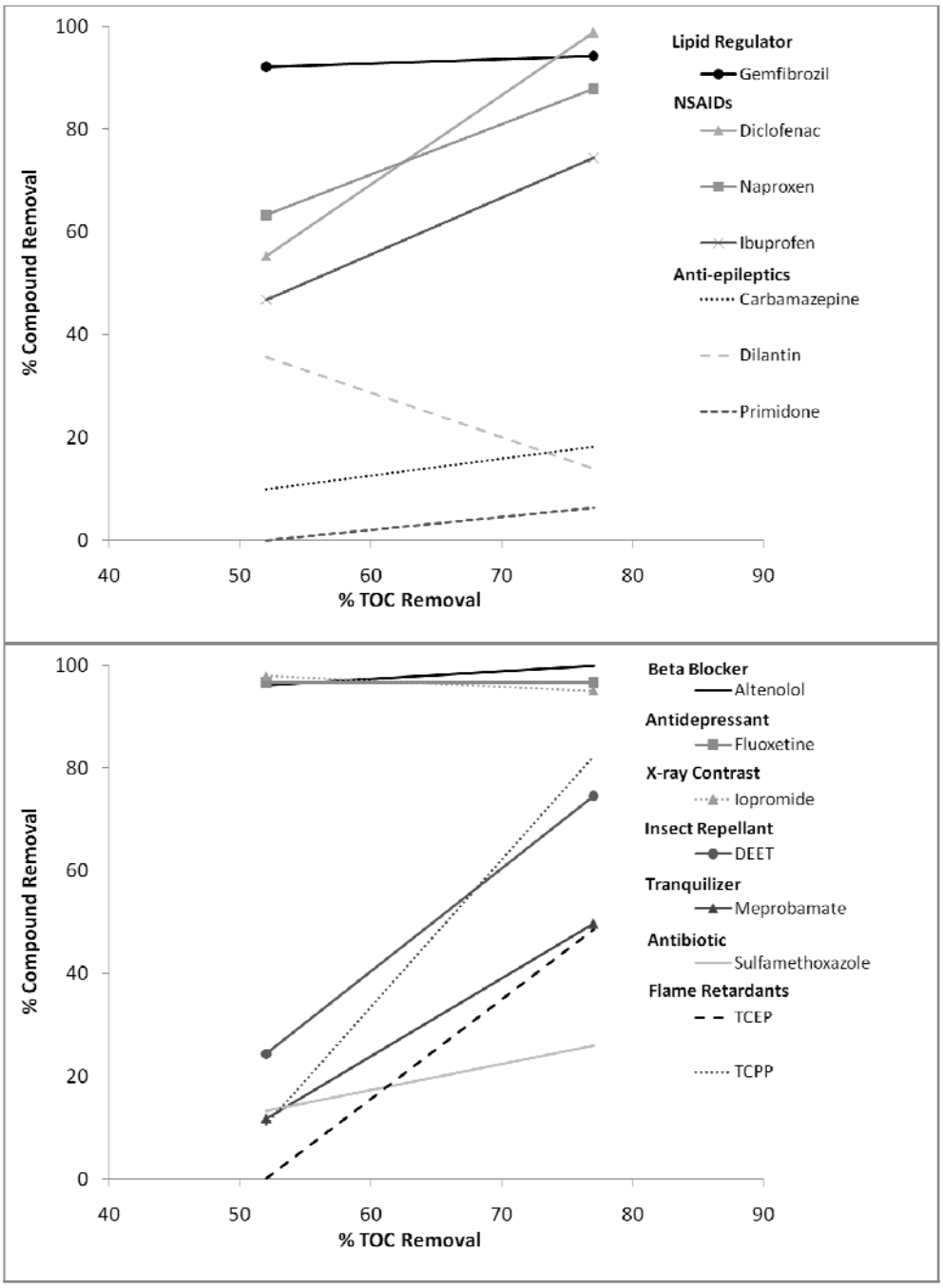


Figure 3.29. Comparison of individiual indicator compounds and total organic carbon removal. The first set of points represents a travel time < 3 days, based on the average removals from WRD's test basin MLS 8 – PR 11 and the second set of points represents a travel time = 60 days, based on the average from PR 8 and PR 10. TOC and UVA_{254} removal delineated on compound removal axis to illustrate compound removal relative to TOC/UVA removal at a travel time = 60 days.

Table 3.12. Pearson's Product Moment Correlation Coefficient for Correlations Between Compound Removal and TOC and TOX Removals

Compound	TOC Correlation (*p*-value)	TOX Correlation (*p*-value)
TCEP	0.954 (0.00308)	0.921 (0.00910)
TDCPP	0.963 (0.00199)	0.987 (0.0131)
Gemfibrozil	0.911 (3.76e-05)	0.748 (0.0129)
DEET	0.983 (0.000439)	0.994 (5.02e-05)
Dilantin	0.941 (0.00516)	0.967 (0.00166)
Benzophenone	0.645 (0.167)	0.718 (0.108)
Naproxen	0.862 (7.49e-05)	0.737 (0.0149)
Ibuprofen	0.862 (0.000310)	0.719 (0.0447)

CHAPTER 4

IDENTIFICATION OF SURROGATES AND INDICATORS TO MONITOR THE REMOVAL OF TRACE ORGANIC COMPOUNDS IN HIGH-PRESSURE MEMBRANE OPERATIONS

4.1 IDENTIFICATION OF SURROGATES AND INDICATOR COMPOUNDS FOR HIGH-PRESSURE MEMBRANE OPERATIONS

In groundwater recharge projects in the United States, treatment of reclaimed water with an integrated membrane system (IMS) consisting of microfiltration (MF) or ultrafiltration followed by RO is a widely used practice for projects that directly inject reclaimed water into a potable aquifer. Reclaimed water applied to reverse osmosis (RO) membranes usually has previously received secondary or tertiary treatment followed by disinfection. Significant research has been conducted to understand the performance of IMS in removing total dissolved solids (TDS), TOC, nutrients, and select trace organic chemicals (Drewes et al., 2003a; Drewes et al., 2005; Snyder et al., 2007; Kim et al., 2007; Bellona and Drewes, 2007; Bellona et al., 2008).

The majority of trace organic chemicals occurring in the nanograms-per-liter concentration represent a molecular size range of 80 to 800 g/mol. Thus, for effective rejection by physical separation processes, tight membranes are required and only treatment processes employing nanofiltration (NF) or RO membranes will be effective in removing these compounds. The primary removal mechanisms during membrane separation for trace organic chemicals include size exclusion, electrostatic repulsion, and adsorption. The dominant mechanism depends on the physicochemical properties of the solute (i.e., molecular size, pK_a, and log K_{ow}) and the membrane (i.e., pore size, surface charge, and hydrophobicity), as well as the feedwater composition (i.e., pH, ionic strength, TOC, and hardness), and operational conditions (i.e., flux and recovery; Bellona et al., 2004).

This chapter highlights how the proposed surrogates and indicators can be applied to assess the performance of treatment systems employing RO or NF membranes. A precursor study (Drewes et al., 2008a) proposed treatment removal categories for indicator compounds of RO and NF systems. Table 4.1 provides a master list of indicator compounds and their removal percentages for RO treatment considering a pretreatment of reclaimed water with MF or ultrafiltration, pH adjustment to 6.5 and operational conditions of a permeate flux of approximately 12 gfd (20 L/m^2 h [LMH]), and a recovery of approximately 80 to 85%.

As demonstrated in previous studies, the vast majority of indicator compounds are efficiently rejected by RO membranes exceeding 90% removal (Snyder et al., 2006; Snyder et al., 2007; Drewes et al., 2008a). Compounds that are nonionic (neutral) and small can exhibit a partial removal, as observed for nitrosamines such as NDMA or 1,4-dioxane (Drewes et al., 2008a). Indicator compounds that are small but exhibit hydrophobic properties can adsorb to the polymeric structure of thin-film composite membranes and partition through the active layer of the membrane into the permeate. For example, one compound meeting these properties is chloroform, which usually exhibits only moderate removal during RO treatment (Drewes et al., 2005; Drewes et al., 2008a). The highly efficient rejection of wastewater-derived

contaminants by RO membranes limits to a few the number of available indicator compounds representing intermediate removal. None of the indicator compounds considered by Drewes et al. (2008a) exhibited poor removal (<25%). Regarding membrane treatment performance monitoring, the most appropriate indicator compounds responding to a partial system failure and membrane integrity issue are those solutes that are small and nonionic and occur at quantifiable levels in the feed water. In order to further validate the master indicator list and to develop correlations with appropriate surrogate parameters, controlled laboratory-, pilot-, and full-scale studies were conducted for performance assessments.

Table 4.1. Treatment Removal Categories for Indicator Compounds of RO Systems[a]

Good Removal (>90%)				Intermediate Removal (90–50%)	Intermediate Removal (50–25%)	Poor Removal (<25%)
Indolebutyric acid[b]	Dichlorprop	Isobutylparaben[b]	Propranolol		Chloro-form	
Acetaminophen	Diclofenac	Ketoprofen	Propylpara		NDM	
Acetyl cedrene[b]	Dilantin	Mecoprop	Salicylic		NDEA	
Atenolol	EDTA	Meprobamate	Simvastatin hydroxy			
Atorvastatin	Erythromycin–H_2O	Methyl dihydrojasmonate[b]	Sulfamethoxazole			
Atorvastatin (*o*-hydroxy)	Estriol	Methyl ionine[b]	TCEP			
Atorvastatin (*p*-hydroxy)	Estrone	Methyl salicylate[b]	TCPP			
Benzyl acetate[b]	Fluoxetine	Metoprolol	TDCPP			
Benzyl salicylate[b]	Galaxolide	Musk ketone	Terpineol[b]			
Bisphenol A	Gemfibrozil	Musk xylene[b]	Tonalide[b]			
Bucinal[b]	Hexyl salicylate[b]	Naproxen	Triclocarba			
Butylated hydroxyanisole[b]	Hexylcinnam-aldehyde[b]	Nonylphenol	Triclosan			
Caffeine	Hydrocodone	Norfluoxetine	Trimethopr			
Carbamazepine	Ibuprofen	OTNE				
Ciprofloxacin[b]	Iopromide	Phenylphenol[b]				
DEET	Isobornyl acetate[b]	Primidone				

[a]Operating conditions: recovery 80%; permeate flux ~12 gfd or 20 LMH; pH = 6.5. Removal of compounds with no footnote was verified through peer-reviewed literature data or experimental data generated during this study.

[b]Removal estimate is based on MW being > 150 g/mol.

4.2 VALIDATION OF SURROGATES AND INDICATOR COMPOUNDS DURING LABORATORY-SCALE MEMBRANE TREATMENT

A laboratory-scale membrane system using spiral-wound elements was employed at CSM. CSM's system consists of 2 stages (1:1) utilizing a microfiltered/non-nitrified secondary effluent from the Denver Metro Wastewater Reclamation District as the feed water (spiked with nitrate), which was pH adjusted to pH 6.1–7.0. The nanofiltration membrane NF 4040 (Dow/Filmtec) was employed for these tests. The system was operated at recoveries of 10 to 80% and a permeate flux of 10 and 16 gfd (in recycle mode by returning permeate and concentrated to the feed container). Table 4.1 lists the indicator compounds that were detected in the feed and permeate streams during CSM's laboratory-scale NF experiments. Indicator compounds were spiked in the feed. For all experimental conditions, all the target compounds occurred at low levels in the permeate, with concentrations of less than 100 ng/L, where most of the compounds were non-detect or exhibited concentrations of less than 10 ng/L. A majority of the compounds showed removal to more than 99% (2-log) regardless of the operational conditions. However, systematic trends of permeate concentrations were observed as a function of the operational conditions.

Some compounds exhibited increasing permeate concentrations while the recovery increased from 22 to 80% at a flux of 16 gfd. These indicator compounds are neutral in character and of a lower molecular weight (<220 g/mol), such as atrazine, caffeine, DEET, and meprobamate, or have prominent aliphatic characteristics, such as atenolol and TCEP. Increasing concentrations of indicator compounds also correlated with increasing concentrations of certain surrogate parameters. This is expected because increasing recovery for a given feed flow rate results in a higher degree of concentration polarization at the membrane surface and lower rejection. Figure 4.1 presents correlations of indicator compounds and certain surrogate parameters. This correlation demonstrates that surrogate bulk parameter concentrations respond to trace organic compound levels. Therefore, slight changes in the levels of a suite of surrogate parameters will indicate changes in the levels of certain organic compounds during NF membrane operation. Obviously, these changes are only noticeable when consistent surrogate parameter concentrations are established and logged during the operation.

Table 4.2 Indicator Concentrations in the Feed and Permeate During CSM's Laboratory-Scale NF Experiments

Flux (gfd)	10						16					
Recovery (%)	12		48		75		22		48		80	
	Feed ng/L	Permeate ng/L	Feed ng/L	Permeate ng/L	Feed ng/L	Permeate ng/L	Feed ng/L	Permeate ng/L	Feed ng/L	Permeate ng/L	Feed ng/L	Permeate ng/L
Atenolol	2700	41.0	3600	50.0	3400	47.0	2300	31.0	2800	38.0	5200	57.0
Atorvastatin	56	<0.5	140	<0.5	100	<0.5	63	<0.5	110	<0.5	170	<0.5
Atrazine	560	6.1	620	6.8	630	7.6	540	4.6	620	6.0	950	8.2
Benzophenone	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
BHA	440	17.0	630	18	520	18.5	520	8.1	530	22	630	28
Bisphenol A	1400	110.0	2000	95	1500	115	1200	99	1300	91	1900	91
Caffeine	1000	31.5	1300	39	1200	38.5	950	22	1100	31	2000	50
Carbamazepine	890	6.9	1200	11	1100	9.5	880	5.1	1100	6.6	1800	12
DEET	1000	10.2	1400	11	1400	13	1100	7.8	1300	10	2000	17
Diazepam	870	0.9	1400	1.3	1100	1.9	920	0.7	1100	2.0	1700	2.2
Diclofenac	620	0.7	870	0.9	800	0.7	630	0.8	770	0.8	1100	1.5
Dilantin	680	5.5	890	6.0	540	6.2	710	4.0	750	5.9	720	7.5
Fluoxetine	500	1.0	620	1.7	530	2.8	510	<0.5	510	2.4	860	2.4
Gemfibrozil	2300	2.7	2900	3.8	2700	3.2	2100	2.2	2700	3.2	4100	5.6
Ibuprofen	730	1.8	940	2.1	800	1.9	740	1.6	760	2.1	1400	3.2
Iopromide	590	<10	760	<10	830	<10	720	<10	680	<10	860	<10
Meprobamate	1200	7.6	1700	10.0	1900	11.0	1400	6.3	1600	8.3	2700	15
Musk Ketone	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Naproxen	1100	3.7	1700	5.0	1600	4.6	1200	3.5	1500	3.3	1900	6.2
Octyphenol	160	<25	310	<25	150	<25	240	<25	170	<25	300	<25
Primidone	640	1.8	730	2.2	740	1.9	590	1.4	640	1.5	820	2.4
Sulfamethoxazole	1300	13	2000	15	1700	11.5	1400	12	1700	9.1	2800	12.0
TCEP	990	19	1300	22	1300	24.5	1000	14	1200	17	2000	31.0
TCPP	2100	<100	2800	<100	2900	<100	2300	<100	2800	<100	4500	<100
Triclosan	6	<1.0	40	<1.0	2.4	<1.0	21	<1.0	5.6	<1.0	6.4	<1.0
Trimethoprim	1100	11	1400	12	1300	11	1100	7.2	1300	8.5	2100	12.0

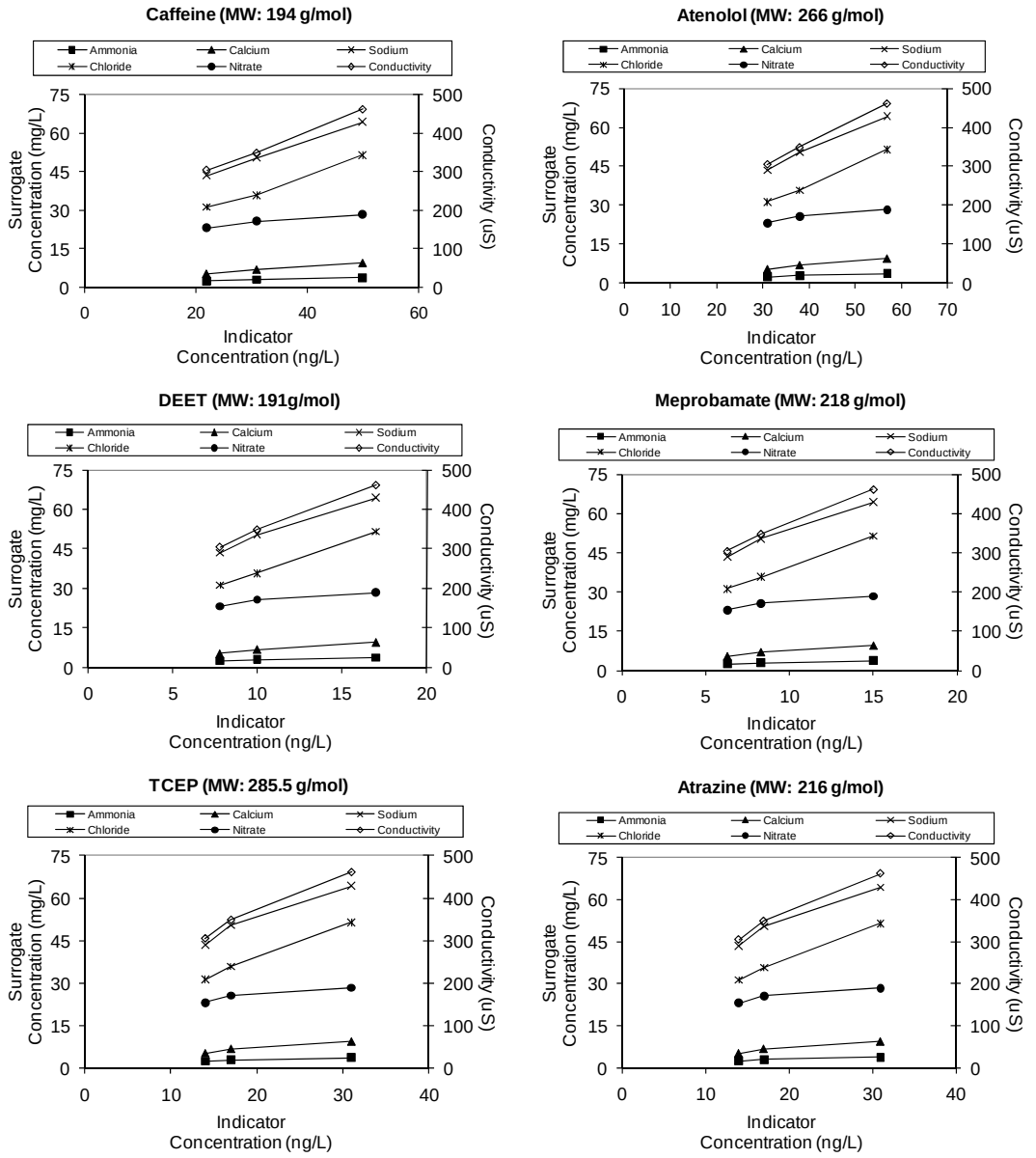


Figure 4.1. Correlations of indicator compound and surrogate levels for NF membrane experiments. Experimental conditions represent a flux of 16 gfd and from left to right reveal the three sets of measurement for a given compound at recoveries of 22, 48, and 80%, respectively.

