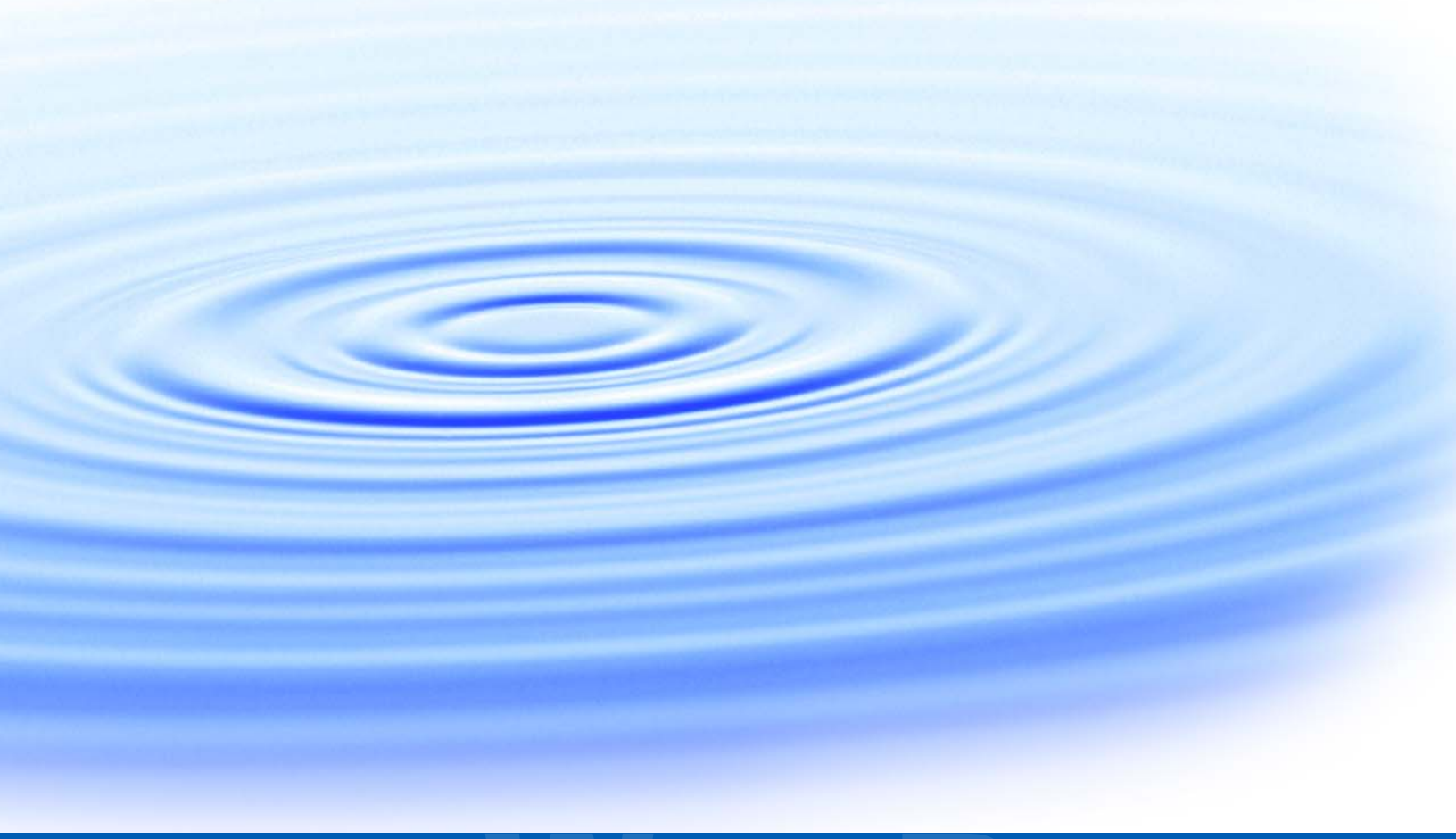
WATEREUSE FOUNDATION

# Development of Indicators and Surrogates for Chemical Contaminant Removal during Wastewater Treatment and Reclamation



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

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The Foundation's funding partners include the U.S. Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations. The Foundation also conducts research in cooperation with the Global Water Research Coalition.

# Development of Indicators and Surrogates for Chemical Contaminant Removal during Wastewater Treatment and Reclamation

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# EXECUTIVE SUMMARY

## PROJECT BACKGROUND AND OBJECTIVES

This research was performed by a team of faculty, scientists, and graduate students from the Colorado School of Mines, the University of California–Berkeley, and the Southern Nevada Water Authority. It was funded by the WateReuse Foundation, the Water Environment Research Foundation, the Bureau of Reclamation, and the California State Water Resources Control Board.

The recent detection of a variety of chemicals in municipal wastewater effluent has raised concerns about the potential presence of wastewater-derived chemical contaminants in water produced by indirect-potable-reuse systems. Regulatory agencies and utilities have struggled with this issue because the wastewater-derived chemicals often are present at extremely low concentrations and because no standardized analytical methods are available. For the majority of the compounds, it is difficult to assess human health or ecological risks associated with indirect potable reuse because chemical and toxicological data for the hundreds of compounds potentially present in recycled 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 indirect-potable-reuse systems has evolved that assumes that certain bulk measurements and 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. This approach may be a reasonable way to circumvent the significant costs associated with analysis of all of the possible chemicals of concern if the analytes monitored are good predictors of the contaminants of concern. However, this proposition has never been tested.

The objectives of this project were (a) to identify surrogate parameters and indicator compounds for wastewater-derived chemical contaminants that might be useful in the assessment of indirect-potable-reuse systems, (b) to identify and assess the performance of analytical methods for the chosen surrogates and indicators, and (c) to validate the ability of chosen surrogates and indicators to predict the occurrence and removal of wastewater-derived contaminants in indirect-potable-reuse systems.

## THE CONCEPT OF INDICATORS AND SURROGATES

The approach for monitoring wastewater-derived contaminants developed in this study is utilizing a combination of surrogate parameters and indicator compounds tailored to monitor the removal efficiency of individual unit processes comprising an overall treatment train. In the context of this study, an indicator compound is an individual chemical occurring at quantifiable level, which represents certain physicochemical and biodegradable characteristics of a family of trace organic constituents that are relevant to fate and transport during treatment, providing a conservative assessment of removal. A surrogate parameter is a quantifiable change of a bulk parameter that can serve as a measure of the performance of individual unit processes or operations in removing trace organic compounds. This approach

utilizes only a limited set of analytes for the evaluation of indirect potable reuse. The approach proposed to select viable indicator compounds is primarily driven 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 compound in various treatment processes. 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 compounds with similar properties. 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 the indicator compound, while normal operating conditions will be indicated by partial or complete compound removal. Predetermined changes of surrogate parameters can be utilized to define and ensure normal operating conditions of a treatment process.

Indicator compounds and surrogate parameters identified were classified into categories of different treatability (Chapter 5). These treatment categories include conventional and advanced water treatment processes commonly employed in indirect-potable-reuse applications. The treatment processes are characterized by key removal mechanisms such as biodegradation (i.e., soil-aquifer treatment [SAT]), chemical oxidation (i.e., ozonation, advanced oxidation, chlorination, and chloramination), photolysis (i.e., low-pressure UV radiation), adsorption (i.e, granular activated carbon [GAC]), or physical separation (i.e., nanofiltration and reverse osmosis). Data currently available on the efficacy of different treatment systems operating under certain conditions in removing individual compounds are limited and imprecise. The properties and occurrence levels of organic micropollutants occurring at the nanograms-per-liter (ng/L) level vary widely, and different analytical methods are required for their quantification (Chapter 3). While multiple methods have been developed and employed during the last 10 years for the detection of these compounds, none of these methods currently are standardized. Interlaboratory comparisons among experienced analytical laboratories conducted during this study revealed that analytical methods targeted for multicomponent analysis exhibited significant variations of recovery and relative standard deviations (RSDs), indicating the degree of uncertainty that is still associated with reporting low ppt-level concentrations. Instead of relying on absolute numbers or threshold levels as a treatment goal or performance measure, we decided to group potential indicator compounds into four removal categories: "good removal (>90%)," "intermediate removal ($90\% < x < 50\%$ and $50\% < x < 25\%$)," and "poor removal (<25%)." This classification of indicators into removal categories of individual unit processes is dependent upon the physicochemical and biodegradable properties of the compounds. Whether the proposed degree of removal is achieved will depend upon operational conditions of the treatment process (e.g., oxidant dose concentration, type of activated carbon, water matrix, and contact time). Along with this classification, relevant operational boundary conditions were defined for each type of treatment.