4.3 VALIDATION OF SURROGATES AND INDICATOR COMPOUNDS DURING PILOT-SCALE MEMBRANE TREATMENT

4.3.1 Pilot-Scale Membrane Experiments at CSM

An experiment was conducted using an 18-gpm membrane skid that employed a nanofiltration membrane (NF-4040, Dow/Filmtec) at CSM's laboratory. For this experiment, city tap water was spiked with a suite of N-nitrosamines at environmentally relevant concentrations. The skid was operated at constant recovery (65%) and increasing feed pressure (50–90–125 psi) and samples were collected from the feed as well as the combined

permeate for each pressure adjustment. The results of this rejection experiment are presented in Figure 4.2. As expected, the rejection of the target nitrosamines increased with increasing permeate flux and was higher for compounds with higher molecular weight. For example, the rejection varied between 0% for N-nitrosodimethylamine (NDMA) to approximately 30 to 60% of N-nitrosodi-n-propylamine. TOC concentration in the feed water varied between 1.75 and 2 mg/L and was consistently below 0.5 mg/L in the combined permeate for each pressure (flux) adjustment.

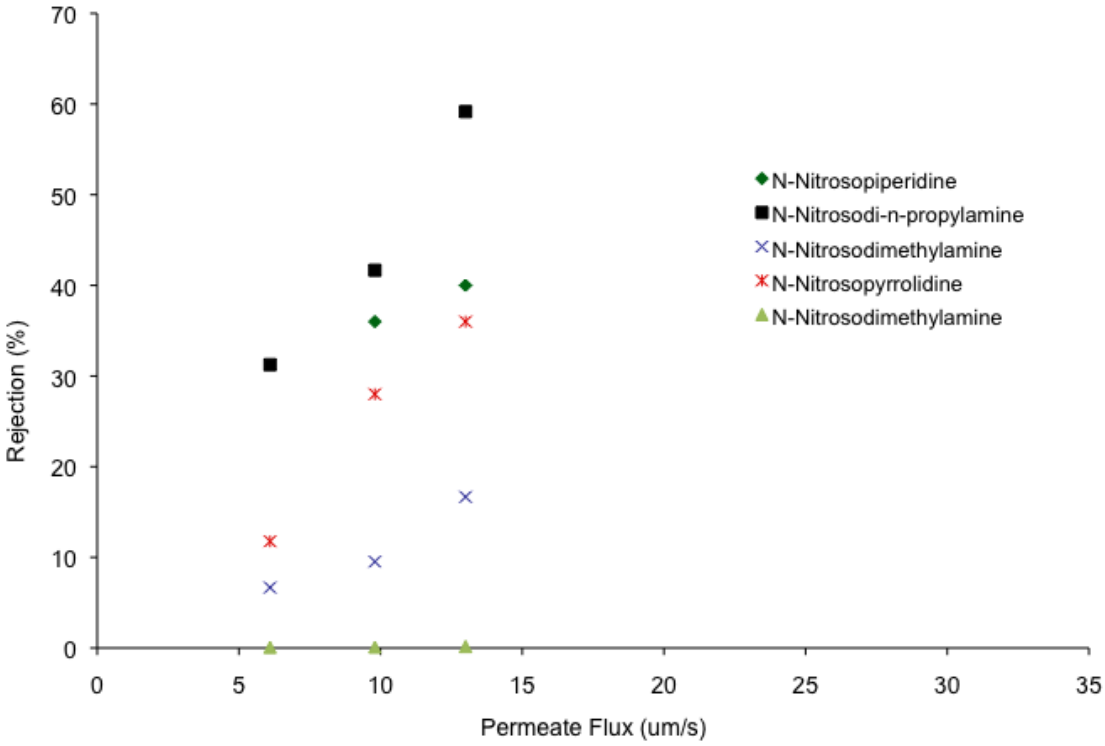


Figure 4.2. Rejection of various nitrosamines with increasing permeate flux for a pilot-scale NF membrane operation.

4.3.2. Pilot-Scale Membrane Experiments at CSDLAC

Additional membrane performance experiments were conducted at a pilot-scale facility operated by CSDLAC employing a conventional RO membrane. The system was fed with a membrane bioreactor (MBR) permeate. During the study, samples were collected from the feed water, 1-stage permeate, and the combined permeate. The measured concentrations for indicator compounds occurring in the feedwater and permeate during the pilot-scale study are summarized in Table 4.2. The concentrations decreased for all the compounds during RO treatment and were below or very close to the detection limits. RO treatment was very efficient at removing most indicator compounds. Table 4.3 lists select bulk water quality measurements for samples from CSDLAC's RO systems. Concentrations for some of the surrogate parameters are effectively reduced to greater than two-log removal (i.e., sulfate, calcium, magnesium). Concentrations for other parameters are reduced by more than 90% (i.e., TOC, conductivity, chloride, potassium and ammonia). However, values for some parameters were only partially reduced (i.e., such as ultraviolet absorbance, sodium, nitrate,

and boron). Most of these water quality parameters can be used to assess RO membrane performance where the easiest parameters to measure are TOC, UV absorbance, and conductivity. The nature of the organic matter in the feed water was further characterized through 3-D fluorescence measurements. As expected, Figure 4.3 illustrates that the intensities of humic- and protein-like peak regions decrease during RO treatment. Although fluorescence measurements are limited to measuring fluorophores, fluorescence provides a *sensitive* surrogate parameter that could be used to detect early deficiencies in the performance of a RO process.

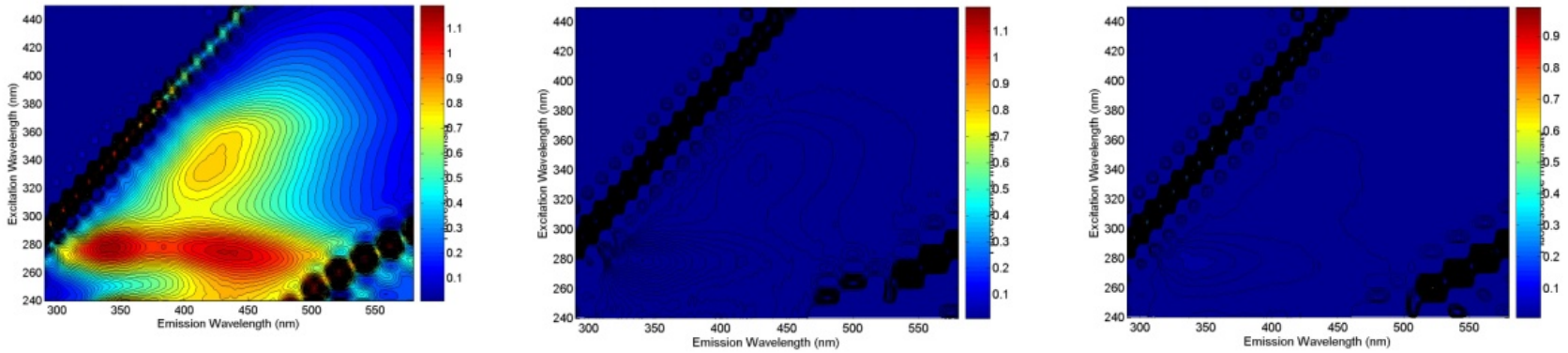
Table 4.3 Concentrations of Indicator Compounds at CSDLAC's Pilot-Scale RO System

Indicator	MBR Permeate ng/L	RO First Stage ng/L	RO Permeate ng/L	Travel Blank ng/L
Atenolol	270	<1.0	<1.0	<1.0
Atorvastatin	4.3	<0.50	<0.50	<0.50
Atrazine	17	<0.25	<0.25	<0.25
Benzophenone	61	<50	<50	<50
BHA	23	<1.0	<1.0	<1.0
Bisphenol A	21	<5.0	<5.0	<5.0
Caffeine	7.3	<5.0	<5.0	<5.0
Carbamazepine	400	<0.50	<0.50	<0.50
DEET	160	<1.0	<1.0	<1.0
Diazepam	2.2	<0.25	<0.25	<0.25
Diclofenac	45	<0.25	<0.25	<0.25
Dilantin	150	<1.0	<1.0	<1.0
Fluoxetine	35	<0.50	<0.50	<0.50
Gemfibrozil	410	<0.25	<0.25	<0.25
Ibuprofen	32	<1.0	<1.0	<1.0
Iopromide	90	<10	<10	<10
Meprobamate	370	<0.25	<0.25	<0.25
Musk Ketone	29	<25	<25	<25
Naproxen	120	<0.50	<0.50	<0.50
Primidone	130	<0.50	<0.50	<0.50
Sulfamethoxazole	1700	0.99	1.2	<0.25
TCEP	230	<10	<10	<10
TCPP	1000	<100	<100	<100
Triclosan	90	<1.0	<1.0	<1.0
Trimethoprim	73	<0.25	<0.25	<0.25

Table 4.4. Water Quality Measurements at CSDLAC's RO System

Sample Location	pH	TOC (mg/L)	UV_{254} (1/cm)	Cond. (mS/cm)	PO_4 (mg/L)	SO_4 (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	K (mg/L)	Na (mg/L)	NO_3 - N (mg/L)	NH_3-N (mg/L)	B (mg/L)
Pilot-Scale RO (May 2, 2008)														
RO Feed	6.45	5.9	0.198	1050	9.5	182	54	17	116	16	145	6.1	NA	0.50
1st Stage Effluent	5.40	0.32	0.070	108	<0.5	0.50	0.08	0.010	0.5	<0.09	21	1.3	NA	0.37
RO Permeate	5.52	0.16	0.062	98	<0.5	0.80	0.08	0.009	1.6	0.25	20	1.1	NA	0.40
Total Removal:	-	*97%*	*68%*	*91%*	*>95%*	*99.6%*	*99.9%*	*99.9%*	*99%*	*98%*	*86%*	*82%*	-	*19%*

Note: NA = not analyzed



MBR permeate – RO Feed *1st stage* *RO permeate*

Figure 4.3. Fluorescence EEMs for samples from CSDLAC's pilot-scale RO system.

4.4 VALIDATION OF SURROGATES AND INDICATOR COMPOUNDS DURING FULL-SCALE MEMBRANE TREATMENT

Orange County Water District (OCWD) operated the Groundwater Replenishment System (GWRS). A centerpiece of the advanced water treatment train was the reverse osmosis treatment followed by an ultraviolet-AOP (UV-AOP) and subsurface direct injection. OCWD's RO system was using a pH adjusted (pH 6.8), microfiltered non-nitrified secondary effluent and operates at a recovery of 85%. The RO train employed the low-pressure RO membrane ESPA 2 (Hydranautics, Oceanside, CA). Table 4.4 summarizes concentrations of indicator compounds measured in the feed and permeate streams during three sampling campaigns. Measured concentrations in AOP-treated and subsurface monitoring well samples are presented in the Appendix (Table A.8). Indicator compounds were not spiked in the feed; therefore, the concentrations observed represent ambient levels of these constituents.

The findings of these monitoring studies revealed that some indicator compounds occurred in the permeate at very low concentrations (less than 110 ng/L), whereas most of the compounds were either not detected or were less than 5 ng/L. The majority of the indicator compounds were removed greater than 99% during all sampling campaigns. However, it is interesting that some systematic trends were observed for permeate concentrations for certain indicator compounds as a function of operational time. Some indicator compounds systematically increased in the permeate the longer the RO operation had been in operation (Figure 4.4). Throughout all sampling campaigns at this facility, the feed concentrations of target compounds were similar across campaigns. Interestingly, the concentration of some neutral and smaller molecular weight compounds did not increase as much as some of the larger molecular weight compounds, such as sulfamethoxazole, triclosan, and trimethoprim. This observation might suggest another type of rejection mechanism other than size exclusion that is important for rejection of solutes with more hydrophilic properties.

Table 4.5. Indicator Concentrations in the Feed and Permeate During OCWD's Full-Scale RO Operation

Indicator Compound	MW	Jul 08 Before RO	Jul 08 After RO	Oct 08 Before RO	Oct 08 After RO	Jan 09 Before RO	Jan 09 After RO
	(g/mol)	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
Atenolol	266	1700	2.2	1800	4.6	1500	14
Atorvastatin	559	56	<0.50	62	<0.50	55	<0.50
Atrazine	216	4.4	<0.25	3.8	<0.25	3.9	<0.25
Benzophenone	182	570	<50	790	94	610	110
BHA	180	78	<1.0	130	<1.0	130	<1.0
Bisphenol A	228	480	<5.0	180	<5.0	480	<5.0
Caffeine	194	600	<5.0	900	<5.0	690	6.8
Carbamazepine	236	190	<0.50	220	<0.50	190	0.79
DEET	191	1600	1.8	570	1.1	400	1.5
Diazepam	285	2.2	<0.25	0.87	<0.25	1.3	<0.25
Diclofenac	296	280	<0.25	180	<0.25	190	<0.25
Dilantin	252	130	<1.0	130	<1.0	160	<1.0
Fluoxetine	309	27	<0.50	33	<0.50	27	<0.50
Gemfibrozil	250	3300	1.7	3300	2.7	3800	4.6
Ibuprofen	206	700	<1.0	1200	<1.0	550	1.1
Iopromide	791	160	<10	130	<10	310	<10
Meprobamate	218	330	0.32	330	0.32	330	0.66
Musk Ketone	294	25	<25	150	<25	56	<25
Naproxen	230	480	0.66	2200	2.2	1100	3.2
Octyphenol	206	190	<25	580	<25	360	<25
Primidone	218	97	<0.50	100	<0.50	110	<0.50
Sulfamethoxazole	253	1500	0.33	1400	1.1	1800	5.8
TCEP	286	530	<10	750	<10	320	<10
TCPP	328	4400	<100	1800	<100	950	<100
Triclosan	290	230	<1.0	430	5.3	510	29
Trimethoprim	290	610	0.38	630	1.1	600	8.1

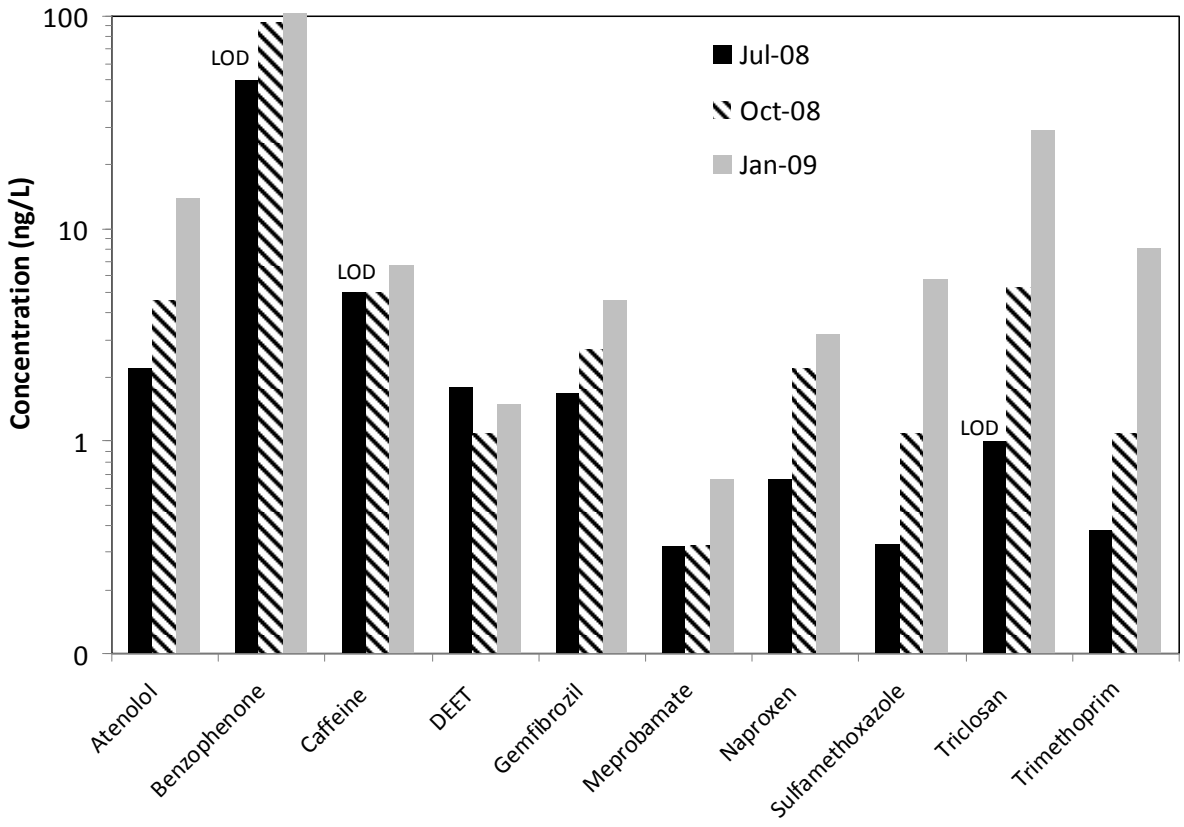


Figure 4.4. Concentration of indicator compounds in OCWD's RO permeate over time.
Note. LOD = limit of detection.

Bulk parameters measured in the feed and combined permeate samples are summarized in Table 4.5. In general, the indicator compound concentration increases also corresponded with increases of certain surrogate parameter levels (data not shown).

Table 4.6. Water Quality Measurements at OCWD's RO System

Sample Location	pH	TOC (mg/L)	UV_{254} (1/cm)	Cond. (□S/cm)	PO_4 (mg/L)	SO_4 (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	K (mg/L)	Na (mg/L)	NO_3 - N (mg/L)	NH_3-N (mg/L)	B (mg/L)	TTHM (mg/L)	NDMA (ng/L)
Full-Scale RO (April 2008)																
RO Feed	7.6	11.8	0.21	1600	0.83	305	80	23	190	18	193	<0.1	28	0.39	1.8	21
RO Permeate	6.5	0.16	0.10	40	<0.5	4.4	0.11	0.02	5.8	0.27	25	<0.1	1.1	0.27	1.0	11
Total Removal:	-	*99%*	*53%*	*97%*	*>40%*	*99%*	*99.9%*	*99.9%*	*97%*	*99%*	*87%*	-	*96%*	*31%*	*44%*	*48%*
Full-Scale RO (July 2008)																
RO Feed	7.8	13.2	0.29	1730	2.8	243	74	21	231	18	225	2.7	22	0.39	1.4	28
RO Permeate	5.9	0.19	0.09	42	<0.5	1.2	0.07	0.02	5.5	0.29	25	0.19	1.5	0.26	0.7	12
Total Removal:	-	*99%*	*70%*	*98%*	*>82%*	*99.5%*	*99.9%*	*99.9%*	*98%*	*98%*	*89%*	*93%*	*93%*	*35%*	*50%*	*57%*
Full-Scale RO (October 2008)																
RO Feed	6.9	12.5	0.28	1760	1.21	290	74	20	227	29	220	1.63	22	0.38	1.3	30
RO Permeate	4.9	0.16	0.08	30	<0.5	0.7	0.11	0.01	4.3	0.97	24	0.12	0.9	*0.24*	0.8	14
Total Removal:	-	*99%*	*72%*	*98%*	*>59%*	*99.7%*	*99.9%*	*100%*	*98%*	*97%*	*89%*	*93%*	*96%*	*37%*	*38%*	*53%*
Full-Scale RO (January 2008)																
RO Feed	6.8	10.9	0.431	1940	1.4	345	81	21	155	18	212	1.53	27	0.41	NM	71
RO Permeate	4.7	0.16	0.09	49	<0.5	1.00	0.16	0.04	9.2	0.83	31.3	0.14	1.2	0.28	NM	35
Total Removal:	-	*99%*	*79%*	*97%*	*>64%*	*99.7%*	*99.8%*	*99.8%*	*94%*	*95%*	*85%*	*91%*	*96%*	*32%*	-	*51%*

Note. NM = not measured

CHAPTER 5

RECOMMENDATIONS FOR MONITORING PROGRAMS

5.1 INDICATOR/SURROGATE FRAMEWORK—THE CONCEPT

5.1.1. Selection of Potential Indicator Chemicals From a Literature Survey

Numerous past studies have reported the occurrence of trace organic chemicals in effluents of North American (U.S. and Canada) conventional wastewater treatment facilities. However, if trace organic chemicals do not occur at concentrations above their detection limits and at high frequencies, many of these compounds may not represent good indicator candidates for monitoring efforts. Using these criteria, compound occurrence data was screened and compounds that did not occur at a frequency above 80% or were not present in secondary or tertiary-treated wastewater at concentrations at least five times higher than their respective limits of quantification were eliminated. Chemicals considered during screening are presented in the Appendix in Table A.1. Based on this analysis a list of 50+ potential indicator chemicals were identified in North American wastewater effluents. In addition, ten full-scale conventional wastewater treatment facilities located in the United States were selected to validate the occurrence of some potential indicator chemicals in conventionally treated secondary- or tertiary-treated effluents. Considering the monitoring results from these facilities, detection ratios and frequencies are in agreement with the proposed indicator chemicals. It is noteworthy that this screening of compounds is biased through the application of analytical methods that targeted compounds that were of interest to the researchers who initiated the study. It is possible that other feasible indicator chemicals are present, but analytical methods may not exist for these chemicals or existing methods have not been applied to measure these chemicals in treated wastewater.

The approach for monitoring trace organic chemicals for groundwater recharge operations developed in this study used a combination of surrogate parameters and indicator chemicals as proposed by Drewes et al. (2008a). In the context of this study, an indicator chemical is an individual chemical occurring at a quantifiable level, which represents certain physicochemical and biodegradable characteristics of a family of trace constituents that are relevant to fate and transport during treatment, thus providing a conservative assessment of removal. A surrogate parameter is a quantifiable change of a bulk parameter that can serve as a measure of individual unit processes or operations' performance in removing trace compounds. This approach utilizes only a limited set of analytes for the evaluation of proper performance of soil-aquifer treatment and high-pressure membrane treatment systems and may be a reasonable way to circumvent the significant costs associated with analysis of a wide range of chemicals of concern, provided that the analytes monitored are good predictors of the contaminants of concern. The approach proposed to select feasible indicator compounds is driven foremost by treatment performance and less so by toxicological relevance. Physicochemical properties (e.g., molecular size, pK_a, log K_{ow}, volatility, and dipole moment) often determine the fate and transport of a chemical in various treatment processes. Thus, selecting multiple indicators representing a broad range of properties will allow accounting for chemicals currently not identified ("unknowns") and new chemicals synthesized and entering the environment in the future (i.e., new pharmaceuticals), provided they fall within the range of properties covered. The underlying concept is that absence or removal of an indicator chemical during a treatment process would also ensure absence or

removal of unidentified chemicals with similar properties. Proper removal is ensured as long as the treatment process of interest is operating according to its technical specifications. It is therefore necessary to define for each treatment process the operating conditions under which proper removal is to be expected. Predetermined changes of surrogate parameters can be utilized to define normal operating conditions according to specification for a given treatment process. Data currently available on the efficacy of different treatment systems operating under certain conditions regarding the removal of individual chemicals are limited and imprecise. Thus, this study focused on defining the operational boundary conditions for surface-spreading and membrane operations under which removal is to be expected and to develop and validate correlations between surrogate parameter and indicator chemicals.

For the surrogate/indicator framework, potential indicator chemicals are classified into four removal categories: "good removal (>90%)", two groups of "intermediate removal (90% < x < 50% and 50% < x < 25%)," and "poor removal (<25%)". This rating of indicators into removal categories of individual unit processes is dependent on the physicochemical and biodegradable properties of the chemicals. Whether the proposed degree of removal is achieved will depend on operational conditions of the treatment process. The most sensitive compounds to assess the performance of a specific treatment process will be those that are partially removed under normal operating conditions. Thus, a system failure will be indicated by poor removal of indicator chemicals classified in the categories "good removal (>90%)" and "intermediate removal (90% < x < 50%)," whereas normal operating conditions will be indicated by partial or complete indicator chemical removal.

The proposed framework is a conservative approach designed to ensure proper removal of identified and unidentified trace organic contaminants and to detect failures in system performance. Assessing system performance of individual unit processes composing an overall treatment train is distinguished into two phases: pilot/start-up and full-scale operation/compliance monitoring. In order to apply the surrogate/indicator framework to a given or proposed treatment train, first operational boundary conditions of treatment processes need to be identified, ensuring the performance of each unit process according to its technical specifications. During a pilot/start-up phase for each unit process, the surrogate or operational parameters that demonstrate a measurable removal (differential) under normal operating conditions ($\Delta X = [X_{in} - X_{out}]/X_{in}$) need to be identified. In parallel, an occurrence study is to be performed confirming that indicator compounds occur at high enough concentrations in the feed water. During piloting of a new treatment process, challenge or spiking tests can be conducted with select indicator chemicals to determine the removal differential ΔY under normal operating conditions. For these tests, 5 to 10 indicator chemicals from the treatment category classified as "good removal" should be selected. During start-up of the full-scale operation, the operational boundary conditions and removal differential ΔX and ΔY for selected surrogate and operational parameters and indicator chemicals should be confirmed. To ensure the proper performance of each full-scale unit operation, select surrogate and operational parameters should be measured on a regular basis. Although it is implied that proper performance of the full-scale treatment train will ensure appropriate removal of wastewater-derived organic contaminants, select indicator chemicals (three to six) for each unit process or/and the overall treatment should be monitored at frequencies in the order of semiannually or annually. The individual steps to develop a surrogate/indicator monitoring framework are summarized in Table 5.1.

Table 5.1. Application of Surrogate/Indicator Framework to an Overall Treatment Train

	Surrogate Parameters	Indicator Compounds
Piloting or/and Start-up		
Step 1	Define operational conditions for each unit process composing the overall treatment train for proper operation according to technical specification	
Step 2	For each unit process, select surrogate parameter that demonstrate a measurable change under normal operating conditions and quantify this differential $\Delta X_i = \left\| (X_{i,in}-X_{i,out}) \right\|$	Conduct occurrence study to confirm detection ratio of feasible indicator compounds is larger than 5 in the feed water of each unit process
Step 3		Conduct challenge or spiking study where feasible with select indicator compounds (5–10) during pilot or start-up to determine the removal differentials under normal operating conditions $\Delta Y_i = (Y_{i,in}-Y_{i,out})/Y_{i,in}$
Step 4	Select feasible surrogate and operational parameters for each unit process	Select 3 to 6 indicator compounds from categories classified as "Good removal"
Full-Scale Operation/Compliance Monitoring		
Step 5	Confirm operational conditions of full-scale operation and removal differential ΔX_i for selected surrogate and operational parameters	
Step 6	**Operational Monitoring**: Monitor differential ΔX_i of select surrogate and operational parameters for each unit process or/and the overall treatment train on a regular basis (daily, weekly)	**Verification Monitoring**: Monitor differential ΔY_i of selected indicator compounds for each unit process or/and the overall treatment train semi-annually/annually

During this study, master lists of indicator compounds were developed and validated for soil-aquifer treatment and high-pressure membrane processes (Tables 5.2 and 5.3). Removal of select surrogate parameters correlated with increasing removal of indicator compounds. Thus, changes of certain surrogate or operational parameters summarized in Table 5.4 were identified as being sensitive in picking up performance deficiencies, which might or might not result in a diminished removal of trace organic chemicals in soil-aquifer treatment. Thus, to ensure proper performance of unit operations regarding the removal of trace organic chemicals, a combination of appropriate surrogate parameters and indicator compounds should be selected.

Table 5.2. Treatment Removal Categories for Indicator Compounds of Surface Spreading Systems

Surface Spreading Systems Conditions (dilution with native groundwater: 0%):

i) Partially nitrified treated wastewater; extensive vadose zone (>100′); subsurface travel time: > 2 weeks

ii) Nitrified/denitrified treated wastewater; shallow vadose zone (<10′); subsurface travel time: > 2 months

Good Removal (>90%)		Intermediate Removal (90–50%)	Intermediate Removal (50–25%)	Poor Removal (<25%)
Acetyl cedrene[b]	Indolebutyric acid[c]	TCEP[1]		Carbamazepine[1]
Atenolol[c,1]	Iopromide[1]	TCPP[1]		Primidone[1]
Atorvastatin[b,1]	Isobornyl acetate[b]		TDCPP[1]	
Benzophenone[1]	Meprobamate[1]		Dilantin[1]	
Benzyl acetate[c]	Methyl			
Benzyl salicylate[d]	Methyl ionine[d]			
Bisphenol A[1]	Methyl salicylate[c]			
BHA[1]	Metoprolol			
Bucinal[d]	Musk ketone[b]			
Caffeine[1]	Musk xylene[b]			
DEET[1]	Naproxen[1]			
Diclofenac[1]	NDMA			
EDTA	Nonylphenol			
Erythromycin[1]	OTNE[b]			
Estrone	Propranolol			
Fluoxetine[1]	Propylparaben[c]			
Galaxolide[b,1]	Sulfamethoxazole[1]			
Gemfibrozil[1]	Terpineol[b]			
Hexyl salicylate[d]	Tonalide[b]			
Hexylcinnamaldehyde[b]	Triclocarban[b]			
Hydrocodone[1]	Triclosan[1]			
Ibuprofen[1]	Trimethoprim[1]			

Note: Removal of compounds with no superscript was verified through peer-reviewed data.

[1] Sulfamethoxazole removal is dependent on predominant redox conditions and is more favorable under anoxic conditions.

[b] Removal estimate is based upon log D being > 3.0 (pH 7).

[c] Removal is estimated as fast biodegradation on the basis of a BioWin prediction.

[d] Removal estimate is based upon log D being > 3.0 (pH 7) and upon fast biodegradation on the basis of a BioWin prediction.

Table 5.3. Treatment Removal Categories for Indicator Compounds of RO Systems[a]

Good Removal (>90%)				Intermediate Removal (90–50%)	Intermediate Removal (50–25%)	Poor Removal (<25%)
Indolebutyric acid[b]	Dichlorprop	Isobutylparaben[b]	Propranolol		Chloroform	
Acetaminophen	Diclofenac	Ketoprofen	Propylparaben[b]		NDMA	
Acetyl cedrene[b]	Dilantin	Mecoprop	Salicylic acid		NDEA	
Atenolol	EDTA	Meprobamate	Simvastatin hydroxy acid			
Atorvastatin	Erythromycin–H_2O	Methyl dihydrojasmonate[b]	Sulfamethoxazole			
Atorvastatin (o-hydroxy)	Estriol	Methyl ionine[b]	TCEP			
Atorvastatin (p-hydroxy)	Estrone	Methyl salicylate[b]	TCPP			
Benzyl acetate[b]	Fluoxetine	Metoprolol	TDCPP			
Benzyl salicylate[b]	Galaxolide	Musk ketone	Terpineol[b]			
Bisphenol A	Gemfibrozil	Musk xylene[b]	Tonalide[b]			
Bucinal[b]	Hexyl salicylate[b]	Naproxen	Triclocarban[b]			
Butylated hydroxyanisole[b]	Hexylcinnamaldehyde[b]	Nonylphenol	Triclosan			
Caffeine	Hydrocodone	Norfluoxetine	Trimethoprim			
Carbamazepine	Ibuprofen	OTNE				
Ciprofloxacin[b]	Iopromide	Phenylphenol[b]				
DEET	Isobornyl acetate[b]	Primidone				

[a]Operating conditions: recovery 80%; permeate flux ~12 gfd or 20 LMH; pH = 6.5.

[b]Removal estimate is based on MW > 150 g/mol.

Note: Removal of compounds with no footnote was verified through peer-reviewed literature data or experimental data generated during this study.