For each treatment process, a master list of indicator compounds was provided by recruiting compounds, for which analytical methods existed, from the final list of viable indicator compounds present in secondary- or tertiary-treated wastewater effluents (Chapter 4). This list was compiled through a comprehensive literature review of over 100 peer-reviewed journal articles and an internal occurrence survey drawing upon yet-to-be-published findings

and ongoing projects among the three principal investigators. The developed treatment removal categories for indicator compounds of each treatment process of interest (i.e., SAT, ozone, advanced oxidation, chlorination, carbon adsorption, and reverse osmosis) was validated through laboratory-, pilot-, and full-scale experiments (Chapter 5). Findings of these studies confirmed the classification of indicator compounds into the different removal categories. As expected, results of these efforts also revealed that surrogate parameters are not strongly correlated with the removal of indicator compounds occurring at nanograms-per-liter concentrations. Partial or complete change of select surrogate parameters, however, can demonstrate the proper operation of a unit operation or treatment train. Certain surrogate parameters were also sensitive enough to pick up beginning performance deficiencies, which might be or might not be resulting in a diminished removal of wastewater-derived contaminants in that treatment process. Thus, to fully access the performance of unit operations in removing wastewater-derived contaminants, a combination of appropriate surrogate parameters and indicator compounds should be used (Chapter 7). This framework is a conservative approach designed to detect the failures of systems to block wastewater-derived contaminants. Adopting the treatment-category framework can also help engineers more properly tailor multiple barriers of treatment processes that have a demonstrated ability to remove wastewater-derived contaminants in indirect-potable-reuse applications.

# CHAPTER 1

# INTRODUCTION

## 1.1 BACKGROUND

An increasing number of utilities are currently obtaining drinking water from source waters under the influence of agricultural runoff, urban stormwater runoff, and/or discharges from municipal wastewater treatment facilities. Faced with increasing water demand and lack of alternative sources, utilities have new incentive to reuse treated municipal wastewater effluent to augment drinking water supplies. In the United States, potable water reuse usually involves the indirect reuse of wastewater effluent after it undergoes infiltration through the vadose zone or direct injection into aquifers. 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 (NRC, 1998), whereas groundwater injection projects usually employ secondary or tertiary treatment followed by microfiltration (MF) and reverse osmosis (RO) (Alexander et al., 2002; Freeman et al., 2002; Drewes et al., 2003a). The recent detection of a variety of chemicals in municipal wastewater effluent has raised concerns about the potential presence of wastewater-derived chemical contaminants in water produced by indirect potable reuse systems. Regulatory agencies and utilities have struggled with this issue because the wastewater-derived chemicals often are present at extremely low concentrations and because no standardized analytical methods are available. In only a few cases have specific compounds been detected at concentrations that pose potential risks to drinking water supplies (CDPH, 2007a) or to aquatic ecosystems (Jobling et al., 1998; Kelce and Wilson, 1997). For the majority of the compounds, it is difficult to assess human health or ecological risks associated with indirect potable reuse because chemical and toxicological data for the hundreds of compounds potentially present in recycled water are lacking and because 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 continual 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.

Concerns about chemical contaminants are not limited to planned indirect-potable-reuse projects. While the traditional maxim for selecting drinking water supplies has been to use the highest-quality source available (Pontius, 2003), many once-pristine river water sources evolved over time into unintentional indirect potable reuse systems, as wastewater from upstream dischargers increased to substantial portions of the stream flow (WEF/AWWA, 1998). The presence of chemical contaminants in these unplanned indirect potable reuse systems is now a concern to utilities and regulators interested in source water protection.

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. For enteric pathogens, monitoring of indicator organisms (e.g., total and fecal coliforms and bacterial viruses) is accepted as a means of assessing pathogen removal (Pontius, 2003; CDPH, 2007b). However, a similar suite of monitoring parameters for chemical contaminants has not been developed.

Traditional water quality methods of measuring bulk organic matter in wastewater, such as measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), or total organic halogen (TOX), continue to be used in monitoring programs, even though their ability to serve as surrogates for chemical contaminants of concern has never been demonstrated. To develop monitoring programs that can be used to assess the performance of indirect potable reuse systems in sufficiently removing wastewater-derived contaminants, the utility of these water quality parameters must be assessed along with other simple-to-measure indicators of wastewater-derived contaminants.

### 1.1.1 Regulatory Framework for Wastewater-Derived Contaminants

In the United States, there are no federal regulations that specifically address potable reuse. The U.S. Environmental Protection Agency (EPA) has published a guidance document on water reuse (U.S. EPA, 2004). However, the document has no regulatory authority and does not make specific recommendations with respect to chemical contaminants.

The majority of "wastewater-derived contaminants" are not regulated in the United States. Moreover, a comprehensive list of "emerging contaminants" is not feasible. For instance, endocrine disrupting compounds (EDCs) are a vast group of chemicals that have a toxicological impact and are not simply a list of chemicals. In fact, endocrine disruption was not specifically named in any U.S. legislation until 1995 with amendments to the Safe Drinking Water Act (bill number S.1316) and Food Quality Protection Act (bill number P.L. 104-170) mandating that chemicals and formulations be screened for potential endocrine activity before they are manufactured or used in certain processes where drinking water and/or food could become contaminated. Under these laws, the EPA is required to "develop a screening program, using appropriate validated test systems and other scientifically relevant information, to determine whether certain substances may have an effect in humans that is similar to an effect produced by a naturally occurring estrogen, or other such endocrine effect as the Administrator may designate." Furthermore, these laws specified that the EPA develop a testing program by 1998, implement the program by 1999, and report to Congress by 2000. This timeline was significantly delayed; therefore, a comprehensive list of EDCs is not possible at this time.

To meet the requirements of this recent legislation, the EPA formed the Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) to provide recommendations on a conceptual framework, priority setting, screening and testing methodologies, and communication and outreach programs. The EDSTAC group consisted of various stakeholders and experts in reproductive toxicology. The committee began deliberations in October 1996 and issued a final report in July 1998 recommending that human and wildlife impacts be considered and that estrogen, androgen, and thyroid (EAT) endpoints be examined (U.S. EPA, 1998). The conceptual framework devised by EDSTAC consists of an initial sorting, prioritization, Tier 1 and 2 testing, and a hazard assessment of an estimated 87,000 chemicals. In addition to discrete chemicals, EDSTAC recommended the evaluation of mixtures of chemicals in breast milk, baby formulas, hazardous waste sites, pesticides and fertilizers, drinking water disinfection by-products (DBPs), and gasoline. The outcome of this screening battery is critical to the water industry, as it is designed to definitively identify EDCs. However, it is important that the current legislation regulates only the industries producing or using raw chemicals but not the water industry. As a result, these actions may have little immediate effect on water and wastewater treatment regulations.

There are currently no federal regulations for pharmaceuticals in drinking or natural waters. The U.S. Food and Drug Administration (FDA) requires ecological testing and evaluation of a pharmaceutical only if an environmental concentration in water or soil is expected to exceed 1 mg/L or 100 μg/kg, respectively (FDA, 1998). In light of the recent data on the occurrence of PPCPs in the aquatic environment, these policies may need to be reconsidered. While extensive monitoring programs are underway, toxicological studies conducted at environmentally relevant concentrations are necessary for intelligible regulations to be established.

While no federal legislation specifically regulates EDCs and pharmaceutical residues in drinking or wastewater, individual states may regulate these compounds in the absence of any federal mandates. Among the states, California and Florida have made the most progress in establishing uniform approaches for assessing planned indirect potable reuse and often serve as examples for regulators in other states. Therefore, it is appropriate to consider their regulations in more detail.