Table 5.4. Sensitive Surrogate Parameters Identified for Different Treatment Categories

Mechanism	Treatment Process	Surrogate for Performance Assessment
Biodegradation	SAT	BDOC; ΔDOC; ΔUVA; ΔTOX; Δammonia; Δnitrate; fluorescence
Physical separation	RO	Δconductivity; Δboron
	NF	Δconductivity; Δcalcium; Δmagnesium

5.2 RECOMMENDATIONS FOR MONITORING DURING PILOT-SCALE STUDIES AND START-UP

5.2.1 Monitoring Framework for SAT

Following the steps outlined in Table 5.1, a feasible, surrogate parameter for an SAT operation could be BDOC or the difference in ammonia, nitrate, DOC, or UVA measurements prior to and after a spreading operation (Table 5.4). During a pilot study or start-up of a full-scale facility, these measurement differentials will be determined. As an example, certain indicator compounds representing different biodegradability levels are suggested in Table 5.4 to be considered in performance-monitoring efforts.

Table 5.5. Monitoring Framework for SAT Systems[a]

Monitoring Level	Good Removal (>90%)	Intermediate Removal (90 < x < 50%)	Intermediate Removal (50 < x < 25%)	Poor Removal (<25%)
Piloting/start-up	ΔAmmonia			
	ΔNitrate			
	ΔDOC			
	Fluorescence			
	BDOC			
	ΔGemfibrozil			ΔPrimidone
	ΔDEET			
	ΔIopromide			
	ΔMeprobamate			
Full-scale operation/ compliance monitoring:	ΔAmmonia			
	ΔUVA			
	ΔTOC			

[a]Conditions: travel time in subsurface > 4 weeks; predominant redox conditions: oxic followed by anoxic; dilution: 0%.

During pilot or start-up, the expected removal differentials for these indicators need to be determined. Monitoring for a compound that behaves conservatively during SAT, such as primidone or carbamazepine, can provide an organic wastewater tracer that allows an assessment of dilution with native groundwater. If the observed removal of the select indicator compounds falls outside the expected removal category, the process is not properly designed or working and adjustments have to be considered. If the indicator compound differentials confirm the proposed removal categories, monitoring for the expected removal differential of selected surrogate compounds will ensure proper removal of wastewater-derived organic compounds during this operation. During full-scale operation, it is necessary only to ensure that the select surrogate parameter differential is achieved.

5.2.2 Monitoring Framework for High-Pressure Membrane Treatment

Following the steps outlined in Table 5.1, a feasible surrogate parameter for an RO operation could be the differential in conductivity, TOC, and boron measurements prior to and after RO treatment (Table 5.5). During a pilot study or start-up of a full-scale facility, these measurement differentials will be determined. As an example, certain indicator compounds representing different solute properties are suggested in Table 5.5 for consideration in performance-monitoring efforts or RO operations.

Table 5.6. Monitoring Framework for RO Systems[a]

Monitoring Level	Good Removal (>90%)	Intermediate Removal (90 < x < 50%)	Intermediate Removal (50 < x < 25%)	Poor Removal (<25%)
Pilot/start-up	ΔConductivity			
	ΔTOC			
	ΔBoron			
	ΔCaffeine		ΔNDMA	
	ΔDEET			
	ΔMeprobamate		ΔChloroform	
	ΔAcetaminophen			
Compliance monitoring	ΔConductivity			
	ΔBoron			

[a]Dilution = 0%.

During pilot or start-up, the expected removal differentials for these indicators need to be determined. If the observed removal of the select indicator compounds falls outside the expected removal category, the process is not properly designed or working and adjustments have to be considered. If the indicator compound differentials confirm the proposed removal categories, monitoring for the expected removal differential of selected surrogate compounds will ensure proper removal of wastewater-derived organic compounds during this operation. During full-scale operation, it is necessary only to ensure that the select surrogate parameter differential is achieved.

CHAPTER 6

CONCLUSIONS

6.1 CONCLUSIONS

The objectives of this project were (a) to identify potential surrogates and indicators for the removal of wastewater-derived chemical contaminants in groundwater recharge projects employing soil-aquifer treatment and high-pressure membrane treatment, (b) to validate the ability of chosen surrogates and indicators to predict the removal of wastewater-derived contaminants in groundwater recharge projects, and (c) to develop guidance and recommendations for the water industry regarding suitable surrogates for groundwater recharge systems using reclaimed water.

Chemicals that were considered suitable to serve as indicators were identified by screening occurrence data of treated wastewater effluents that met a detection frequency above 80% and a level of occurrence that was at least five times higher than their respective limit of quantification. Based on this analysis, a list of more than 50 potential indicator chemicals were identified in North American wastewater effluents. Indicator chemicals identified represented a broad range of physicochemical properties and were characterized by different removal categories that represent good (>90%), moderate (90–25%), and poor removal (<25%) for both soil-aquifer treatment and high-pressure membrane treatment. Although most indicator compounds occur in a similar concentration range, the absolute concentration was used to determine percentage removal in this classification. The removal classification was confirmed through monitoring efforts at multiple SAT sites and membrane facilities. In order to quantify indicator chemicals occurring at the parts-per-trillion level, internal standards and isotope dilution and other QA/QC measures were employed to assure a high degree of precision and certainty in the concentrations reported. The precision and variability achieved by these methods is smaller than the variability of field operations and therefore reported results are suitable to illustrate differences that are due to field performance. It is important to note that the occurrence of indicator compounds in reclaimed water is not static given the release of new chemicals, phasing out of certain pharmaceuticals, or termination of certain product lines. Thus, it is highly suggested that the suitability of suggested indicator compounds is reviewed on a regular basis (3-5 year timeframe) to adjust to potential changes in the use of chemicals.

For SAT operations, several surrogate parameters were identified as differential measures (i.e., BDOC; ΔDOC; ΔUVA; ΔTOX; Δammonia; Δnitrate; fluorescence) that were considered suitable for performance assessment of this treatment process. To assess proper operation of high-pressure membrane applications, electrical conductivity and boron were proposed.

6.1.1 Soil Aquifer Treatment Operations

Based on findings derived from conducting field monitoring efforts at five field sites, redox conditions and feed water types did not seem to impact the removal of indicator chemicals during SAT. The results indicate that removals for biodegradable indicator chemicals are similar across sites for similar travel times despite differences in the extent of vadose zones, which supports the robustness and reliability of SAT operations regarding the removal of biodegradable trace organic chemicals. Considering the travel times across different field sites, the results suggest that removal of DEET, diclofenac, ibuprofen, and meprobamate

were characterized by slower kinetics and required a travel time of more than 1 week to achieve a removal in excess of 90%. The chlorinated flame retardant compounds (i.e., TCEP, TCPP, TDCPP) were not well removed after 6 days under oxic or anoxic conditions and for various feed water types. This is in general agreement with observations from full-scale monitoring efforts, where these compounds were not well attenuated and persist for travel times exceeding many months. The antiepileptic compounds (i.e., primidone, dilantin, carbamazepine), sulfamethoxazole, and atrazine were not well removed after 5 days under either oxic or anoxic conditions, which also agrees with observations from full-scale monitoring. Indicator chemicals that exhibit persistent behavior (removal category of less than 25%) can serve as conservative tracers in SAT operations (e.g., primidone, carbamazepine) and can be used to assess the degree of dilution with native groundwater that is not influenced by wastewater recharge.

A more expanded suite of indicator compounds was examined using feed water with low organic carbon (~0.2 mg/L) and inorganic nitrogen concentrations. Under these feed water conditions, most of the biodegradable indicator chemicals were removed by more than 90% after 5 days of travel time under both oxic and anoxic conditions. This is an agreement with full-scale observations, where all of these compounds were removed in excess of 90% with travel times greater than 1 week.

Removal of indicator chemicals was correlated with removal of surrogate parameters, such as TOC, TOX, and UVA. In general, select indicator chemicals, with the exception of benzophenone, exhibited a significant correlation (p-value < 0.05) with both TOC and TOX. These results demonstrate that changes in TOC and TOX do correlate with changes of indicator chemicals in the subsurface. However, based on laboratory soil-column experiments using feed water with a low carbon concentration (~0.2 mg/L), the same indicator compounds exhibited similar substantial reductions despite no changes in TOC concentrations being observed. This suggests that for sites using feed water qualities that are characterized by a low TOC concentration (< 2 mg/L), TOC monitoring would not be a sufficient surrogate parameter to assess the removal of trace organic chemicals during spreading-basin operation.

6.1.2 High-Pressure Membrane Operations

As demonstrated in previous studies, the vast majority of indicator chemicals are efficiently rejected by RO membranes exceeding 90% removal. Chemicals that are nonionic (neutral) and small can exhibit a partial removal, as observed for nitrosamines, such as NDMA, or 1,4-dioxane. Indicator compounds that are small but exhibit hydrophobic properties can adsorb to the polymeric structure of thin-film composite membranes and partition through the active layer of the membrane into the permeate (e.g., chloroform). The highly efficient rejection of wastewater-derived contaminants by RO membranes limits to a few the number of available indicator chemicals representing intermediate removal. None of the indicator chemicals considered in this study exhibited poor removal (<25%).

The findings of monitoring studies at a full-scale RO facility revealed that some indicator compounds occurred in the permeate at very low concentrations (less than 110 ng/L), whereas most of the compounds were either not detected or were less than 5 ng/L. The majority of the indicator compounds were removed greater than 99% during all sampling campaigns.

6.2 FUTURE RESEARCH NEEDS

- Future research should evaluate the use and precision of appropriate analytical methods to quantify indicator chemicals in water reuse applications. These methods should be validated through round-robin efforts.
- To increase the use of surrogate parameters rather than favoring the measurement of individual chemicals, additional or suggested surrogate parameters that can be measured in real time should be explored.
- A better relationship should be developed between removal of indicator chemicals and travel time during SAT operations, resulting in rate constants for biotransformation. These rate constants could be used for contaminant transport models that can assist in design and operation of managed aquifer recharge facilities.
- A better understanding of pathways of biotransformation can also assist in a better classification of indicator compounds that are not solely based on observed removal efficiencies but on molecular fragments that are subject to a biological attack. The relationships can guide in the development of quantitative structure property relationship models that, coupled with contaminant transport models, could provide an *a priori* assessment of emerging chemicals that have not yet been studied or monitored.
- Methods for quantifying suggested surrogate parameters, such as BDOC or fluorescence, should be standardized.

REFERENCES

Agenson, K. O.; Urase, T. Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications. *Separation & Purification Technology* **2007**, 55, 147–156.

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. *Environmental Monitoring & Assessment* **2006**, 129, 1–3, 19–26.

APHA; AWWA; WEF, *Standard methods for the examination of water and wastewater*. 20th ed.: Washington, DC, **1998**.

Bellona, C.; Drewes, J. E.; Xu, P.; Amy, G. Factors affecting the rejection of organic solutes during NF/RO treatment. *Water Research* **2004**, 38 (12), 2795–2809.

Bellona, C.; Drewes, J. E. Viability of a low pressure nanofilter in treating recycled water for water reuse applications—A pilot-scale study. *Water Research* **2007**, 41, 3948–3958.

Bellona, C.; Drewes, J. E.; Oelker, G.; Luna, J.; Filteau, G.; Amy, G. Comparing nanofiltration and reverse osmosis for drinking water augmentation. *Journal of American Water Works Association* **2008**, 100 (9), 102–116.

California Department of Health (CDPH). Draft groundwater recharge regulations. Title 22. Section 3. Department of Public Health, Sacramento, CA, **2003**.

California Department of Health (CDPH). Draft groundwater recharge regulations. Title 22. Section 3. Department of Public Health, Sacramento, CA, **2008**.

Clark, J. F.; McDermott, J.; Avisar, D. The Montebello Forebay sulfur hexafluoride tracer experiment, Final Report, Dept. of Geological Sciences, University of California, Santa Barbara, CA, **2005**.

Chefetz, B.; Mualem, T.; Ben-Ari, J. Sorption and mobility of pharmaceutical compounds in soil irrigated with wastewater. *Chemosphere* **2008**, 73, 1335–1343.

Cordy. G.; Duran, N. L.; Bouwer, H.; Rice, R. C.; Furlong, E. T.; Zaugg, S. D.; Meyer, M. T.; Barber, L. B.; Kolpin, D.W. Do phamaceuticals, pathogens, and other organic waste water compounds persist when waste water is used for recharge? *Ground Water Monitoring & Remediation* **2004**, 24 (2), 58–69.

Crook, J.; Huiltquist, R.; Sakaji, R. New and improved draft groundwater recharge criteria in California. Proceedings of the American Water Works Association Annual Meeting, Denver, Colorado, **2000**.

Daigger, G. T. Evolving urban water and residuals management paradigms: Water reclamation and reuse, decentralization, and resource recovery. *Water Environment Research* **2009**, 81 (8), 810–823.

Diaz-Cruz, S.; Baceló, D. Trace organic chemical contamination in groundwater recharge. *Chemosphere* **2008**, 72, 333–342.

Dickenson, E. R. V.; Drewes, J. E.; Sedlak, D. L.; Wert, E. C.; Snyder. S. A. Applying surrogates and indicators to assess removal efficiency of trace organic chemicals during

chemical oxidation of wastewaters. *Environmental Science & Technology* **2009**, 43 (16), 6242–6247.

Drewes, J. E.; Jekel, M. Behavior of DOC and AOX using advanced treated wastewater for groundwater recharge. *Water Research* **1998**, 32 (10), 3125–3133.

Drewes J. E; Fox, P. Fate of natural organic matter (NOM) during groundwater recharge using reclaimed water. *Water Science & Technology* **1999**, 40 (9), 241–248.

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

Drewes, J. E.; Fox, P. Source Water Impact Model (SWIM)—A new planning tool for indirect potable water reuse systems. *Water Science & Technology* **2001**, 43 (10), 267–275.

Drewes, J. E.; Reinhard, M.; Fox, P. Comparing microfiltration-reverse osmosis and soil-aquifer treatment for indirect potable reuse of water. *Water Research* **2003a**, 37, 3612–3621.

Drewes, J. E.; Heberer, T.; Rauch, T.; Reddersen, K. Fate of pharmaceuticals during groundwater recharge. *Ground Water Monitoring & Remediation* **2003b**, 23 (3), 64–72.

Drewes, J. E.; Bellona, C.; Oedekoven, M.; Xu, P.; Kim, T.-U.; Amy, G. Rejection of wastewater-derived micropollutants in high-pressure membrane applications leading to indirect potable reuse. *Environmental Progress* **2005**, 24 (4), 400–409.

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

Drewes, J. E.; Quanrud, D. M.; Amy, G. L.; Westerhoff, P. K. Character of organic matter in soil-aquifer treatment systems. *Journal of Environmental Engineering* **2006b**, 1447–1458.

Drewes, J. E.; Sedlak, D.; Synder, S.; and Dickenson, E. *Development of Indicators and Surrogates for Chemical Contaminant Removal during Wastewater Treatment and Reclamation.* WaterReuse Foundation, **2008a**.

Drewes, J. E.; Bellona, C.; Xu, P.; Amy, G.; Filteau, G.; Oelker, G. Comparing nanofiltration and reverse osmosis for treating recycled water. AWWA Research Foundation: Denver, CO, **2008b**.

Drewes, J. E. Groundwater replenishment with recycled water—Water quality improvements during managed aquifer recharge. *Ground Water* **2009**, 47 (4), 502–505.

Drewes, J. E.; Khan, S. Water reuse for drinking water augmentation. In *Water Quality & Treatment,* 6th ed. Edzwald, J. K., Ed. American Water Works Association: Denver, CO, **2010**.

EPHSC (Environment Protection and Heritage Standing Committee) Productivity Commission. Chemicals and plastics regulation. Research report. Melbourne, Australia, **2008**.

Focazio, M. J.; Kolpin, D. W.; Barnes, K. K.; Furlong, E. T.; Meyer, M. T.; Zuagg, S. D.; Barber, L. B.; Thurman, M. E. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States – II. Untreated drinking water. *Science of the Total Environment* **2008**, 402, 201–216.

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**.

Geselbracht, J.; Crook, J. A proposed alternate means of meeting TOC requirements for groundwater-recharge projects. Proceedings of the American Water Works Association Annual Meeting, Denver, CO, **2000**.

Godfrey, E.; Woessner, W. W.; Benotti, M. J. Pharmaceuticals in on-site sewage effluent and ground water, western Montana. *Ground Water* **2007**, *45* (3), 263–271.

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

Guest, J. S.; Skerlos, S.T. A new planning and design paradigm to achieve sustainable resource recovery from wastewater. *Environemntal Science and Technology* **2009**, 43, 6126–6130.

Guo, Y.C.; Krasner, S.W. Occurrence of primidone, carbamazepine, caffeine, and precursors for N-nitrosodimethylamine in drinking water resources impacted by wastewater. *Journal of the American Water Works Association* **2009**, *45*, 58–67.

Heberer, T.; Mechlinski, A.; Fanck, B.; Knappe, A.; Massmann, G.; Pekdeger, A.; Fritz, B. Field studies on the fate and transport of pharmaceutical residues in bank filtration. *Ground Water Monitoring & Remediation* **2004**, *24* (2), 70–77.

Henderson, R. K.; Baker, A.; Murphy K. R.; Hambly, A.; Stuetz, R. M.; Khan, S. J. Fluorescence as a potential monitoring tool for recycled water systems: A review. *Water Research* **2009**, 43, 863–881.

Her, N.; Amy, G.; Foss, D.; Cho, J. Variations of molecular weight estimation by HP-size exclusion chromatography with UVA versus online DOC detection. *Environmental Science and Technology* **2002**, 36 (15), 3393–3399.

Her, N.; Amy, G.; McKnight, D.; Sohn, J.; Yoon, Y. Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. *Water Research* **2003**, 37, 4295–4303.

Imai, A.; Fukushima, T.; Matsushige, K.; Kim, Y.; Choi, K. Characterization of dissolved organic matter in effluents from wastewater treatment plants. *Water Research* **2002**, 36, 859–870.

Kim, T-U.; Drewes, J. E.; Summers, R.S.; Amy, G. Solute transport model for trace organic neutral and charged compounds through nanofiltration and reverse osmosis. *Water Research* **2007**, *41*, 3977–3988.

Kolpin, D. W., Skopec, M., Meyer, M. T., Furlong, E. T., Zaugg, S. D. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. *Science of the Total Environmental* **2004**, 328, 119–130.

La Farré, M.; Peréz, S.; Kantiani, L.; Barceló, D. Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. *Trends in Analytical Chemistry* **2008**, 27 (1), 991–1007.

Leenheer, J. A.; Rostad, C. E.; Barber, L. B.; Schroeder, R.; Anders, R.; Davisson, M. L. Nature and chlorine reactivity of organic constituents from reclaimed water in

groundwater, Los Angeles County, California. *Environmental Science and Technology* **2001**, 35, 3869–3876.

Lin, W-C.; Chen, H-C.; Ding, W-H. Determination of pharmaceutical residues in waters by solid-phase extraction and large-volume on-line derivatization with gas chromatography-mass spectrometry. *Journal of Chromatography A* **2005**, 1065, 279–285.

Lin, C.; Eshel, G.; Negev, I.; Banin, A. Long-term accumulation and material balance of organic matter in the soil of an effluent infiltration basin. *Geoderma* **2008**, 148, 35–42.

Mansell, J.; Drewes, J. E. Fate of steroidal hormones during soil-aquifer treatment. *Ground Water Monitoring & Remediation* **2004**, 24 (2), 94–101.

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

McKnight, D. M.; Boyer, E. W.; Westerhoff, P. K.; Doran, P. T.; Kulbe, T.; Andersen, D. T. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography* **2001**, *46* (1), 38–48.

Mompleat, S.; Le Bot, B.; Thomas, O. Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. *Enviromental International* **2009,** 35 (5), 803–814.

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

Müller, M. B.; Frimmel, F. H. A new concept for the fractionation of DOM as a basis for its combined chemical and biological characterization. *Water Research* **2002**, 36, 2643–2655

Nam, S-N.; Krasner, W.K.; Amy G. L. Chapter 20: Differentiating effluent organic matter (EfOM) from natural organic matter (NOM): Impact of EfOM on drinking water sources. In *Advanced Environmental Monitoring*; Kim, Y. J.; Platt, U., Eds. Springer: New York, **2007**.

National Research Council. Issues in potable reuse. National Academy Press: Washington, DC, **1998**.

Nellor, M.; Soller, J. Tools to assess and understand the relative risks of indirect potable reuse projects. Preliminary TDIs, DWELs, and risk metrics. (WRF-06-018). WateReuse Foundation: Alexandria,VA, **2009**.

Ng, H. Y.; Elimelech, M. Influence of colloidal fouling on rejection of trace organic contaminants by reverse osmosis. *J. Membrane Science* **2004**, 244, 215–226.

Nghiem, L. D.; Schäfer, A. I.; Elimelech, M. Pharmaceutical retention mechanisms by nanofiltration membranes. *Environmental Science & Technology* **2005**, 39 (19),7698–7705.

Nghiem, L. D.; Hawkes, S. Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size. *Separation and Purification Technology* **2007**, 57, 176–184.

Osenbrück, K.; Gläser, H.-R.; Knöller, K.; Weise, S. M.; Möder, M.; Wennrich, R.; Schirmer, M.; Reinstorf, F.; Busch, W.; Strauch, G. Sources and transport of selected organic micropollutants in urban groundwater underlying the city of Halle (Saale), Germany. *Water Research* **2007**, *41* (15), 3259–3270.

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

Quanrud, D. M.; Hafer, J.; Karpiscak, M. M.; Zhang, J.; Lansey, K. E.; Arnold, R. G. Fate of organics during soil-aquifer treatment: Sustainability of removals in the field. *Water Research* **2003,** 37, 3401–3411.

Rauch, T.; Drewes, J. E. A novel approach for quantifying biological bulk organic carbon removal in groundwater recharge systems. *Journal of Environmental Engineering* **2005**, 131 (6), 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 Research* **2006**, 961–968.

Rauch-Williams, T.; Hoppe-Jones, C.; Drewes, J. E. The role of organic matter in the removal of trace organic chemicals during managed aquifer recharge. *Water Research* **2009**, 44 (2), 449–460.

Reddersen, K.; Heberer, T. Multi-compound methods for the detection of pharmaceutical residues in various waters applying solid phase extraction (SPE) and gas chromatography with mass spectrometric (GC-MS) detection. *Journal of Separation Science* **2003**, 26, 1443–1450.

Robeck, G. (Ed.). *Report of the scientific advisory panel on groundwater recharge with reclaimed water*. Prepared for State of California, State Water Resources Control Board, Dept. of Water Resources, and California Dept. Health Services. Dept. Water Resources: Sacramento, CA, **1987**.

Rodriguez, C.; Van Buynder, P.; Lugg, R.; Blair, P.; Devine, B.; Cook, A.; Weinstein P. Indirect potable reuse: A sustainable water supply alternative. *International Journal Environment Res Public Health* **2009**, 6, 1174–1209.

Scheytt, T.; Mersmeann, P.; Ledig, M.; Pekdeger, A.; Herberer, T. Transport of pharmaceutically active compounds in saturated laboratory columns. *Ground Water* **2004**, 42 (5) 767–773.

Scheytt, T. J.; Mersmann, P.; Herberer T. Mobility of pharmaceuticals carbamazepine, diclofenca, ibuprofen, and propyphenazone in miscible-displacement experiments. *Journal of Contaminant Hydrology* **2006**, 83, 53–69.

Schriks, M.; Heringa, M. B.; van der Kooi, M. M.; de Voogt, P.; van Wezel, A. P. Toxicological relevance of emerging contaminants for drinking water quality. *Water Research* **2009**, 44 (2), 461–476.

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.* USGS Water Resources Investigations Report 03-4146, Department of the Interior: Sacramento, CA, **2003**.

Schwab, B. W.; Hayes, E. P.; Fiori, J. M.; Mastrocco, F. J.; Roden, N. M.; Cragin, D.; Meyerhoff, R. D.; D'Aco, V. J.; Andersen, P. D. Human pharmaceuticals in U.S. surface

waters: A human health risk assessment. *Regulatory Toxicology and Pharmacology* **2005**, 42, 296–312.

Sloss, E. M.; Geschwind, S. A.; McCaffrey, D. F.; Ritz, B. R. Groundwater recharge with reclaimed water. An epidemiologic assessment in Los Angeles County, 1987–1991. Prepared for the Water Replenishment District of Southern California, Rand, Santa Monica, California. 1996, 124.

Sloss, E.M.; McCaffrey, D.F.; Fricker, R.D.; Geschwind, S.A.; Ritz, B.R. Groundwater Recharge with Reclaimed Water. Birth Outcomes in Los Angeles County, 1982–1993. Prepared for the Water Replenishment District of Southern California, Rand, Santa Monica, CA, **1999**, 148.

Snyder S. A.; Westerhoff, P.; Yoon, Y.; Sedlak, D. L. Pharmaceuticals, personal care products and endocrine disrupters in water: Implications for water treatment. *Environmental Engineering Science* **2003**, 20, 449–469.

Snyder, S.; Adham, S.; Redding, A. M.; Cannon, F. S.; DeCarolis, J.; Oppenheimer, J.; Wert, E. C.; Yoon, Y. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* **2007**, 202, 56–181.

Snyder, S.; Trenholm, R. A.; Snyder, E. M.; Bruce, G. M.; Pleus, R. C.; Hemming, J. Toxicological relevance of EDCs and pharmaceuticals in drinking water. Awaa Research Foundation: Denver, CO, **2008**.

Strauch, G. Möder, M. Wennrich, R. Osenbrück, K. Gläser, H-R. Schladitz, T. and C. Müller. Indicators for assessing the impact on urban surface and groundwater. *Journal of Soils and Sediments* **2008**, 8(1),23-33.

Ternes, T. A.; Bonerz, M.; Herrmann, N.; Teiser, B.; Andersen, H. R. Irrigation of treated wastewater in Braunschweig, Germany: An option to remove pharmaceuticals and musk fragrances. *Chemosphere* **2007,** 66, 894–904.

United States Environmental Protection Agency (USEPA). Guidelines for water reuse. Washington, DC, **1992**.

United States Environmental Protection Agency (USEPA). Guidelines for water reuse. Washington, DC, **2004**.

Vanderford, B. J.; Pearson, R. A.; Rexing, D. J.; Snyder, S. Analysis of endocrine disruptors, pharmaceuticals and personal care products in water using liquid chromatography/tandem mass spectrometry. *Analytical Chemistry* **2003**, 75 (22), 6265–6274.

Vanderford, B. J.; Snyder, S. Analysis of pharmaceuticals in water by isotope dilution liquid chromatography/tandem mass spectrometry. *Environmental Science & Technology* **2006** 40, 7312–7320.

Water Replenishment District of Southern California (WRD). Regional groundwater monitoring report for water year 2006/2007, Table 2.1. **2008a**.

Water Replenishment District of Southern California (WRD. Groundwater replenishment at the Montebello Forebay Spreading Grounds, Technical Bulletin, Volume 14, Water Replenishment District of Southern California. **2008b**.

Water Replenishment District of Southern California (WRD). Regional groundwater monitoring report for water year 2009. **2010**.

Wells, M. J. M.; Morse, A.; Bell, K. Y.; Pellegrin, M.-L.; Fono, L. J. Emerging pollutants. *Water Environment Research* **2009,** 81 (10) 2211–2254.

Xu, P.; Drewes, J. E.; Kim T.; Bellona C.; Amy, G. Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications, *Journal of Membrane Science* **2006***,* 279, 165–175.

Xue, S.; Zhao, Q.-L.; Wei, L.-L.; Ren, N.-Q. Behavior and characteristics of dissolved organic matter during soil column studies of soil aquifer treatment. *Water Research* **2009**, 43, 499–507.

Ying, G.; Toze, S.; Hanna, J.; Yu, X.; Dillion, P. J.; Kookana, R. S. Decay of endocrine disrupting chemicals in aerobic and anoxic groundwater. *Water Research* **2008,** 42, 1133–1141.

Yu, L.; Fink, G.; Wintgens, T.; Melin, T.; Ternes, T. A. Sorption behavior of potential organic wastewater indicators with soils. *Water Research* **2009,** 23, 951–960.

APPENDIX

A.1 SUPPLEMENTAL INFORMATION

Table A.1. List of Compounds Considered During Indicator Compound Selection

Compound Category	Compounds Evaluated in Secondary/Tertiary-Treated Effluents
Pharmaceuticals	
Analgesic	Acetaminophen, Bezafibrate, Diclofenac, Ketoprofen, Naproxen, Ibuprofen, Fenoprofen, Indometacin, Propyphenazone, Hydrocodone, Codeine, Meclofenamic acid, Tolfenamic acid
Antibiotic	Carbadox, Chlorotetracycline, Ciprofloxacin, Clarithromycin, Democyclocycline, Doxycycline, Enrofloxacin, Erythromycin, Norfloxacin, Ofloxacin, Olaquindox, Oxolinic acid, Oxytetracycline, Pipemidic acid, Roxithromycin, Sulfacetamide, Sulfachloropyridazine, Sulfadiazine,Sulfadimethoxine, Sulfaguanidine, Sulfamerazine, Sulfamethazine, Sulfamethizole, Sulfamethoxazole, Sulfamethoxypyridazine, Sulfamoxole, Sulfapyridine, Sulfaquinoxaline, Sulfasomidin, Sulfathiazole, Tetracycline, Trimethoprim, Tylosin, Lincomycin, Minocycline,
Anticonvulsant	Sarafloxacin
Antihypertensive	Carbamazepine, Primidone, Dilantin
Lipid regulator	Propanolol, Metoprolol, Diltiazem
Anxiolytic	Clofibric acid, Gemfibrizol, Fenofibrate
Bronchodilator	Diazepam, Meprobamate
Antidepressant	Salbutamol, Albuterol
Antihistamine	Fluoxetine
Antidiabetic	Diphenhydramine, Ranitidine, Cimetidine
X-ray contrast agent	Metformin
Stimulant	Iopromide
Anticoagulant	Pentoxifylline
	Warfarin
Hormones	
Estrogen	
Androgen	Estrone,17β-Estradiol, 17α-Ethinylestradiol, Estriol, Mestranol
Progestogen	Testosterone
Other	Progesterone
	Androstenedione, Hydrocortisone
Personal Care Products	
Antimicrobial	Triclosan, Triclocarban, Methyl Triclosan, Methylparaben, Isobutylparaben, Propylparaben, Chloroxylenol, o-Phenylphenol, Phenoxyethanol
Antiacne	Salicylic acid
Fragrance	Acetyl Cedrene, Benzyl Acetate, Benzyl Salicylate, Galaxolide, *g*-Methyl Ionine, Hexyl Salicylate, Hexylcinnamaldehyde, Isobornyl Acetate, Methyl Dihydrojasmonate, Methyl Salicylate, Musk Ketone, Musk Xylene, OTNE, *p-t*-Bucinal, Terpineol, Tonalide, Camphor, Vanillin
Antipruritic	Menthol
Surfactant	Nonylphenol, Octylphenol
Antioxidant	Butylated hydroxyanisole, Butylated hydroxytoluene
Insecticide	DEET
Antiseptic	Acriflavine
Chelating agent	EDTA
UV blocker	Benzophenone, Oxybenzone
Other	
DBP	NDMA
Flame retardant	TCEP, TDCPP, hexabromododecane
Stimulant	Caffeine, Paraxanthine, Nicotine, Cotinine
Plasticizer	Bisphenl A, Bis(2-ethylhexyl) phthalate, Dibutyl phthalate, Dimethyl phthalate
Silicone	Polydimethylsiloxane
Sterol	Cholesterol, Coprostanol
Plant hormone	Indole-3-butyric acid
Pesticide	Atrazine, Trifluralin, Simazine

Table A.2. Physicochemical Properties of Select Indicator Compounds[a]

Name	Formula	CAS No.	MW (g/mol)	log K_{ow}	log D (pH = 7)	pK_a	Charged/ Uncharged (pH 7)	Biodegradability Probability[7]	Application
Acetaminophen	$C_8H_9NO_2$	103-90-2	151.2	0.34[3] 0.46[1]	0.34[3]	9.38 (acid)[1] 9.46 (acid)[4]	Uncharged	LM: Fast (1.0) NLM: Fast (0.99)	PhAC analgesic
Acetyl cedrene	$C_{17}H_{26}O$	32388-55-9	246.4	5.17[3]	5.17[3]	n.a.	Uncharged	LM: Slow (0.27) NLM: Slow (0.01)	PCP fragrance
Atenolol	$C_{14}H_{22}N_2O_3$	29122-68-7	266.3	0.56[4]	−2.23[4]	9.87 (base)[4]	Charged (+)	LM: Fast (1.3) NLM: Fast (1.0)	PhAC beta blocker
Atorvastatin	$C_{33}H_{34}FN_2O_5$	134523-00-5	558.6	6.36[2]				LM: Fast (0.58) NLM: Slow (0.003)	PhAC lowers cholesterol
Atorvastatin (*o*-hydroxy atorvastatin)									Metabolite of atorvastatin
Atorvastatin (*p*-hydroxy atorvastatin)									Metabolite of atorvastatin
Benzyl acetate	$C_9H_{10}O_2$	140-11-4	150.2	1.93[3] 1.96[1]	1.93[3]	n.a.	Uncharged	LM: Fast (0.98) NLM: Fast (1.0)	PCP fragrance
Benzyl salicylate	$C_{14}H_{12}O_3$	118-58-1	228.2	4.0[3] 4.31[2]	3.97[3]	8.11 (acid)[3]	Uncharged	LM: Fast (1.06) NLM: Fast (1.0)	PCP fragrance
Bisphenol A	$C_{15}H_{16}O_2$	80-05-7	228.3	3.32[1]	3.34[5]	9.85 (acid)[6] 11.05 (acid)[6]	Uncharged	LM: Fast (1.0) NLM: Fast (0.99)	HHC plasticizer
Bucinal (*p*-*t*-bucinal)	$C_{14}H_{20}O$	80-54-6	204.3	4.07[3] 4.36[2]	4.07[3]	n.a.	Uncharged	LM: Fast (0.75) NLM: Fast (1.0)	PCP fragrance
Butylated hydroxyanisole (BHA)	$C_{11}H_{16}O_2$	25013-16-5	180.3	3.5[2]	3.5[5]	11.19 (acid)[6]	Uncharged	LM: Fast (0.73) NLM: Fast (0.87)	PCP antioxidant
Caffeine	$C_8H_{10}N_4O_2$	58-08-2	194.1926	−0.07[1] −0.79[4]	−0.79[4]	1.5 (base)[4]	Uncharged	LM: Fast (0.65) NLM: Fast (0.56)	stimulant
Carbamazepine	$C_{15}H_{12}N_2O$	298-46-4	236.3	2.67[3] 2.45[1]	2.67[3]	0.37 (base)[4] −3.55 (base)[4]	Uncharged	LM: Fast (0.63) NLM: Slow (0.41)	PhAC antiepileptic
Chloroform	$CHCl_3$	67-66-3	119.4	1.97[2]	1.97[5]	n.a.	Uncharged	LM: Slow (0.36) NLM: Slow (0.01)	DBP