#### *1.1.1.1 State of California*

In the late 1980s, the California Department of Public Health (CDPH), formerly known as California Department of Health Services (CalDHS), 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 have never been approved or finalized. The CDPH draft groundwater recharge criteria are designed to ensure a groundwater supply that meets all the drinking water standards and other requirements more specific to water derived from wastewater effluent (CDPH, 2007b). 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 organics (Geselbracht and Crook, 2000). After receiving the final report prepared by a science advisory panel (SAP) submitted to the state in 1987, CDPH selected 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 DOC 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, 2007b) 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). The current draft regulations require that subsurface injection projects produce water with TOC of wastewater origin less than or equal to 0.5 mg/L at the point where the recycled water (with or without dilution water) mixes with native groundwater. Subsurface injection projects are required to treat 100% of the reclaimed water by RO to provide sufficient removal of organics and must meet the TOC limit at the point of injection. If the RWC exceeds 50%, 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 recycled 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 wastewater-derived contaminants, CDPH also included additional monitoring requirements in the 2003 draft criteria (CDPH, 2003). The new criteria require regular monitoring of specific wastewater-derived chemical contaminants (Table 1.1) including chemicals with a State Action Level and a suite of EDCs, pharmaceuticals, and personal care products for which action levels have not been established. The list of compounds was based upon expert judgment, public perception, and available data. The inclusion of compounds for which no action level had been established was controversial among water professionals because the basis for the selection criteria was unclear and because little guidance was presented on analytical methods or detection limits required. CDPH has indicated that monitoring for all of the EDCs, pharmaceuticals, and personal care products listed in the draft regulations will not be required and that compounds likely will be selected for monitoring on a case-by-case basis.

**Table 1.1. Monitoring Requirements for Wastewater-Derived Contaminants Included in the Current CDPH Draft Criteria**[a]

| Compound | Classification | Compound | Classification |
|---|---|---|---|
| *n*-Butylbenzene | Industrial chemical | Nonylphenol | Endocrine |
| Sec-butylbenzene | Industrial chemical | APECs | Endocrine |
| Tert-butylbenzene | Industrial chemical | PBDEs | Endocrine |
| Carbon disulfide | Insecticide | Acetaminophen | Pharmaceutical |
| Chlorate | Industrial chemical, | Amoxicillin | Pharmaceutical |
| 2-Chlorotoluene | Solvent, chemical | Azithromycin | Pharmaceutical |
| Diazinon | Insecticide | Caffeine | Stimulant |
| 1,4-Dioxane | Industrial chemical | Carbamazepine | Pharmaceutical |
| Formaldehyde | Industrial chemical | Ciprofloxacin | Pharmaceutical |
| Isopropylbenzene | Industrial chemical, solvent | Ethylenediamine tetra-acetic acid | Surfactant |
| *n*-Propylbenzene | Solvent | Gemfibrozil | Pharmaceutical |
| 1,2,4-Trimethylbenzene | Petroleum product | Ibuprofen | Pharmaceutical |
| 1,3,5-Trimethylbenzene | Petroleum product | Iodinated contrast agents | Pharmaceutical |
| N-nitrosodimethlyamine | DBP | Lipitor | Pharmaceutical |
| N-nitrosodiethylamine | DBP | Methadone | Pharmaceutical |
| *N*-Nitrosopyrolidine | DBP | Morphine | Pharmaceutical |
| 17β-Estradiol | Endocrine disruptor | Salicylic acid | Pharmaceutical |
| 17α-Ethynylestradiol | Endocrine disruptor | Triclosan | Pharmaceutical |
| Estrone | Endocrine disruptor | | |
| Bisphenol A | Endocrine disruptor | | |

[a]Adopted from CDPH, 2007b.

#### *1.1.1.2 State of Florida*

Florida's water reuse regulations (Florida Department of Environmental Protection, 1999) include sections addressing high-rate infiltration basin systems and soil-absorption field systems, both of which may result in groundwater recharge. Because nearly all groundwater in Florida is

classified as G-II, which is defined as groundwater containing 10,000 mg or less of total dissolved solids (TDS)/L and is designated as a potable supply source, any land application system located over G-II groundwater could function as an indirect potable reuse system. If more than 50% of the wastewater applied to the system is collected after percolation, the system is classified as an effluent disposal system and not as beneficial reuse. Loading to these systems is limited to 9 in./day, and wetting and drying cycles must be used. For systems having higher loading rates or a more direct connection to an aquifer than is normally encountered, the reclaimed water must receive secondary treatment, filtration, and high-level disinfection (no detectable fecal coliforms per 100 mL in at least 75% of the samples analyzed over a 30-day period, maximum of 25 fecal coliforms/100 mL in any sample, total-suspended-solid limit of 5.0 mg/L, and a minimum total chlorine residual of 1.0 mg/L after at least 15 min of contact at peak hour flow) and must meet primary and secondary drinking water standards. These reclaimed water treatment and quality rules are similar to those in the California regulations for surface spreading of reclaimed water (CDPH, 2007b).

The Florida regulations also include criteria directed at planned indirect potable reuse by injection into water supply aquifers and augmentation of surface supplies. The injection regulations pertain to G-I, G-II, and F-I groundwaters, all of which are classified as potable aquifers. Secondary treatment, filtration, and high-level disinfection are required. Reclaimed water must meet G-II groundwater standards prior to injection. G-II groundwater standards are very similar to primary and secondary drinking water standards. For injection into formations of the Floridan and Biscayne aquifers where the concentration of TDS does not exceed 500 mg/L, the regulations are more restrictive and specify that reclaimed water must meet drinking water standards, undergo activated carbon adsorption as an organic removal process, and meet average TOC and TOX limits of 5.0 mg/L and 0.2 mg/L, respectively, in the product water.

### 1.1.2 Previous Use of Surrogates and Indicators in Monitoring Programs

The approach for monitoring wastewater-derived contaminants that was adopted by CDPH in the 2007 draft guidelines (CDPH, 2007b) inherently assumes that TOC and a limited list of wastewater-derived contaminants can be used to assess the removal of all of the wastewater-derived contaminants of concern. This approach may be a reasonable way to circumvent the significant costs associated with analysis of all of the possible chemicals of concern if the analytes monitored are good predictors of the contaminants of concern. However, this proposition has never been tested. Advanced treatment technologies (such as ozonation, activated carbon adsorption, membranes, and SAT) commonly employed in surface and subsurface spreading operations as well as surface water augmentation projects differ in their predominant removal mechanism (such as chemical oxidation, physical adsorption, and physical separation versus biotransformation). It has been demonstrated that the fate and transport of wastewater-derived contaminants are correlated with the type of unit operation employed and depend upon both physicochemical properties and biodegradability of the contaminant (Chang et al., 2002; Snyder et al., 2003a; Drewes et al., 2003b; Bellona et al., 2004). Therefore, one limited set of analytes may not be appropriate for the evaluation of all of the possible combinations of unit processes.

While 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., 2001b). Different approaches have been proposed to distinguish between naturally and wastewater-derived organics 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., 2006). While these methods are promising and provide more insight into the origin of organic matter, they are often semiquantitative and require a significant degree of expertise for proper assessment.

There are several approaches that can be used to evaluate the presence of chemical contaminants in indirect potable reuse systems. Each approach has advantages and disadvantages that must be considered when designing a monitoring scheme. The approaches that are appropriate for monitoring of chemical contaminants are defined below:

- *Monitoring of surrogates for wastewater-derived chemical contaminants of concern:* The use of TOC or another bulk parameter as a substitute for wastewater-derived contaminants is referred to in this report as the use of a surrogate. This approach has been criticized because, as described above, the removal of a bulk parameter may not always be correlated with removal of wastewater-derived contaminants. 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 DOC (BDOC) in conjunction with DOC could serve as an indicator of the presence of organic compounds that are not derived from humic substances. Conversely, integrity measures for membrane applications, such as conductivity and turbidity, could serve as a surrogate for system performance. The main advantage of bulk chemical parameters is that they are more easily measured than are chemical contaminants and in some cases could be included as online monitoring devices.

- *Monitoring of indicators for wastewater-derived chemical contaminants of concern:* Direct measurement of a limited number of wastewater-derived contaminants is referred to in this report as the use of indicators. Indicator wastewater-derived chemical contaminants would most likely include those compounds that occur at relatively high concentrations in wastewater effluent and can be analyzed with instruments that are available in commercial and utility laboratories. Although standard analytical methods are not available for many potential indicators, some of the compounds can be analyzed by adaptation and modification of standard methods that have been used for pesticides and other organic contaminants. The main advantage of this approach is that it limits the expenses associated with monitoring and allows for comparison of system performance among indirect-potable-reuse projects. The main disadvantages associated with this approach are the possibility that certain compounds of interest may not be removed as easily as the indicators and that the less sophisticated methods usually have higher detection limits and are limited to compounds with certain physicochemical properties.