Table A.2. Physicochemical Properties of Select Indicator Compounds[a]

Name	Formula	CAS No.	MW (g/mol)	log K_{ow}	log D (pH = 7)	pK_a	Charged/ Uncharged (pH 7)	Biodegradability Probability[7]	Application
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	85721-33-1	331.3	1.31[3] 0.28[1]	−1.2[3]	2.74 (most acidic)[3] 8.76 (most basic)[3]	Charged (− and +)	LM: Slow (-0.4) NLM: Slow (0)	PhAC antibiotic
DEET	$C_{12}H_{17}NO$	134-62-3	191.3	1.96[3] 2.18[1]	1.96[3]	n.a.	Uncharged	LM: Fast (0.92) NLM: Fast (0.97)	PCP insecticide
Dichlorprop	$C_9H_8Cl_2O_3$	120-36-5	235.1	3.43[1] 2.94[3]	−1.1[5]	3.1 (acid)[1]	Charged (−)	LM: Slow (0.48) NLM: Slow (0.19)	HHC pesticide
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	15307-86-5	296.2	3.28[3] 3.97[4]	1.28[3]	4.15 (acid)[1] 4.0 (acid)[4] −2.18 (base)[4]	Charged (−)	LM: Slow (0.13) NLM: Slow (0.003)	PhAC analgesic
Dilantin	$C_{15}H_{12}N_2O_2$	57-41-0	252.3	2.47[1] 2.28[4]	2.27[4]	8.33(acid)[1] 9.13 (acid)[4] 19.83 (acid)[4]	Uncharged	LM: Fast (0.7) NLM: Fast (0.79)	PhAC anticonvulsant
EDTA	$C_{10}H_{16}N_2O_8$	60-00-4	292.2	−0.43[3]	−5.84[3]	2.13 (most acidic)[3] 11.2 (most basic)[3]	Charged (− and +)	LM: Slow (0.49) NLM: Slow (0.05)	PCP complexing metal agent
Erythromycin–H_2O (structure and properties from erythromycin)	$C_{37}H_{67}NO_{13}$	114-07-8	733.9	2.83[3]	1.66[3]	13.1 (most acidic)[3] 8.1 (most basic)[3] 7.6 (most basic)[6]	Charged (+)	LM: Slow (-1.4) NLM: Slow (0)	PhAC antibiotic
Estriol (E3)	$C_{18}H_{24}O_3$	50-27-1	288.4	2.94[3] 2.45[1]	2.94[3]	10.4 (most acidic)[3]	Uncharged	LM: Fast (0.96) NLM: Fast (0.81)	Steroidal hormone
Estrone (E1)	$C_{18}H_{22}O_2$	53-16-7	270.4	3.69[3] 3.13[1]	3.69[3]	10.34 (acid)[3] 10.37 (acid)	Uncharged	LM: Fast (0.67) NLM: Slow (0.28)	Steroidal hormone
Fluoxetine	$C_{17}H_{18}F_3NO$	54910-89-3	309.3	4.35[3] 4.05[1]	1.57[3]	10.05 (base)[3]	Charged (+)	LM: Slow (0.49) NLM: Slow (0.13)	PhAC antidepressant

Table A.2. Physicochemical Properties of Select Indicator Compounds[a]

Name	Formula	CAS No.	MW (g/mol)	log K_{ow}	log D (pH = 7)	pK_a	Charged/ Uncharged (pH 7)	Biodegradability Probability[7]	Application
Galaxolide (HHCB)	$C_{18}H_{26}O$	1222-05-5	258.4	5.95[3]	5.95[3]	n.a.	Uncharged	LM: Slow (-.04) NLM: Slow (0)	PCP fragrance
Gemfibrozil	$C_{15}H_{22}O_3$	25812-30-0	250.3	4.39[3] 4.77[2]	1.78[3]	4.75 (acid)[3]	Charged (−)	LM: Fast (0.76) NLM: Fast (0.86)	PhAC lipid regulator
Hexyl salicylate	$C_{13}H_{18}O_3$	6259-76-3	222.3	5.06[2] 4.89[3]	4.86[3]	8.17 (acid)	Uncharged	LM: Fast (1.0) NLM: Fast (1.0)	PCP fragrance
Hexylcinnam-aldehyde	$C_{15}H_{20}O$	101-86-0	216.3	5.33[3]	5.33[3]	n.a.	Uncharged	LM: Fast (1.2) NLM: Fast (1.0)	PCP fragrance
Hydrocodone	$C_{18}H_{21}NO_3$	125-29-1	299.4	2.0[3] 2.16[2]	0.51[3]	8.48 (base)	Charged (+)	LM: Fast (0.54) NLM: Slow (0.36)	PhAC analgesic
Ibuprofen	$C_{13}H_{18}O_2$	15687-27-1	206.3	3.97[1]	1.88[5]	4.91 (acid)[1]	Charged (−)	LM: Fast (0.83) NLM: Fast (0.87)	PhAC analgesic
Indolebutyric acid (3-indolebutyric acid)	$C_{12}H_{13}NO_2$	133-32-4	203.2	2.3[3] 2.3[1]	0.18[3]	4.7 (acid)[2] 4.83 (acid)[3] 0.4 (base)[3]	Charged (−)	LM: Fast (0.78) NLM: Fast (0.79)	PCP plant growth regulator
Iopromide	$C_{18}H_{24}I_3N_3O_8$	73334-07-3	791.1	−3.24[3] −2.05[1]	-3.24[3]	10.6 (most acidic)[3]	Uncharged	LM: Slow (-0.98) NLM: Slow (0)	PhAC iodinated X-ray media
Isobornyl acetate	$C_{12}H_{20}O_2$	125-12-2	196.3	3.6[3]	3.6[3]	n.a.	Uncharged	LM: Slow (0.46) NLM: Fast (0.70)	PCP fragrance
Isobutylparaben	$C_{11}H_{14}O_3$	4247-02-3	194.2	3.28[3] 3.4[2]	3.25[3]	8.17 (acid)[3]	Uncharged	LM: Fast (0.95) NLM: Fast (0.99)	PCP antimicrobial cosmetics
Ketoprofen	$C_{16}H_{14}O_3$	22071-15-4	254.3	3.12[1] 2.81[3]	0.04[5]	4.45 (acid)[1] 4.23 (acid)[3]	Charged (−)	LM: Fast (0.88) NLM: Fast (0.89)	PhAC analgesic
Mecoprop	$C_{10}H_{11}ClO_3$	93-65-2	214.6	3.13[1] 2.835[3]	−1.08[5]	3.1 (acid)[1]	Charged (−)	LM: Fast (0.72) NLM: Fast (0.80)	HHC pesticide
Meprobamate	$C_9H_{18}N_2O_4$	57-53-4	218.3	0.7[3] 0.7[1]	0.7[3]	10.9 (most basic)[4]	Charged (+)	LM: Fast (0.62) NLM: Fast (0.55)	PhAC antianxiety
Methyl dihydrojasmonate	$C_{13}H_{22}O_3$	24851-98-7	226.3	2.5[3]	2.5[3]	n.a.	Uncharged	LM: Fast (0.92) NLM: Fast (0.99)	PCP fragrance
Methyl ionone (*g*-methyl ionone)	$C_{14}H_{22}O$	127-51-5	206.3	4.41[3]	4.41[3]	n.a.	Uncharged	LM: Slow (0.47) NLM: Slow (0.11)	PCP fragrance

Table A.2. Physicochemical Properties of Select Indicator Compounds[a]

Name	Formula	CAS No.	MW (g/mol)	log K_{ow}	log D (pH = 7)	pK_a	Charged/ Uncharged (pH 7)	Biodegradability Probability[7]	Application
Methyl salicylate	$C_8H_8O_3$	119-36-8	152.1	2.23[3] 2.55[1]	2.23[3]	9.76 (acid)[3] 9.87 (acid)[1]	Uncharged	LM: Fast (0.97) NLM: Fast (1.0)	PCP fragrance
Metoprolol	$C_{15}H_{25}NO_3$	37350-58-6	267.4	1.79[3]	−0.34[3]	13.9 (acid)[3] 9.17 (base)[3]	Charged (+)	LM: Fast (0.77) NLM: Fast (0.7)	PhAC beta blocker
Musk ketone	$C_{14}H_{18}N_2O_5$	81-14-1	294.3	3.86[3]	3.86[3]	n.a.	Uncharged	LM: Slow (-0.07) NLM: Slow (0)	PCP fragrance
Musk xylene	$C_{12}H_{15}N_3O_6$	81-15-2	297.3	3.83[3] 4.45[2]	3.83[3]	n.a.	Uncharged	LM: Slow (-0.38) NLM: Slow (0)	PCP fragrance
Naproxen	$C_{14}H_{14}O_3$	22204-53-1	230.26	3.18[1]	0.33[5]	4.15 (acid)[1]	Charged (−)	LM: Fast (0.90) NLM: Fast (0.96)	PhAC analgesic
NDMA	$C_2H_6N_2O$	62-75-9	74.1	−0.64[3] −0.57[1]	−0.64[3]	3.56 (base)[3]	Uncharged	LM: Slow (0.19) NLM: Slow (0.21)	DBP
Nonylphenol	$C_{15}H_{24}O$	25154-52-3	220.4	5.71[2]	5.71[5]	10.3 (acid)[1]	Uncharged	LM: Fast (0.92) NLM: Fast (0.96)	PCP surfactant
Norfluoxetine									Metabolite of fluoxetine
Ofloxacin	$C_{18}H_{20}FN_3O_4$	83380-47-6	361.4	1.49[3]	−1.35[3]	2.27 (most acidic)[3] 6.81 (most basic)[3]	Charged (−)	-	PhAC antibiotic
OTNE	$C_{16}H_{26}O$	54464-57-2	234.2	5.29[3]	5.29[3]	n.a.	Uncharged	LM: Slow (0.27) NLM: Slow (0.05)	PCP fragrance
Phenylphenol (*o*-phenylphenol)	$C_{12}H_{10}O$	90-43-7	170.2	2.94[3] 3.09[1]	2.94[3]	9.99 (acid)[3] 9.97 (base)[1]	Uncharged	LM: Fast (0.91) NLM: Fast (0.96)	PCP antimicrobial
Primidone	$C_{12}H_{14}N_2O_2$	125-33-7	218.3	−0.844[3] 0.91[1]	−0.81[3]	12.3 (most acidic)[3] 11.13 (acid)[4] 12.25 (acid)[4]	Uncharged	LM: Fast (1.0) NLM: Fast (0.99)	PhAC antiepileptic
Propranolol	$C_{16}H_{19}NO_2$	525-66-6	259.3	3.1[3] 3.48[1]	0.99[3]	13.84 (acid)[3] 9.14 (base)[3] 9.42 (base)[1]	Charged (+)	LM: Fast (1.07) NLM: Fast (0.98)	PhAC beta blocker

Table A.2. Physicochemical Properties of Select Indicator Compounds[a]

Name	Formula	CAS No.	MW (g/mol)	log K_{ow}	log D (pH = 7)	pK_a	Charged/ Uncharged (pH 7)	Biodegradability Probability[7]	Application
Propylparaben	$C_{10}H_{12}O_3$	94-13-3	180.2	2.93[3] 3.04[1]	2.93[3]	8.23 (acid)[3] 8.5 (acid)[4]	Uncharged	LM: Fast (0.95) NLM: Fast (0.99)	PCP antimicrobial cosmetics
Salicylic acid	$C_7H_6O_3$	69-72-7	138.1	2.26[3] 1.19[1]	−1.68[3]	3.01 (most acidic)[3] 2.97 (most acidic)[1]	Charged (−)	LM: Fast (0.97) NLM: Fast (0.99)	PhAC analgesic
Simvastatin hydroxy acid (structure and properties from simvastatin)	$C_{25}H_{38}O_5$	79902-63-9	418.6	4.68[1]	4.68[5]	15.06 (acid)[4]	Uncharged	LM: Fast (0.87) NLM: Fast (0.99)	Metabolite of simvastatin (PhAC lowers cholesterol)
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	723-46-6	253.4	0.89[3] 0.89[1]	−0.33[3]	6.16 (acid)[4] 1.97 (base)[4] 0.24 (base)[4]	Charged (−)	LM: Slow (0.45) NLM: Slow (0.13)	PhAC antibiotic
TCEP (Tris[2-chloroethyl]phosphate)	$C_6H_{12}Cl_3O_4P$	115-96-8	285.5	0.48[3] 1.44[1]	0.48[3]	n.a.	Uncharged	LM: Fast (0.59) NLM: Fast (1.0)	PCP flame retardant
TCPP (Tris[2-chloroisopropyl]phosphate)	$C_9H_{18}Cl_3O_4P$	13674-84-5	327.6	1.52[3] 2.59[1]	1.52[3]	n.a.	Uncharged	LM: Fast (0.57) NLM: Fast (1.0)	PCP flame retardant
TDCPP (Tris[1,3-dichloro-2-propyl]-phosphate)	$C_9H_{15}Cl_6O_4P$	13674-87-8	430.9	1.79[3] 3.65[1]	1.79[3]	n.a.	Uncharged	LM: Fast (0.19) NLM: Fast (1.0)	HHC flame retardant
Terpineol	$C_{10}H_{18}O$	8000-41-7	154.3	3.33[2]	3.33[5]	19.2 (acid)[6]	Uncharged	LM: Slow (0.49) NLM: Slow (0.29)	PCP fragrance
Tonalide (AHTN)	$C_{18}H_{26}O$	21145-77-7 1506-02-1	258.4	6.37[3]	6.37[3]	n.a.	Uncharged	LM: Slow (0.32) NLM: Slow (0.02)	PCP fragrance
Triclocarban	$C_{13}H_9Cl_3N_2O$	101-20-2	315.6	5.74[3] 4.90[2]	5.74[3]	10.6 (acid)[4] 17.1 (acid)[4]	Uncharged	LM: Slow (0.05) NLM: Slow (0)	PCP antimicrobial
Triclosan	$C_{12}H_7Cl_3O_2$	3380-34-5	289.5	5.8[3] 4.76[1]	5.75[3]	7.8 (acid)[3]	Uncharged	LM: Slow (0.31) NLM: Slow (0.02)	PCP antimicrobial l

Table A.2. Physicochemical Properties of Select Indicator Compounds[a]

Name	Formula	CAS No.	MW (g/mol)	log K_{ow}	log D (pH = 7)	pK_a	Charged/ Uncharged (pH 7)	Biodegradability Probability[7]	Application
Trimethoprim	$C_{14}H_{18}N_4O_3$	738-70-5	290.3	0.79[3] 0.91[1]	0.28[3]	7.34 (most basic)[3] 7.12 (most basic)[1] 7.16 (base)[4] −0.9 (base)[4]	Uncharged & Charged (+)	LM: Fast (0.59) NLM: Fast (0.92)	PhAC antibiotic

[1] measured values obtained from Syracuse Research Corporation at http://www.syrres.com/esc/physprop.htm

[2] estimated values obtained from Syracuse Research Corporation at http://www.syrres.com/esc/physprop.htm

[3] estimated values calculated from Advanced Chemistry Development (ACD/Labs) Software Solaris V4.67

[4] estimated values calculated from United States National Library of Medicine's ChemID Plus Advanced Software located at http://chem.sis.nlm.nih.gov/chemidplus/

[5] estimated values calculated from provided log K_{ow} and pK_a values

[6] estimated values calculated from SPARC On-Line Calculator at ibmlc2.chem.uga.edu/sparc/

[7] estimated probabilities calculated from US EPA's Software BioWin V4.1 (LM: Linear Model; NLM: Nonlinear Model; fast degradation > 0.5; slow degradation < 0.5)

n.a. = not applicable

Table A.3. Indicator Compound Concentrations (ng/L) Observed at Tucson Water's SWRF (analytical methods denoted)

		Campaign #1 (Jan-Feb 2007)			Campaign #2 (July 2007)			Campaign #3 (Dec. 2007)			Campaign #4 (April 2008)		
Analyte	**Lab**	**RB**	**MW 5**	**WR-199A**	**RB**	**MW 5**	**WR-199A**	**RB**	**MW 5**	**WR-199A**	**RB**	**MW 5**	**WR-199A**
Atenolol	SNWA[a]	1900	91	<0.25	1100	30	<0.25	na	na	na	1700	61	<1.0
Atorvastatin	SNWA[a]	24	22	<0.25	<0.25	0.69	<0.25	na	na	na	8.5	<0.50	<0.50
Atrazine	SNWA[a]	1.1	1.1	2.6	2.8	4.0	3.2	na	na	na	2.4	2	2.5
Benzophenone	SNWA[a]	na	na	na	na	na	na	na	na	na	510	330	<50
Benzophenone	SNWA[b]	580	230	<25	400	45.0	<25	na	na	na	na	na	na
BHA	SNWA[a]	na	na	na	na	na	na	na	na	na	93	<1.0	<1.0
BHA	SNWA[b]	200	<25	<25	75	<25	<25	na	na	na	na	na	na
Bisphenol A	SNWA[a]	13	3100	<5.0	<5.0	10000	<5.0	na	na	na	<5.0	2850	<5.0
Caffeine	CSM[c]	605	nd	nd	na	na	na	na	na	na	na	na	na
Caffine	SNWA[a]	na	na	na	na	na	na	na	na	na	380	81	<5.0
Carbamazepine	SNWA[a]	440	380	530	510	440	400	na	na	na	320	435	490
Carbamazepine	CSM[d]	517	374	269	na	na	na	387	438	495	na	na	na
DEET	SNWA[a]	na	na	na	na	na	na	na	na	na	310	135	4.1
DEET	SNWA[b]	940	610	<25	601	190	<25	na	na	na	na	na	na
Diazepam	SNWA[a]	13	4.4	2.7	5.7	4.9	3.5	na	na	na	3.9	5.2	3.5
Diclofenac	SNWA[a]	190	110	<0.25	130	8.9	<0.25	na	na	na	200	67.5	<0.25
Diclofenac	CSM[c]	105	40	<25	na	na	na	67	<10	<10	98	63	21
Dilantin	SNWA[a]	280	240	25	310	97	42	na	na	na	810	260	32
Dioctyl phtalate	SNWA[b]	1200	<50	<50	170	<50	<50	na	na	na	na	na	na
Enalapril	SNWA[a]	2.8	<0.25	<0.25	<0.25	<0.28	<0.25	na	na	na	na	na	na
Fluoxetine	SNWA[a]	67	<0.50	<0.50	44	<0.56	<0.50	na	na	na	55	<0.50	<0.50
Galaxolide	SNWA[b]	5900	35	<25	na	na	na	na	na	na	na	na	na
Galaxolide	SNWA[b]	5900	35	<25	2000	<25	<25	na	na	na	na	na	na
Gemfibrozil	SNWA[a]	3500	2000	<0.25	1800	170	<0.25	na	na	na	4500	2300	<0.25
Gemfibrozil	UCB	na	na	na	na	na	na	na	na	na	na	na	na
Gemfibrozil	CSM[d]	1509	668	nd	na	na	na	na	na	na	na	na	na
Gemfibrozil	CSM[c]	1128	398	nd	na	na	na	2222	1081	<25	2807	1187	67
Ibopbromide	SNWA[a]	na	na	na	na	na	na	na	na	na	680	430	<10
Ibuprofen	SNWA[a]	na	na	na	na	na	na	na	na	na	92	150	<1.0
Ibuprofen	UCB	na	na	na	na	na	na	na	na	na	na	na	na
Ibuprofen	CSM[c]	292	76	nd	na	na	na	764	234	<10	1075	239	26
Linuron	SNWA[a]	<0.50	<0.50	<0.50	0.98	0.57	<0.50	na	na	na	na	na	na
Meprobamate	SNWA[a]	680	520	30	670	250	30	na	na	na	630	600	43
Musk Ketone	SNWA[a]	na	na	na	na	na	na	na	na	na	44	<25	<25
Musk Ketone	SNWA[b]	56	25	<25	94	68	<25	na	na	na	na	na	na
Naproxen	SNWA[a]	1600	640	<0.50	700	55	<0.50	na	na	na	210	270	<0.50
Naproxen	UCB	na	na	na	na	na	na	na	na	na	na	na	na
Naproxen	CSM[d]	801	250	nd	na	na	na	290	117	<0.50	na	na	na
Naproxen	CSM[c]	787	222	nd	na	na	na	473	113	<10	193	93	25
Nonylphenol	SNWA[b]	10000	610	58	310	190	73	na	na	na	na	na	na
Norfluoxetine	SNWA[a]	28	<0.50	<0.50	8.0	<0.56	<0.50	na	na	na	na	na	na
Octylphenol	SNWA[a]	290	51	<25	na	na	na	na	na	na	<25	295	<25
Octylphenol	CSM[d]	274	126	47	na	na	na	na	na	na	na	na	na
o-Hydroxy atorvastatin	SNWA[a]	12	11	<0.50	<0.50	<0.50	<0.50	na	na	na	na	na	na
p-Hydroxy atorvastatin	SNWA[a]	33	28	<0.50	<0.50	<0.50	<0.50	na	na	na	na	na	na
Primidone	SNWA[a]	na	na	na	na	na	na	na	na	na	150	150	140
Primidone	CSM[d]	190	96	75	na	na	na	1540	nd	1146	na	na	na
Risperidone	SNWA[a]	2.1	<0.25	<0.25	0.92	0.66	<0.25	na	na	na	na	na	na
Salicylic acid	CSM[c]	na	na	na	na	na	na	15958	418	<10	3422	255	20
Simvastatin	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.28	<0.25	na	na	na	na	na	na
Simvastatin hydroxy acid	SNWA[a]	<0.25	1.7	<0.25	<0.25	<0.28	<0.25	na	na	na	na	na	na
Sulfamethoxazole	SNWA[a]	1000	1100	51	690	610	71	na	na	na	1100	2400	86
TCEP	SNWA[a]	na	na	na	na	na	na	na	na	na	680	490	120
TCEP	SNWA[b]	740	630	243	840	610	160	na	na	na	na	na	na
TCEP	CSM[c]	500	361	320	na	na	na	na	na	na	362	390	44
TCPP	SNWA[b]	860	820	227	940	1100	140	na	na	na	na	na	na
TCPP	CSM[c]	647	1065	710	na	na	na	na	na	na	na	na	na
TDCPP	SNWA[a]	na	na	na	na	na	na	na	na	na	1900	1150	160
TDCPP	CSM[c]	735	422	409	na	na	na	1267	1010	357	861	698	274
Tonalide	SNWA[b]	880	180	<25	250	120	<25	na	na	na	na	na	na
Traseolide	SNWA[b]	120	<25	<25	na	na	na	na	na	na	na	na	na
Triclosan	SNWA[a]	66	6.8	<1.0	4.0	4.7	<1.0	na	na	na	14	25	<1.0
Triclosan	CSM[d]	433	34	14	na	na	na	na	na	na	na	na	na
Trimethoprim	SNWA[a]	730	33	<0.25	270	23	<0.25	na	na	na	720	32.5	<0.25

na-not analyzed '<' lower than detection limit [a]LC-MS/MS [b]GC-MS/MS [c]GC-MS-PFB [d]GC-MS-MTB

Table A.4. Indicator Compound Concentrations (ng/L) Observed at MFSG's SGCB (analytical methods denoted)

		Campaign #1 (March-May 2007)				Campaign #2 (June-August 2007)				Campaign #3 (Nov 2007-Jan 2008)				Campaign #4 (Feb-August 2008)			
Analyte	**Lab**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 1612T**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 1612T**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 1612T**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 100090**
a-BHC	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
Acetaminophen	CSM[d]	n.d.	n.d.	n.d.	n.d.	na	na	na	na	na	na	na	na	na	na	na	na
Atenolol	SNWA[a]	350	0.72	<0.25	<0.25	870	0.27	<0.25	<0.25	1450	3	0.39	0.45	1340	<1.0	<0.25	<1.0
Atorvastatin	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.50	<0.50	<0.50
Atrazine	SNWA[a]	4.8	3.9	3	4.1	5.4	4.4	5	4.4	6.1	9	5.7	2.6	4.1	2.35	3.8	3.25
b-BHC	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
Benzophenone	SNWA[b]	79	<25	<25	35	83	<25	<25	<25	na	na	na	na	na	na	na	na
Benzophenone	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	89	<50	<50	<50
BHA	SNWA[b]	<25	<25	<25	<25	<25	<25	<25	<25	na	na	na	na	na	na	na	na
BHA	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	<1.0	<1.0	<1.0	<1.0
BHT	SNWA[b]	<25	<25	<25	<25	<25	<25	<25	<25	na	na	na	na	na	na	na	na
Bisphenol A	CSM[d]	n.d.	n.d.	9	n.d.	na	na	na	na	na	na	na	na	na	na	na	na
Bisphenol A	SNWA[a]	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5.65	<5.0	<5.0	na	34	<5.0	<5.0	<5.0
Butylbenzyl phtha	SNWA[b]	<50	<50	<50	60	<50	61	<50	<50	na	na	na	na	na	na	na	na
Caffine	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	280	<5.0	<5.0	<5.0
Carbamazepine	CSM[d]	150	94	144	108	na	na	na	na	na	na	na	na	na	na	na	na
Carbamazepine	SNWA[a]	98	96	110	110	190	160	200	180	225	230	210	na	200	97	110	100
Clofibric acid	CSM[c]	n.d.	n.d.	n.d.	n.d.	<10	<10	<10	<10	<10	<10	<10	na	<10	<10	<10	na
d-BHC	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
DEET	SNWA[b]	31	<25	<25	<25	350	<25	<25	<25	na	na	na	na	na	na	na	na
DEET	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	100	1.6	6.3	<1.0
Diadzinon	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
Diazepam	SNWA[a]	0.94	0.57	0.44	0.48	2	0.89	0.82	0.68	1.65	2.2	1.1	na	<0.25	2.45	7.5	0.335
Dichlorprop	CSM[c]	n.d.	n.d.	n.d.	n.d.	<10	<10	<10	<10	<10	<10	<10	na	<10	<10	<10	na
Diclofenac	CSM[d]	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Diclofenac	SNWA[a]	0.72	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	22	<0.25	<0.25	na	24	<0.25	<0.25	<0.25
Dilantin	SNWA[a]	77	8.3	31	38	180	39	75	160	215	180	66	na	160	10.65	41	195
Dioctyl phthalate	SNWA[b]	<50	<50	<50	51	<50	<50	<50	<50	na	na	na	na	na	na	na	na
Enalapril	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	na	na	na	na	na
Fenofibrate	CSM[c]	n.d.	n.d.	n.d.	n.d.	<50	<50	<50	<50	<50	<50	<50	na	<50	<50	6	na
Fluoxetine	SNWA[a]	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	6.3	5.1	4.1	na	0.91	<0.50	<0.50	<0.50
Galaxolide	SNWA[b]	88	65	<25	<25	200	<25	<25	<25	na	na	na	na	na	na	na	na
g-BHC	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
Gemfibrozil	CSM[d]	375	n.d.	n.d.	n.d.	na	na	na	na	na	na	na	na	na	na	na	na
Gemfibrozil	CSM[c]	64	n.d.	n.d.	n.d.	64	<25	<25	<25	301	<25	<25	na	503	<25	<25	na
Gemfibrozil	SNWA[a]	740	<0.25	<0.25	<0.25	160	<0.25	<0.25	<0.25	460	1.8	<0.25	na	610	<0.25	11	<0.25
Ibuprofen	CSM[c]	<10	n.d.	n.d.	n.d.	36	14	28	20	<10	<10	<10	na	39	<10	<10	na
Ibuprofen	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	50	<1.0	<1.0	<1.0

na-not analyzed n.d.-not detected '<' lower than detection limit [a]LC-MS/MS [b]GC-MS/MS [c]GC-MS-PFB [d]GC-MS-MTB

Table A.4. Cont. Indicator Compound Concentrations (ng/L) Observed at MFSG's SGCB (analytical methods denoted)

		Campaign #1 (March-May 2007)				Campaign #2 (June-August 2007)				Campaign #3 (Nov 2007-Jan 2008)				Campaign #4 (Feb-August 2008)			
Analyte	**Lab**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 1612T**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 1612T**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 1612T**	**SGRB**	**MW 100914**	**MW 1620RR**	**MW 100090**
Iopromide	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	920	<10	<10	<10
Ketorpofen	CSM[c]	n.d.	n.d.	n.d.	n.d.	<25	<25	<25	<25	<25	<25	<25	na	<25	<25	<25	na
Linuron	SNWA[a]	1.3	<0.50	<0.50	<0.50	1.3	<0.50	<0.50	<0.50	3.65	3.1	<0.50	na	na	na	na	na
Mecoprop	CSM[c]	n.d.	n.d.	n.d.	n.d.	23	<10	<10	<10	<10	<10	<10	na	<10	<10	<10	na
Meprobamate	SNWA[a]	170	4	11	9.7	340	2.9	11	8.6	385	290	16	na	290	2.15	31	0.745
Methoxychlor	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
Metolachlor	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
Musk Ketone	SNWA[b]	<25	<25	<25	<25	<25	<25	<25	<25	na	na	na	na	na	na	na	na
Musk Ketone	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	<25	<25	<25	<25
Naproxen	CSM[c]	detect (<25)	n.d.	n.d.	detect (<10)	9.6	7.7	35	10.2	<10	<10	<10	na	<10	<10	<10	na
Naproxen	SNWA[a]	13	<0.50	<0.50	<0.50	4.7	<0.50	<0.50	<0.50	65.5	<0.50	<0.50	na	22	<0.50	0.91	<0.50
Nonylphenol	SNWA[b]	110	<50	61	230	160	68	69	71	na	na	na	na	na	na	na	na
Norfluoxetine	SNWA[a]	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	0.645	<0.50	<0.50	na	na	na	na	na
Octachlorostyren	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na
octylphenol	SNWA[b]	<25	<25	<25	<25	32	<25	<25	<25	na	na	na	na	na	na	na	na
Octylphenol	CSM[d]	116	<50	<50	n.d.	na	na	na	na	na	na	na	na	na	na	na	na
Octylphenol	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	<25	<25	<25	<25
o-Hydroxy atorva	SNWA[a]	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	na	na	na	na	na
Phenacetine	CSM[c]	n.d.	n.d.	n.d.	n.d.	na	na	na	na	na	na	na	na	na	na	na	na
p-Hydroxy atorva	SNWA[a]	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	na	na	na	na	na
Primidone	CSM[d]	133	37	45	n.d. - 43	na	na	na	na	na	na	na	na	na	na	na	na
Primidone	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	130	55	75	75
Risperidone	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	0.78	<0.25	<0.25	<0.25	<0.25	na	na	na	na	na
Salcylic acid	CSM[c]	na	na	na	na	665	15	12	31	6894	141	71	na	1224	413	51	na
Simvastatin	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	na	na	na	na	na
Simvastatin hydr	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	na	na	na	na	na
Sulfamethoxazole	SNWA[a]	320	26	71	46	110	27	86	56	395	490	170	na	270	15.5	100	120
TCEP	SNWA[b]	370	77	120	<50	790	<50	<50	<50	na	na	na	na	na	na	na	na
TCEP	CSM[c]	177	25	37	<25	802	<50	<50	<50	na	na	na	na	354	82	81	na
TCEP	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	240	36	46	19
TCPP	CSM[c]	438	165	106	73	262	27	48	<50	na	na	na	na	795	197	104	na
TCPP	SNWA[a]	na	na	na	na	na	na	na	na	na	na	na	na	1000	480	390	145
TCPP (Fyrol PCF)	SNWA[b]	420	210	150	96	860	230	89	<50	na	na	na	na	na	na	na	na
TDCPP	CSM[c]	200	101	63	<50	452	117	113	66	772	460	278	na	680	416	324	na
Tonalide	SNWA[b]	<25	<25	<25	<25	30	<25	<25	<25	na	na	na	na	na	na	na	na
Traseolide	SNWA[b]	<25	<25	<25	<25	<25	<25	<25	<25	na	na	na	na	na	na	na	na
Triclosan	CSM[d]	80	28	29	19	na	na	na	na	na	na	na	na	na	na	na	na
Triclosan	SNWA[a]	1.5	<1.0	<1.0	<1.0	2.3	<1.0	<1.0	<1.0	9.4	<1.0	<1.0	na	1.1	<1.0	<1.0	<1.0
Trimethoprim	SNWA[a]	120	0.63	<0.25	<0.25	29	0.66	0.28	<0.25	92	3.4	0.42	na	88	0.655	<0.25	<0.25
Vinclozolin	SNWA[b]	<10	<10	<10	<10	<10	<10	<10	<10	na	na	na	na	na	na	na	na

na-not analyzed n.d.-not detected '<' lower than detection limit [a]LC-MS/MS [b]GC-MS/MS [c]GC-MS-PFB [d]GC-MS-MTB

Table A.5 Indicator Compound Concentrations (ng/L) Observed at IEUA's 8th St. Basin (analytical methods denoted)

RB – recharge basin; Lysimeter is a composite sample; Perimeter – perimeter monitoring well