- *Direct measurement of all or most of the wastewater-derived chemical contaminants of concern*: Approximately 100 to 200 different wastewater-derived chemical contaminants have been detected in municipal wastewater effluent by using state-of-the-art analytical techniques such as high-performance liquid chromatography/tandem mass spectrometry (HPLC-MS/MS) and gas chromatography/tandem mass spectrometry (GC-MS/MS). The instruments used for these analyses typically are not available in commercial or utility laboratories. Therefore, including these compounds in a routine monitoring program

would require the development of standard methods and a significant investment of resources on the part of commercial or utility laboratories. This approach has the highest degree of reliability and the highest expense. However, this approach may not be protective of newly developed and introduced synthetic organic compounds.

Ultimately, the monitoring system adopted may include a combination of the three approaches listed above 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 system testing followed by annual monitoring of indicators and weekly measurement of surrogates. The ultimate goal is that monitoring by using a combination of indicator and surrogate parameters will ensure the absence of unknown and potentially harmful contaminants, thus ensuring the safety of a proposed project.

Evaluation of the relative merits of these different monitoring approaches cannot be made without additional research. The purpose of this project was to provide water utilities, regulators, and engineers with guidance on monitoring requirements for wastewater-derived organic contaminants in a variety of source waters, including highly engineered indirect potable reuse systems and surface waters that are subjected to wastewater effluent discharges.

## 1.2 OBJECTIVES

The objectives of this project were (a) to identify surrogates and indicators for wastewater-derived chemical contaminants that might be useful in the assessment of indirect potable reuse systems, (b) to identify and assess the performance of analytical methods for the chosen surrogates and indicators, and, (c) to validate the ability of chosen surrogates and indicators to predict the occurrence and removal of wastewater-derived contaminants in indirect potable reuse systems. The proposed project consisted of three major phases. The research was initiated with a comprehensive literature review to summarize available surrogates and indicators. The second phase of the project consisted of 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 or facilities located in different regions of the continental 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.

This study was conducted by a team of students, faculty, and research scientists of the Colorado School of Mines (CSM), the University of California–Berkeley (UC), and the Southern Nevada Water Authority (SNWA), with support by the staff of participating utilities and consulting scientists and engineers. In addition, a Stakeholder Advisory Committee provided additional oversight and input on issues relevant to the development of regulations and monitoring programs to meet the needs of the water industry.

# CHAPTER 2

# PROJECT APPROACH

## 2.1 THE CONCEPT OF TREATMENT CATEGORIES

Engineered treatment systems applied in indirect-potable-reuse projects, which can be used to control wastewater-derived chemical contaminants, employ physical, chemical, and biological processes to remove or transform the compounds. Previously published research on the mechanisms through which treatment processes act suggests that the extent of removal can be predicted for compounds exhibiting similar properties, provided that those properties determine the behavior of the compound in the treatment process (Chang et al., 2002; Snyder et al., 2003a; Drewes et al., 2003b; Bellona et al., 2004). These similarities in the behavior of wastewater-derived contaminants in treatment systems as well as the relationship between the removal of wastewater-derived contaminants and readily accessible parameters may provide a basis for simplifying the evaluation and monitoring of engineered treatment systems' ability to remove trace organic compounds.

The compounds most sensitive in assessing 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 the indicator compound, while normal operating conditions will be indicated by partial or complete compound removal. If an indicator compound that is easily removed by the treatment system is chosen, the indicator will be less sensitive to partial failure, whereas the selection of an indicator that is poorly removed under normal operating conditions will provide little insight into system performance under any conditions. Because data on the efficacy of different treatment systems regarding the removal of individual compounds are limited and imprecise, we decided to rank potential indicator compounds in four removal categories: "good removal (>90%)," "intermediate removal (25% < x < 50%)" and "intermediate removal (50% < x < 90%)," and "poor removal (<25%)." This grouping was determined for individual treatment processes that are characterized by a predominant removal mechanism. Because this study was tailored toward performance monitoring of indirect potable reuse systems, only conventional and advanced treatment processes going beyond secondary/tertiary wastewater treatment processes were considered in this project. However, this grouping can be developed for any other unit operation as well. The processes selected include biological treatment (i.e., SAT and membrane bioreactors [MBRs]), chemical oxidation (i.e., chlorination, chloramination, ozonation, and AOPs), photolysis (i.e., UV radiation), and adsorption (i.e., powdered activated carbon [PAC] and granular activated carbon [GAC]), as well as physical separation (i.e., RO and nanofiltration [NF]). The treatment processes of interest are summarized in Table 2.1.

**Table 2.1. Treatment Categories for Treatment Processes of Interest**

| Predominant Removal Mechanisms | Treatment Processes |
|---|---|
| Biodegradation | SAT; riverbank filtration; aquifer storage and recovery; MBR |
| Chemical oxidation | Ozone; advanced oxidation; chlorine; chloramination |
| Photolysis | Low- and medium-pressure UV radiation |
| Adsorption | GAC and PAC adsorption |
| Physical separation | NF; RO |

The selection of viable indicator compounds occurring in secondary- or tertiary-treated wastewater effluents is documented in Chapter 4, whereas the grouping and ranking of indicator compounds in individual treatment and removal categories for individual unit processes are described in Chapter 5.

Traditionally, the treatment performance of a unit process or operation is assessed by measuring the partial or complete removal of a bulk parameter, e.g., BOD, turbidity, conductivity, or nitrate. Therefore, measurements of bulk or operational parameters might serve as surrogates to assess the efficiency of individual unit operations to remove or transform wastewater-derived contaminants, provided the removal of bulk or operational parameters is correlated to the removal of trace organics. While bulk parameters can be more easily measured by using standardized methods than by using indicator compounds occurring at the nanograms-per-liter level, some of these parameters might not necessarily be sensitive enough to pick up a partial system failure resulting in a reduced removal of wastewater-derived contaminants. Thus, this research study investigated the suitability of a wide range of bulk measurements or surrogate parameters to assess process performance and failure. Potentially suitable surrogate parameters considered in this study are described in Chapter 3. Since surrogate parameters also exhibit different degrees of removal or transformation by individual unit processes, similar to degrees displayed by wastewater-derived contaminants, these parameters were also grouped into different treatment categories to develop relationships between the efficiency of removal of indicator compounds and efficiency of removal of surrogate parameters. This surrogate and indicator framework was validated through performance-monitoring efforts using laboratory-, pilot-, and full-scale facilities. Findings from this phase of the study are presented in Chapter 5.

## 2.2 DEFINITIONS

In order to meet the requirements for serving as an indicator compound, a wastewater-derived contaminant has physicochemical and/or biodegradable properties that are representative for a broader class of compounds, has to occur at concentrations that are both representative of environmental concentrations of the broader class of compounds and high enough to determine a meaningful degree of reduction through a unit process or a sequence of processes, has fate and transport characteristics that can be linked to a predominant removal mechanism (e.g., biodegradation and oxidation) allowing to group this compound into a treatment removal category, and is quantifiable with a peer-reviewed analytical method. Suitable surrogate parameters in this sense are commonly available or emerging bulk measurements that are sensitive enough to provide a quantifiable measurement differential that is related to the removal of wastewater-derived contaminants. In the context of this study,

we offer the following definitions for indicator compounds for wastewater-derived contaminants and surrogate parameters.

### 2.2.1 Definitions of Indicator Compounds and Surrogate Parameter

#### *2.2.1.1 Indicator Compounds*

An indicator compound is an individual chemical occurring at a quantifiable level that represents certain physicochemical and biodegradable characteristics of a family of trace organic constituents that are relevant to fate and transport during treatment. It provides a conservative assessment of removal.

#### *2.2.1.2 Surrogate Parameter*

A surrogate parameter is a quantifiable change of a bulk parameter that can measure the performance of individual unit processes or operations in removing trace organic compounds.