		8TH ST. Campaign #1 (Sept-Oct 2007)			8TH ST. Campaign #2 (March-April 2008)		
Analyte	**Lab**	**RB**	**Lysimeter**	**Perimeter**	**RB**	**Lysimeter**	**Perimeter**
Atenolol	SNWA[a]	200	0.71	<0.25	80	1.35	<1.0
Atorvastatin	SNWA[a]	<0.25	<0.25	<0.25	<0.50	<0.50	<0.50
Atrazine	SNWA[a]	0.38	1.1	100	1.5	0.78	99
Benzophenone	SNWA[b]	83	89	<25	na	na	na
Benzophenone	SNWA[a]	na	na	na	110	55	<50
BHA	SNWA[a]	na	na	na	<1.0	<1.0	<1.0
Bisphenol A	SNWA[a]	27	1400	<5.0	27	47.5	5.3
Caffeine	SNWA[a]	na	na	na	270	<5.0	<5.0
Carbamazepine	SNWA[a]	89	43	0.43	30	64	<0.50
clofibric acid	CSM[c]	<10	<10	<10	<10	<10	<10
Diazepam	SNWA[a]	1.1	0.25	<0.25	0.35	0.345	<0.25
dichlorprop	CSM[c]	<10	<10	<10	<10	<10	<10
Diclofenac	SNWA[a]	5.4	5	<0.25	0.59	<0.25	<0.25
Diclofenac	CSM[c]	na	<10	na	<10	<10	na
DEET	SNWA[a]	na	na	na	44	50	<1.0
Dilantin	SNWA[a]	94	93	<1.0	87	98	<1.0
Enalapril	SNWA[a]	<0.25	<0.25	<0.25	na	na	na
fenofibrate	CSM[c]	<50	<50	<50	<50	<50	<50
Fluoxetine	SNWA[a]	5.2	<0.50	<0.50	2	<0.50	<0.50
Gemfibrozil	SNWA[a]	0.37	2	<0.25	0.69	0.88	0.37
gemfibrozil	CSM[c]	<25	<25	<25	<25	<25	<25
ibuprofen	CSM[c]	27	43	19	16	7.6	<1.0
Ibuprofen	SNWA[a]	na	na	na	<10	<10	<10
ibuprofen	CSM[c]	na	na	na	<10	<10	<10
ketoprofen	CSM[c]	<25	<25	<25	<25	<25	<25
Linuron	SNWA[a]	4.2	12	<0.50			
mecoprop	CSM[c]	64	84	<10	133	23	<10
Meprobamate	SNWA[a]	680	280	0.73	240	275	<0.25
Musk Ketone	SNWA[a]	na	na	na	<25	<25	<25
Naproxen	SNWA[a]	<0.50	1.9	<0.50	1.4	<0.50	<0.50
naproxen	CSM[c]	<10	<10	<10	<10	0	<10
Norfluoxetine	SNWA[a]	<0.50	<0.50	<0.50	na	na	na
Octylphenol	SNWA[b]	46	26	<25	na	na	na
Octylphenol	SNWA[a]	na	na	na	<25	<25	<26
o-Hydroxy atorvastatin	SNWA[a]	<0.50	<0.50	<0.50	na	na	na
p-Hydroxy atorvastatin	SNWA[a]	<0.50	<0.50	<0.50	na	na	na
Primidone	SNWA[a]	na	na	na	40	66	<0.50
Risperidone	SNWA[a]	<0.25	<0.25	<0.25	na	na	na
salicylic acid	CSM[c]	528	2421	<10	317	80	28
Simvastatin	SNWA[a]	<0.25	<2.5	<0.25	na	na	na
Simvastatin hydroxy acid	SNWA[a]	<0.25	<0.25	<0.25	na	na	na
Sulfamethoxazole	SNWA[a]	4.2	7.6	<0.25	2.3	18	0.3
TCEP	CSM[c]	1015	669	<50	733	259	<50
TCEP	SNWA[a]	na	na	na	730	385	<10
TCEP	SNWA[b]	890	590	<50	na	na	na
TCPP	CSM[c]	NA	NA	NA	1802	718	<50
TCPP	SNWA[a]	na	na	na	1700	980	<100
TDCPP	CSM[c]	1077	372	48	884	574	<50
TDCPP	SNWA[b]	1300	850	<50	na	na	na
Triclosan	SNWA[a]	11	3.7	<1.0	1.9	<1.0	<1.0
Trimethoprim	SNWA[a]	0.97	<0.25	<0.25	0.35	<0.25	<0.25

na-not analyzed '<' lower than detection limit [a]LC-MS/MS [b]GC-MS/MS [c]GC-MS/MS-PFB

Table A.6. Indicator Compound Concentrations (ng/L) Observed at IEUA's Brooks and Hickory Basins (analytical methods denoted)

		BROOKS		BROOKS		HICKORY		
		Campaign #1 (Sep 2008)		Campaign #2 (Oct 08)		Campaign #1 (March-April 2008)		
Analyte	Lab	RB	Lysimeter	RB	Lysimeter	RB	Lysimeter	Perimeter
Atenolol	SNWA[a]	<1.0	<1.0	20	<1.0	81	5.6	<1.0
Atorvastatin	SNWA[a]	<0.50	<0.50	<0.50	<0.50	<0.50	<0.58	<0.50
Atrazine	SNWA[a]	0.53	0.81	0.44	0.97	0.59	1.1	20
Benzophenone	SNWA[a]	103.5	76	120	79	98	<58	<50
BHA	SNWA[a]	<1.0	<1.0	<1.0	<1.0	<1.0	<1.2	<1.0
Bisphenol A	SNWA[a]	<5.0	140	<5.0	68	<5.0	6	<5.0
Caffeine	SNWA[a]	99.5	6	32	<5.0	9	<5.8	<5.0
Carbamazepine	SNWA[a]	47	44	64	65	12.5	87	1.3
DEET	SNWA[a]	34	56	38	52	38	49	1.1
Diazepam	SNWA[a]	<0.25	<0.25	0.28	0.82	0.27	0.85	0.29
Diclofenac	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.29	<0.25
Dilantin	SNWA[a]	105	97	100	140	69	49	7.2
Fluoxetine	SNWA[a]	2.1	0.54	1.1	<0.50	5.35	0.58	<0.50
Gemfibrozil	SNWA[a]	1.7	<0.25	<0.25	0.68	<0.25	<0.29	<0.25
Ibuprofen	SNWA[a]	2.8	<1.0	7.2	4.8	5.1	5.5	<1.0
Iopromide	SNWA[a]	27.5	<10	110	23	<10	<12	<10
Meprobamate	SNWA[a]	320	260	440	440	255	31	0.29
Musk Ketone	SNWA[a]	<25	<25	<25	<25	<25	<29	<25
Naproxen	SNWA[a]	<0.50	<0.50	<0.50	<0.50	<0.50	<0.58	<0.50
Octylphenol	SNWA[a]	<25	<25	<25	<25	32	<29	<25
Primidone	SNWA[a]	55	69	67	69	29.5	87	0.89
Sulfamethoxazole	SNWA[a]	1	4.5	7.8	8	<0.25	42	4.2
TCEP	SNWA[a]	655	500	580	510	730	430	<10
TCPP	SNWA[a]	3050	2100	2400	2000	2050	270	<100
Triclosan	SNWA[a]	<1.0	<1.0	6.7	<1.0	1.6	<1.2	<1.0
Trimethoprim	SNWA[a]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.29	5.1

<' lower than detection limit [a]LC-MS/MS

Table A.7. Indicator Compound Concentrations (ng/L) Observed at City of Auburndale's RIB (analytical methods denoted)

		Auburndale (March 2008)		
Analyte	Lab	RIB Basin	Down-gradient Well	Up-gradient Well
Atenolol	SNWA[a]	86	<1.0	<1.0
Atorvastatin	SNWA[a]	2.05	<0.50	<0.50
Atrazine	SNWA[a]	240	280	18.5
Benzophenone	SNWA[a]	<50	<50	<50
BHA	SNWA[a]	15	<1.0	<1.0
Bisphenol A	SNWA[a]	12.5	2300	2300
Caffeine	SNWA[a]	11	14	23
Carbamazepine	SNWA[a]	190	170	190
DEET	SNWA[a]	36	280	49.5
Diazepam	SNWA[a]	1.04	0.71	<0.25
Diclofenac	SNWA[a]	11	<0.25	<0.25
Dilantin	SNWA[a]	230	85	150
Fluoxetine	SNWA[a]	26	<0.50	<0.50
Gemfibrozil	SNWA[a]	130	<0.25	15.5
Ibuprofen	SNWA[a]	<1.0	<1.0	<1.0
Iopromide	SNWA[a]	<10	<10	<10
Meprobamate	SNWA[a]	295	2.5	66
Musk Ketone	SNWA[a]	<25	<25	<25
Naproxen	SNWA[a]	4.75	<0.50	<0.50
Octylphenol	SNWA[a]	<25	<25	<25
Primidone	SNWA[a]	160	91	115
Sulfamethoxazole	SNWA[a]	565	200	145
TCEP	SNWA[a]	215	<10	25.5
TCPP	SNWA[a]	990	350	225
Triclosan	SNWA[a]	76	2.8	12.5
Trimethoprim	SNWA[a]	16	<0.25	<0.25

<' lower than detection limit [a]LC-MS/MS

Table A.8. Indicator Compound Concentrations (ng/L) During the Operation of Orange County Water District's GWRS (analytical methods denoted)

		Campaign #1 (July 2008)			Campaign #2 (October 2008)				Campaign #3 (January 2009)			
Description	Lab	Before RO	After RO	After AOP	Before RO	After RO	After AOP	Monitoring Well M37/4	Before RO	After RO	After AOP	Monitoring Well M37/4
Atenolol	SNWA[a]	1700	2.2	<1.0	1800	4.6	<1.0	<1.0	1500	14	<1.0	<1.0
Atorvastatin	SNWA[a]	56	<0.50	<0.50	62	<0.50	<0.50	<0.50	55	<0.50	<0.50	<0.50
Atrazine	SNWA[a]	4.4	<0.25	<0.25	3.8	<0.25	<0.25	0.36	3.9	<0.25	<0.25	0.29
Benzophenone	SNWA[a]	570	<50	<50	790	94	<50	<50	610	110	<50	<50
BHA	SNWA[a]	78	<1.0	<1.0	130	<1.0	<1.0	<1.0	130	<1.0	<1.0	<1.0
Bisphenol A	SNWA[a]	480	<5.0	<5.0	180	<5.0	<5.0	32	480	<5.0	<5.0	98
Caffeine	SNWA[a]	600	<5.0	<5.0	900	<5.0	<5.0	<5.0	690	6.8	<5.0	<5.0
Carbamazepine	SNWA[a]	190	<0.50	<0.50	220	<0.50	<0.50	0.59	190	0.79	<0.50	0.67
DEET	SNWA[a]	1600	1.8	<1.0	570	1.1	<1.0	<1.0	400	1.5	<1.0	<1.0
Diazepam	SNWA[a]	2.2	<0.25	<0.25	0.87	<0.25	<0.25	<0.25	1.3	<0.25	<0.25	<0.25
Diclofenac	SNWA[a]	280	<0.25	<0.25	180	<0.25	<0.25	<0.25	190	<0.25	<0.25	<0.25
Dilantin	SNWA[a]	130	<1.0	<1.0	130	<1.0	<1.0	0.97	160	<1.0	<1.0	0.55
Fluoxetine	SNWA[a]	27	<0.50	<0.50	33	<0.50	<0.50	<0.50	27	<0.50	<0.50	<0.50
Gemfibrozil	SNWA[a]	3300	1.7	<0.25	3300	2.7	<0.25	<0.25	3800	4.6	<0.25	<0.25
Ibuprofen	SNWA[a]	700	<1.0	<1.0	1200	<1.0	<1.0	<1.0	550	1.1	<1.0	<1.0
Iopromide	SNWA[a]	160	<10	<10	130	<10	<10	<10	310	<10	<10	<10
Meprobamate	SNWA[a]	330	0.32	<0.25	330	0.32	<0.25	2.0	330	0.66	<0.25	1.0
Musk Ketone	SNWA[a]	25	<25	<25	150	<25	<25	<25	56	<25	<25	<25
Naproxen	SNWA[a]	480	0.66	<0.50	2200	2.2	<0.50	<0.50	1100	3.2	<0.50	<0.50
Octylphenol	SNWA[a]	190	<25	<25	580	<25	<25	<25	360	<25	<25	<25
Primidone	SNWA[a]	97	<0.50	<0.50	100	<0.50	<0.50	0.77	110	<0.50	<0.50	0.92
Sulfamethoxazole	SNWA[a]	1500	0.33	<0.25	1400	1.1	<0.25	0.81	1800	5.8	<0.25	0.47
TCEP	SNWA[a]	530	<10	<10	750	<10	<10	<10	320	<10	<10	<10
TCPP	SNWA[a]	4400	<100	<100	1800	<100	<100	<100	950	<100	<100	<100
Triclosan	SNWA[a]	230	<1.0	<1.0	430	5.3	<1.0	<1.0	510	29	<1.0	<1.0
Trimethoprim	SNWA[a]	610	0.38	<0.25	630	1.1	<0.25	<0.25	600	8.1	<0.25	<0.25

<' lower than detection limit

[a]LC-MS/MS

Table A.9. Trace Organic Contaminant Concentrations in the Research Basin (RB) and Subsurface Sampling Locations

Travel times noted in parentheses. Average concentrations for MLS 8 – PR 11 representative of upper aquifer.
Average values for PR 8, PR 10 representative of lower aquifer.

Compound	MRL[a]	RB	RB-dup	MRL[b]	MLS 8 (10 hrs)	WP Z (12 hrs)	MLS 14 (26 hrs)	MLS 20 (42 hrs)	PR 9 (51 hrs)	PR 11 (70 hrs)	Avg. (MLS 8-PR 11)	PR 8 (60 days)	PR 10 (60 days)	PR 10-dup (60 days)	Avg. (PR8, PR10)
Altenol	20	830	830	1	3.2	14	15	95	19	45	32±34	<MRL	<MRL	<MRL	<MRL
Atorvastatin	10	<MRL	<MRL	0.50	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Atrazine	5.0	<MRL	<MRL	0.25	5.5	5.8	5.4	5.1	5.1	5.2	5±0.2	4	3.9	4.1	4.0 ± 0.1
Benzophenone	1000	<MRL	<MRL	50	67	<MRL	<MRL	68	120	55	68±27	<MRL	<MRL	<MRL	<MRL
Caffeine	100	<MRL	<MRL	5.0	<MRL	17	<MRL	<MRL	5.8	<MRL	7±5	<MRL	<MRL	<MRL	<MRL
Carbamazepine	10	330	340	5.0	280	330	320	280	270	330	302±28	170	170	170	170 ± 0
DEET	20	320	310	10	130	230	260	300	280	230	238±60	36	57	56	50 ± 12
Diazepam	5.0	<MRL	<MRL	0.25	2.1	2.4	2.6	2.5	2.9	2.4	2±0.3	1.2	1.6	1.8	1.5 ± 0.3
Dilantin	20	150	170	1.0	130	100	99	94	97	98	103±13	94	78	84	85 ± 8
Fluoextine	10	13	17	0.50	<MRL	0.89	<MRL	<MRL	<MRL	<MRL	0.57±0.16	<MRL	<MRL	<MRL	<MRL
Iopromide	200	2700	3100	10	25	84	20	130	44	59	60±41	110	77	81	89 ± 18
Meprobamate	5.0	430	42	2.5	300	360	400	420	360	410	375±45	97	150	150	132 ± 31
Primidone	10	150	160	5.0	140	180	120	220	130	220	168±45	92	91	87	90 ± 2.6
Sulfamethoxazole	5.0	460	440	2.5	180	390	330	550	490	400	390±129	220	200	200	207 ± 12
TCEP	200	400	400	10	390	410	400	420	410	380	402±15	83	150	150	128 ± 39
TCPP	2000	7200	7300	1000	6000	7000	6700	7800	6100	5300	6,483±875	580	910	900	797 ± 188
Trimethroprim	5.0	54	54	0.25	29	26	83	99	29	81	58±33	6.5	1.9	2.1	3.5 ± 2.6
BHA	1.0	<MRL	<MRL	1.0	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Bisphenol-A	5.0	<MRL	<MRL	5.0	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Diclofenac	0.50	24	20	0.50	7	9.8	9.7	10	13	9.5	10±2	<MRL	<MRL	<MRL	<MRL
Gemfibrozil	5.0	880	900	0.25	6.3	28	20	130	75	160	70±63	35	30	30	32 ± 2.9
Ibuprofen[c]	1.0	10	11	1.0	6.3	10	1.7	6.1	4.6	4.8	12±8	<MRL	1.3	1.3	1.3 ± 0
Musk Ketone	25	<MRL	<MRL	25	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Naproxen	0.50	32	32	0.50	1.9	8.2	5.3	23	12	20	6±3	2.4	2.4	2.4	2.4 ± 0
Octylyphenol	25	<MRL	<MRL	25	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Triclosan[d]	1.0	6.5	8.2	1.0	1.6	8.4	7.1	8.9	2.9	9.1	6±3	<MRL	<MRL	<MRL	<MRL

[a]Minimum reporting level for research basin.
[b]Minimum reporting level for subsurface.
[c]Detected in travel blank at 3.1 ng/L
[d]Detected in travel blank at 1.3 ng

Advancing the Science of Water Reuse and Desalination

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