## 2.3 FIELD SITES AND SAMPLING STRATEGIES

Field investigations for this study were carried out at 11 participating water reclamation facilities located in six different states within the continental United States operating 12 wastewater treatment plants. These facilities represent a wide range of capacities and operations such as secondary treatment (i.e., partly nitrifying, nitrifying/denitrifying, and chemical phosphorus removal), rapid-sand filtration, ultrafiltration, MBRs, disinfection (i.e., chlorine, chloramination, UV, and ozone), constructed wetlands, high-rate infiltration basins, SAT, and integrated membrane systems (IMSs) (i.e., MF followed by RO), as well as different applications leading to indirect potable reuse (i.e., surface spreading, direct injection, and surface water augmentation). During the initial phase of the study, the research team conducted a survey at all participating utilities to determine unit processes and operations employed, process parameters, water qualities, and service area characteristics for each individual wastewater treatment plant participating in this study. The survey represented the basis for selecting field sites, unit operations, and logistics for full-scale sampling. Table 2.2 summarizes the treatment specifics and sampling locations of each plant selected for this study. The participating utilities assisted with sampling logistics and provided operational information and data for the time of sampling.

### 2.3.1 Sampling Collection and Handling

#### *2.3.1.1 Sampling Equipment*

Each facility was instructed to follow sampling guidelines provided by the research team. Efforts were made to reduce if not eliminate the use of plastics during the sampling process because they can either cause adsorptive losses of target compounds or leak compounds targeted in the study into the sample. Only glass or metal collection containers were used during sample collections, and if plastic tubing was employed, it was well conditioned. Also, efforts were made to minimize caffeine contamination as caffeinated products were not consumed during sample collections. Sampling bottles were precleaned, contained the appropriate preservative or quenching agent if needed, and were provided by the individual utility, CSM, SNWA, and UC laboratory facilities.

#### *2.3.1.2 Sample Collection*

Synoptic samples were collected as composites over a short period (2 to 4 h) or as grabs prior to a unit process and by considering the hydraulic retention time after the particular treatment process. Prior to sampling, the proper operation of the plant was confirmed by operational parameters provided by the facility during the initial survey. Care was also taken not to sample the facilities within 48 h following rain. Samples were collected by using existing dedicated facility autosamplers employed for quality and compliance purposes or were collected manually. Autosamplers were set up to collect time-based samples over a 2- to 4-h period. Samples were collected directly in a single, large 20-L glass container. The participating utility assisted with sampling logistics and provided operational information (e.g., flow, BOD loading, and solid and hydraulic retention times) and operational data for the time of sampling (e.g., pH, total suspended solids, mixed liquor total suspended solids, COD or BOD, ammonia, and nitrate).

**Table 2.2. Treatment Specifics and Sampling Locations at Full-Scale Facilities**

| Facility | Type of Reuse | Capacity | Treatment Train | Sampling Locations: Unit Processes | Sampling Locations: Receiving Streams |
|---|---|---|---|---|---|
| Facility 1 | Plant 1a: Surface spreading | 15 mgd 57 ML/day | Primary,[a] secondary[b] (nitrifying/ denitrifying), tertiary filtration, disinfection (chlorine), surface spreading | Tertiary effluent Spreading basin Monitoring wells | — |
| | Plant 1b: Pilot MBR (ZeeWeed™ 500c) | 25 gpm 95 L/min | Primary,[a] MBR | Primary effluent After MBR | — |
| Facility 2 | Plant 2: Stream flow augmentation | 88.5 mgd 335 ML/day | Primary,[a] secondary[b] (partly nitrifying/denitrifying), tertiary filtration, disinfection (UV) | Tertiary effluent After UV | — |
| Facility 3 | Plant 3: Provision of feed to Plant 4 | | Primary,[a] secondary[b] treatment | Secondary effluent prior to MF | — |
| Facility 4 | Plant 4: Direct injection | 6 mgd 23 ML/day | Feed from Plant 3, disinfection (chloramine), MF, RO, UV/$H_2O_2$, direct injection | After MF After RO After AOP | — |
| Facility 5 | Plant 5: Surface water augmentation | 20 mgd 76 ML/day | Primary,[a] secondary[b] (nitrifying), chemical P-removal, tertiary filtration/ultrafiltration, pre-ozonation, GAC, disinfection (ozone) | Secondary effluent After ultrafiltration After pre-ozone After BAC After ozone | — |
| Facility 6 | Plant 6: Stream flow augmentation | 21 mgd 79 ML/day | Primary,[a] secondary[b] (partly nitrifying/denitrifying), tertiary filtration, disinfection (chloramine) | Tertiary effluent After chloramination | — |
| Facility 7 | Plant 7: Surface spreading | 40 mgd 151 ML/day | Primary,[a] secondary[b] (partly nitrifying), disinfection (chloramine), surface spreading | Secondary effluent After chloramination Spreading basin Monitoring wells | Discharge (after chloramination) River/ riverbank wells |
| Facility 8 | Plant 8: Direct injection | 14 mgd 53 ML/day | Primary,[a] secondary,[b] tertiary treatment, disinfection (chloramine), MF, RO, direct injection | Tertiary effluent After chloramination After MF After RO Monitoring wells | — |
| Facility 9 | Plant 9: Surface spreading | 2.5 mgd 9.5 ML/day | Primary,[a] secondary[b] (partly nitrifying/denitrifying), disinfection (chloramine), rapid infiltration basin | Secondary effluent After chloramination Monitoring wells | — |
| Facility 10 | Plant 10: Surface spreading | 5 mgd 19 ML/day | MBR, disinfection (UV), spreading basins, RO, UV/$H_2O_2$ | Before MBR After MBR After UV Prior and after RO | — |
| Facility 11 | Plant 11: Surface water augmentation | 120 mgd 454 ML/day | Primary,[a] secondary[b] (partly nitrifying/denitrifying) disinfection (chlorine) | — | River |

[a]Primary treatment: mechanical treatment.

[b]Secondary treatment: biological treatment, usually by activated sludge (Facility 7 is employing trickling filters).

BAC – biologically-active carbon filtration

ML/day – Million liters per day; mgd – million gallons per day

#### *2.3.1.3 Shipment and Storage*

Once the samples were collected, they were split on site and, if needed, shipped overnight to SNWA, UC, and CSM in ice-packed coolers. Upon arrival, samples were logged and stored at 4 °C pending further analysis. For GC/MS, GC/MS-MS, and LC/MS-MS analyses, samples were extracted within 2 weeks. The extracts were stored at 4 °C until analyses of extracts were completed. Field and laboratory blanks were processed like field samples.

## 2.4 LABORATORY- AND PILOT-SCALE UNIT OPERATIONS

In addition to full-scale evaluations of individual unit operations, experiments were conducted to assess the removal of surrogate parameters and indicator compounds in laboratory- and pilot-scale facilities. By spiking of the laboratory- and pilot-scale facilities with a mixture of wastewater-derived contaminants, findings related to contaminant removal in various full-scale unit operations were verified without the complications associated with fluctuations in influent concentrations and uncertainties associated with quantification of contaminants near detection limits during monitoring of full-scale facilities. For this task, representative unit operations, such as SAT, advanced oxidation (i.e., ozone/hydrogen peroxide), NF, and RO treatment, as well as an MBR, were employed.

### 2.4.1 Soil-Column System Simulating SAT

The fate and transport of surrogate parameter and indicator compounds present in recycled water during SAT were investigated under controlled conditions by using an existing laboratory-scale soil-column system at CSM. The column setup consisted of four 1-m acrylic glass columns (15-cm inner diameter) in series connected through Teflon tubing (Figure 2.1). The soil used in the column system represents aquifer material of the Aqua Fria River alluvial in Arizona ($d_{50}$ = 0.8 mm), which is low in soil organic carbon content (less than 0.1%). The soil in this system provides a surface to which microorganisms can attach. The important element of SAT is the thriving biologically active community in these soil columns that is common to all SAT projects and representative of full-scale operations.

**Figure 2.1. Soil-column system at CSM simulating anoxic, saturated flow conditions.**

The column system was operated in plug-flow mode under anoxic and saturated flow conditions and at a flow rate of 1.0 mL/min or a loading rate of approximately 0.8 m/day. The hydraulic travel time in this column system consisting of four 1-m columns was approximately 6 days per 1-m column, simulating a total of 25 days of subsurface treatment. Travel times were previously determined through breakthrough tests using conservative tracers (Rauch, 2005). The columns had been continuously fed with secondary or tertiary treated-type wastewater for over 9 years. The column feed was regularly sparged with nitrogen to keep dissolved oxygen concentrations below 2.0 mg/L. Sample water flowed through the column for approximately 3 months. The system was fed with water from the South Platte River, which is primarily comprised of treated wastewater from the Denver metropolitan area. Liquid samples for water quality analysis were collected from the feedwater, the first and fourth columns of the system representing different travel times. Samples from these locations were analyzed for surrogate parameters and indicator compounds.

### 2.4.2 Laboratory-Scale Ozonation Facility

Laboratory-scale oxidation studies were conducted at SNWA's laboratory-scale ozonation facility. The laboratory-scale plant design consists of a 12-cell, continuous-flow ozone contactor constructed with inert materials such as glass, fluorocarbon polymers, and stainless steel (Figure 2.2). The 12-contactor cells each have a hydraulic residence time of 2 min, for a total of 24 min. A 55-gal (200-L) stainless steel drum was used to feed tertiary-treated wastewater effluent samples from Facility 2 at a design flow rate of 1 L/min into the system. The applied ozone dose varied among 2, 3.6, and 7 mg as $O_3$ per L. The experimental conditions for the experiments are summarized in Table 2.3. Grab samples were collected prior to and during the spiking experiment. Ozone was injected into cell 1 with countercurrent flow through a fritted glass diffuser producing a bubble size of 10 to 20 μm. Samples were collected after contact times of 6 and 18 min (2 and 3.6 mg of ozone/L) and 2, 6, and 18 min (7.0 mg of ozone/L) where the ozone residual concentration was measured as zero at these contact times. Additional experiments were performed with hydrogen peroxide ($H_2O_2$) applied in addition to ozone with dosages varying among 1, 2, and 3.5 mg/L. Experimental conditions including the use of hydrogen peroxide are also summarized in Table 2.3.

**Figure 2.2. Laboratory-scale ozonation testing setup.**

**Table 2.3. Experimental Conditions Employed in Laboratory-Scale Ozonation Facility**

| Experiment No. | Ozone Concn (mg/L) | Hydrogen Peroxide Concn (mg/L) | Contact Time (min) |
|---|---|---|---|
| 1 | 2.0 | — | 6 |
| 2 | 3.6 | — | 18 |
| 3 | 7.0 | — | 2, 6, 18 |
| 4 | 2.0 | 1.0 | 10 |
| 5 | 2.0 | 2.0 | 10 |
| 6 | 7.0 | 3.5 | 2, 6, 10 |

### 2.4.3 Pilot-Scale NF Membrane Skid

During this study, CSM operated a mobile two-stage pilot-scale membrane skid with a capacity of approximately 18 gpm (68 L/min) using MF-treated feedwater at Facility 8 (Figure 2.3). The membrane skid was utilizing 4040 spiral wound NF-4040 elements (Dow/Filmtec) capable of simulating the hydraulics and recovery of a full-scale two-stage RO train. The membranes were configured in a 2:2:1:1 pressure vessel array with each pressure vessel holding 4, 3, 4, and 3 elements, respectively. This design has been proven to simulate a two-stage full-scale train employing seven 8040 elements per vessel. The pilot is equipped with a customized supervisory control and data acquisition system to monitor and log flux, pressure, and selected water quality parameters online (e.g., pH, temperature, and conductivity). For further details, please see Drewes et al., 2008.

**Figure 2.3. Pilot-scale membrane skid operational at a full-scale RO facility.**

The skid was operated at a specific flux of approximately 0.1 gfd/psi (0.028 L/m$^2$ h kPa) and a recovery of 85%, simulating full-scale RO facilities. The spiking experiment was executed during operation of the NF membrane while the system was fed with microfiltered tertiary effluent from full-scale Facility 8 (see Table 2.2). During the sampling campaign, a spike solution of selected target compounds was added to the feed for 1 h. Grab samples were collected from the influent and permeate prior to and after the addition of the spike solution.

### 2.4.4 Pilot-Scale MBR

The pilot-scale MBR was fed with domestic primary effluent (40 gpm or 150 L/min) provided from the full-scale wastewater treatment plant of Facility 1. The MBR consisted of two anoxic tanks, one aeration tank, and one membrane tank in series with a total working capacity of approximately 11,700 gal (45 m$^3$) (Figure 2.4). Each anoxic tank was equipped with a mechanical mixer with an approximate working volume of 1670 gal (6.3 m$^3$). The primary effluent is fed to the first anoxic tank through a 7.5-cm feed spool. The water level in the first anoxic tank was monitored to control the feed. The first anoxic tank also recovered mixed liquor from the aeration tank. The aeration tank had a working volume of approximately 6700 gal (25.3 m$^3$), which uses process air via 38 10-in. fine bubble diffusers. A 5-hp recirculation pump in the aeration tank pumped mixed liquor to both the membrane tank (120 gpm or 454 L/min) and the first anoxic tank (120 gpm or 454 L/min). Sludge was wasted from the aeration tank. The membrane tank had an aerobic operating volume of 1588 gal (6 m$^3$): two membrane cassettes, each containing 10 Zenon hollow-fiber ZeeWeed™ 500c membrane elements, were situated in the membrane tank. The total membrane area is 4730 ft$^2$ (439 m$^2$). The nominal membrane pore size was 0.04 μm. The membrane tank included a recycle stream to the aeration tank at 80 gpm (302 L/min). Before the experiment, the influent was sampled to determine baseline conditions. During the experiment, grab samples were collected from MBR permeate after the appropriate residence time.

**Figure 2.4. Pilot-scale MBR at Facility 1.**

# CHAPTER 3

# METHODS TO QUANTIFY SURROGATES AND INDICATOR COMPOUNDS

## 3.1 ANALYTICAL METHODS FOR SURROGATES EMPLOYED IN THIS STUDY

### 3.1.1 Organic Bulk Surrogates

#### *3.1.1.1 Surrogates Related to EfOM*

Organic matter in municipal wastewater is referred to as effluent organic matter (EfOM). EfOM consists of (a) NOM derived from drinking water sources, (b) organic chemicals of anthropogenic origin, and (c) SMPs generated during biological wastewater treatment by the decomposition of organic matter. SMPs consist of polysaccharide-like and fulvic acid-like material (Drewes and Fox, 2000a). Different approaches have been proposed to distinguish between nature- and wastewater-derived organics by using differences in functional groups, structural properties, molecular size distribution, aromaticity, reactivity, or acid/base solubility.

**TOC**

TOC is a useful parameter that can quantify EfOM in wastewater effluents. TOC consists of particulate organic carbon (POC) and dissolved organic carbon (DOC) (operationally defined as 0.45 μm filtered). TOC has been proposed as a surrogate for water quality concerns (Chang et al., 1998). The California Department of Public Health (2007a) developed draft criteria for the use of reclaimed municipal wastewater to recharge groundwater basins that are sources of domestic water supply, which include a limit on TOC concentration. The draft guidelines inherently assume that TOC can be used as a surrogate to assess the removal of wastewater-derived contaminants of concern. Unfortunately, TOC is somewhat limiting, since it cannot be used to differentiate between biologically oxidizable matter and inert organic matter.

**BDOC**

BDOC quantifies the dissolved biodegradable organic matter. The latter consists of organic compounds that undergo microbial biotransformation (i.e., polysaccharide-like SMPs) and mineralization. BDOC in conjunction with DOC serves as a surrogate for the presence of organic compounds that are not derived from humic substances. BDOC is an effective surrogate for assessing the biological performance of SAT systems (Drewes and Fox, 1999; Drewes and Jekel, 1998; Fox et al., 2001; Drewes and Fox, 2000b).

**Hydrophobic DOC and Hydrophilic DOC**

Hydrophobic DOC and hydrophilic DOC are used to differentiate between the “humic” and “nonhumic” substances. The XAD resin method is used for fractionation of hydrophobic and hydrophilic DOC (Leenheer, 1981; Aiken et al., 1992). Hydrophobic and hydrophilic DOC fractions are effective surrogates for assessing the performance of oxidation (i.e., ozone), activated carbon adsorption, biodegradation, and membrane (i.e., RO) processes. In general,

the hydrophobic DOC is more effectively removed by ozonation, activated carbon adsorption, and membrane rejection, and the hydrophilic DOC is preferentially removed by biodegradation (Dickenson and Amy, 2000). Rauch and Drewes (2005) reported that in addition to organic colloids, quantification of hydrophobic and hydrophilic carbon can be used to predict the biodegradability of domestic wastewater effluents during groundwater recharge.

### Color

Color mainly results from dissolved materials, most often organics. Color typically indicates the presence of organic debris, such as leaves and wood in various stages of decomposition. Tannins, humic acid, and humates from the decomposition of lignin are considered the principal sources of color in natural waters (Sawyer et al., 1994). Receiving waters with high color is indicative of wastewaters containing lignin derivatives, such as from pulping operations in the paper industry, and dye wastes, such as from dyeing operations in the textile industry. A typical domestic wastewater is light brown. Color at 436 nm has been shown to be removed by oxidation processes (i.e., ozone), activated carbon adsorption, and membrane processes (i.e., RO), and thus color could be a simple and effective surrogate for assessing the performance of these treatment processes.

### COD

COD measures the gross amounts of organic carbon and is widely used for determining the strength of wastewaters. COD is the quantity of oxygen required for oxidation of carbon to carbon dioxide and water. The oxidation occurs through the chemical action of strong oxidizing agents under acidic conditions. COD has been proposed as a surrogate for water quality concerns (Chang et al., 1998). COD can be used as a surrogate for TOC, as well as for BDOC (Babcock et al., 2001). Unfortunately, COD cannot be used to differentiate between biologically oxidizable organic matter and inert organic matter.

### BOD

BOD measures the gross amounts of organic carbon and is the principal test used for determining the pollutional strength of wastewaters. BOD is the amount of oxygen consumed by living organisms (mainly bacteria) while utilizing the organic matter present in the wastewater sample. BOD can be used as a surrogate for BDOC in conventional and advanced wastewater-treated effluents (Babcock et al., 2001). The BOD and COD parameters can be used together to indicate toxic conditions and the presence of biologically resistant organic substances. BOD has limited potential as a surrogate for advanced biological treatment processes, such as SAT and biological activated carbon (BAC) systems, since a BOD measurement of less than 2 mg/L is unreliable.

### UV Spectrometry

The electronic absorbance of UV irradiation of aqueous samples is mostly due to the dissolved compounds containing chromophores, which are covalently unsaturated groups, such as C=C and C=O. In NOM the electronic absorption is linked to chromophores (e.g., $\pi$ bonds) within aromatic rings. The absorbance spectrum at wavelengths of 200 to 400 nm is associated with the aromaticity of NOM (Chin et al., 1994). Most researchers use a single UV absorbance (UVA) at 254 or 272 nm to monitor UV-absorbing components of NOM. To better compare the UVA at 254 nm for different waters, the UVA is normalized by the DOC concentration of the sample, expressed in units of liters per milligram-meter. This is defined as the specific UVA (SUVA). Edswald and Van Benschoten (1990) found that SUVA was a good indicator of the humic content of raw waters. This was supported by strong correlations

between SUVA and the aromatic content of humic and fulvic acids (Aiken and Leenheer, 1993; Chin et al., 1994; Croué et al., 1999). Also, Croué et al. (1999) and Hwang et al. (2001) observed that SUVA decreases with the increasing hydrophilic character of a NOM fraction. This agrees with findings by Amy and Drewes (2006), in which SUVA increased during travel in subsurface systems for wastewater effluents applied to SAT systems.

### Fluorescence Spectrometry

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. Presently, fluorescence research is focusing on the acquisition and interpretation of the fluorescence excitation-emission matrix (EEM) (McKnight et al., 2001; Amy and Drewes, 2006). 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. Amy and Drewes (2006) used differential EEM spectra to assess the performance of SAT of wastewater effluents. They reported that both humus-like and protein-like EfOM was removed over the short term, while additional humus-like EfOM was removed over the long term. Fluorescence spectrometry can be used to distinguish humus-like organic matter from protein-like organic matter. In this study, fluorescence intensity for protein-like organic matter was quantified at an excitation wavelength of 330 nm and an emission wavelength of 270 nm. Humus- and fulvic acid-like intensities were quantified at excitation wavelengths of 420 and 440 nm and at emission wavelengths of 330 and 240 nm, respectively. The specific fluorescence (SFLUOR) intensity is defined as the protein or humic fluorescence intensities (see wavelengths above) divided by DOC times 10.

### MW

The molecular weight (MW) for a heterogeneous mixture of organic matter is represented by an average MW or an MW distribution. It can be measured by the size exclusion chromatography (SEC) method using UV detection and/or DOC detection (Her et al., 2002a). The majority of MW data reported in the literature are for whole water samples, humic substances, and hydrophobic fractions (Her et al., 2002b). NOM present can differ in its MW and can range from a few hundred to a high of several thousands. SEC-UV can be potentially used to classify NOM as being relatively more humus-like or protein-like by use of a UV index ratio (URI, $UVA_{210}/UVA_{254}$) (Her et al., 2008). Her et al. (2004) observed the URI decreased after ozonation of river water; thus, URI could be an effective surrogate assessing the performance of oxidation processes. SEC-DOC has also been used to reveal transformation/removal patterns of the following EfOM fractions: polysaccharides, humic substances, and low-MW acids (Amy and Drewes, 2006). Amy and Drewes (2006) reported that SAT of wastewater effluent preferentially removed nonhumic components (e.g., proteins, polysaccharides) of EfOM over short travel times/distances, while humic components (e.g. humic substances) were removed over longer travel times/distances.

### Adsorption Analysis

Adsorption analysis can be used to describe the competitive adsorption of different DOC fractions onto activated carbon. The analysis is based upon the ideal-adsorbed-solution theory and operationally defines fictive DOC fractions of different adsorbability (Drewes and Jekel, 1997). Adsorption analysis has been previously employed to describe the change of DOC adsorbability during conventional wastewater treatment and SAT (Drewes and Jekel, 1997; Drewes and Fox, 1999).

**TOX**

TOX, sometimes referred to as adsorbable organic halides, is a bulk parameter that measures the total organically bound halogens. TOX has been used to describe mainly halogenated organics of anthropogenic origin in water as well as the formation of halogenated species during chlorination. If one couples TOX with ion chromatography, the halogens can be distinguished into chlorinated (TOCl), brominated (TOBr), and iodinated (TOI) organics. While TOCl and TOBr are formed mainly during wastewater chlorination, TOI is comprised mainly of iodinated contrast media used during X-rays in hospitals and medical centers. While TOX is sensitive to chloride, bromide, and iodide, it is not sensitive to fluoride. TOX can be used to monitor the breakthrough of some synthetic organic compounds in water treatment processes and/or to estimate the level of formation of chlorinated organic by-products after disinfection. However, TOX yields no information about the structure or nature of the organic compounds to which the halogens are bound.

### 3.1.2 Other Bulk Surrogates

**Turbidity**

Turbidity is used to assess the clarity of water and is caused by a wide variety of suspended materials, which range in size from colloidal to coarse dispersions. Turbidity can serve as a surrogate to assess the system performance and integrity of membranes, such as ultrafiltration, NF, and RO types.

**Hardness**

Hardness is caused by multivalent metallic cations. The principal hardness-causing cations are the divalent calcium, magnesium, strontium, ferrous iron, and manganous ions.

**Alkalinity**

The alkalinity of water is a measure of its capacity to neutralize acids. The alkalinity is caused primarily by the salts of weak acids. Alkalinity is used to a great extent in wastewater treatment practice for determining the buffering capacity. Alkalinity is also an important factor in determining the amenability of wastewaters to biological treatment (i.e., SAT).

**Nitrogen**

In aquatic systems the dominant nitrogen forms are ammonia, nitrogen ($N_2$), nitrite, nitrate, and organic nitrogen. Organically bound nitrogen is usually associated with amino acids, amines, amides, imides, nitro derivatives, and a number of other compounds. Ammonia and organic nitrogen analyses are important in determining whether sufficient available nitrogen is present for biological treatment (i.e., SAT and BAC).

**Phosphorus**

In wastewater the dominant phosphorus forms are the inorganic phosphorus forms, orthophosphates and polyphosphates, and organically bound phosphorus. Organically bound phosphates are formed primarily by biological processes, such as biological treatment processes and those governing body wastes and food residues. Phosphorus is important in determining whether sufficient available phosphorus is present for biological treatment (i.e., SAT and BAC).

### Conductivity

The conductivity of a solution is a measure of its ability to carry an electrical current and varies both with the number and type of ions the solution contains. Conductivity can serve as a surrogate to assess the system performance and integrity of membranes, such as UF, NF, and RO types.

### TDS

TDS is the dissolved portion of solid matter in aqueous samples. In water, TDS consists mainly of inorganic salts, a small amount of organic matter, and dissolved gases. The operational definition is the matter that remains as residue upon evaporation and drying at 180 °C. The TDS correlates well with hardness. So, like conductivity, TDS can serve as a surrogate to assess the system performance of membranes, such as UF, NF, and RO types.

The analytical methods employed to quantify bulk surrogate parameters are summarized in Table 3.1.

**Table 3.1. List of Select Surrogate Parameters Investigated during This Study**[a]

| Surrogate | Phase | Physicochemical Properties | Reference or Method |
|---|---|---|---|
| Total organic carbon (TOC) | Liquid | Heterogeneous carbon | SM 5310 C |
| Dissolved organic carbon (DOC) | Liquid | Dissolved carbon mixture | SM 5310 C |
| BDOC | Liquid | BDOC | Rauch and Drewes (2004) |
| Hydrophobic/hydrophilic DOC | Liquid | "Humic" and "nonhumic" | Aiken et al. (1992) |
| Color (COL) | Liquid | Hydrophobic/aromatic | SM 2120 C |
| Chemical oxygen demand (COD) | Liquid | Organic strength | SM 5220 B |
| Biochemical oxygen demand (BOD) | Liquid | Biodegradable organics | SM 5210 B |
| UV light absorption (UVA) | Liquid | Aromaticity | SM 5910 B |
| Fluorescence | Liquid | Humic-like vs. protein-like | McKnight et al. (2001) |
| MW | Liquid | Size, humic vs. nonhumic | Her et al. (2002a) |
| Adsorption analysis | Liquid | Hydrophobicity/adsorbability | Drewes and Jekel (1997) |
| Turbidity (TURB) | Liquid | Suspended solids | SM 2130 B |
| Alkalinity (ALK) | Liquid | Buffering capacity | SM 2320 B |
| Hardness | Liquid | Multivalent metallic cations | SM 2340 C |
| Conductivity (COND) | Liquid | Function of number and types of | SM 2510 B |
| Total dissolved solids (TDS) | Liquid | Inorganic salts | SM 2540 C |
| $NH_4$-N, $NO_2$-N, $NO_3$-N, $PO_4$-P | Liquid | Nutrients for biological | SM 4110 B |
| Boron | Liquid | Low-MW acid | SM 3125B |
| Total organic halides (TOX) | Liquid | Organically bound halides | SM 5320 B |
| Total organic iodide (TOI) | Liquid | Iodinated contrast media | Oleksy-Frenzel et al. (2000) |
| Trihalomethanes (THMs) | Liquid | Volatile, low-MW DBPs | EPA Method 551.1 |
| Haloacetic acids (HAAs) | Liquid | Polar, low-MW DBPs | SM 6251 B |

[a] APHA (2005); EPA Method, U.S. EPA, 1995.

**Boron**

Boron occurs in water as boric acid ($H_3BO_3$). At elevated pH ($pK_a = 9.24$), boric acid dissociates as tetrahydroxyborate anion [$B(OH)_4^-$]. With an MW of 61.8 or 78.8 g/mol depending upon speciation, boron is usually poorly rejected by RO and NF membranes (Drewes et al., 2008).

## 3.2 ANALYTICAL METHODS FOR INDICATORS EMPLOYED IN THIS STUDY

The properties and occurrence level of organic micropollutants occurring at the nanograms-per-liter (ng/L) level vary widely, and different analytical methods are required for their quantification. During the last 10 years, multiple methods have been developed and employed for the detection of these compounds and in most cases include GC/MS usually coupled with derivatization and LC/MS (Barber et al., 1995; Snyder et al., 1999; Snyder et al., 2001; van Stee et al., 2002; Reddersen and Heberer, 2003; Vanderford et al., 2003). The use of LC/MS allows the identification of highly polar contaminants without derivatization. To gain enhanced selectivity and sensitivity, tandem MS is increasingly being used for the measurement of organic trace compounds in various environmental matrices (Zwiener and Frimmel, 2004; Richardson and Ternes, 2005). The limitation of GC/MS applications is that analytes need to be transferred to the gas phase either directly or after an appropriate derivatization step. The drawback of LC/MS analysis is the sensitivity to matrix effects resulting in ion suppression. Ion suppression in LC/MS can occur when coeluting ionic and ionizable constituents of the sample and the sample matrix suppress the ionization of the sample molecules in a mass spectrometer's source. To overcome matrix effects, researchers have proposed deuterated or $^{13}C$-labeled internal standards to ensure recovery (Richardson and Ternes, 2005; Vanderford and Snyder, 2006), more-effective steps to remove matrix components (Kloepfer et al., 2005), and alternative interfaces (e.g., atmospheric pressure chemical ionization) (Richardson and Ternes, 2005).

While some of the techniques require expensive and technically challenging instrumentation, others could be used directly or adapted for use in the laboratories of many utilities and contractors. For instance, several utilities have GC/MS systems for the measurement of semivolatile compliance compounds and DBPs. GC/MS can be used directly for the measurement of certain indicators (e.g., octylphenol and phthalates), while other compounds can be derivatized to expand the range of GC-amenable compounds (Lee and Peart, 1998; Huang and Sedlak, 2001; Reddersen and Heberer, 2003; Soliman et al., 2004). In addition, utilities often have GC with other detectors that may be applicable for indicator analysis (e.g., electron capture detectors for halogenated by-products, nitrogen-phosphorus detectors for nitrosamines, and flame ionization detectors for several organic compounds). Many utility laboratories have the ability to measure metals in water as part of CWA and SDWA compliance requirements. These instruments can prove valuable for the measurement of emerging contaminants such as iodinated contrast media and organotins (Snyder et al., 2003c). Likewise, utilities often have ion-chromatography systems with conductivity or spectrometric detection. Several ionic pharmaceuticals (e.g., clofibric acid) and endocrine disruptors (e.g., perchlorate) would be amenable to standard ion-chromatography analysis. Immunoassays represent another class of simple yet sensitive analytical tools that show promise for the analysis of trace organics in wastewater. For instance, immunoassays have been applied in the compliance testing of drinking water for the presence of triazine herbicides. In addition, immunoassays have been used successfully to monitor estrogenic hormones in wastewater effluents (Aherne et al., 1985; Aherne and Briggs, 1989; Snyder et

al., 1999; Huang and Sedlak, 2001; De Alda and Barcelo, 2001; Koda and Soya, 2002; Matsunaga and Ueki, 2002; Snyder et al., 2003b). Spectrometric instruments are readily available at most utilities and contract laboratories. For instance, HPLC with UV diode-array and/or fluorescence detectors has been used to successfully monitor environmentally relevant levels of alkylphenols in wastewater effluents (Naylor et al., 1992; de Voogt et al., 1997; Belfroid et al., 1999; Snyder et al., 1999).

The analytical methods employed to quantify wastewater-derived contaminants in this study are described below.

### 3.2.1 GC/MS (CSM)

Pharmaceuticals, pesticides, and chlorinated flame retardants were extracted by using C-18 solid-phase extraction (SPE) material followed by derivatization and GC/MS as described by Reddersen and Heberer (2003). Samples were acidified to a pH of 2 by using residue-free 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 SPE. Analytes were then pressure extracted via a vacuum from the filtrate (5 to 8 mL/min) by using 1 g of preconditioned RP-C-18 SPE material. The C-18 cartridges were then dried overnight with a gentle stream of medical-grade nitrogen.

#### *3.2.1.1 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 a 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 h. The residue was resuspended again in toluene (100 µL) and transferred to 200-µL glass inserts.

#### *3.2.1.2 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 during intervals 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 h. The remaining solution was transferred to 200-µL glass inserts.

### 3.2.2 GC/MS-MS (UC)

#### *3.2.2.1 Method for Steroid Hormones*

Steroid hormones were extracted by using C-18 SPE disks followed by derivatization and GC/MS-MS as described by Kolodziej et al. (2004). The surrogate standard mesterolone was spiked into the filtered samples at a concentration of 100 ng/L. Steroid hormones were then pressure extracted from the filtrate by using preconditioned 90-mm Empore C-18 SPE disks.

To remove polar organic matter from the extraction disks, the C-18 disks were washed twice with 25 mL of a 70:30 (v/v) water:methanol solution prior to elution of the steroid analytes with 20 mL of a 10:90 (v/v) water:methanol solution. The eluent was then dried under vacuum, resuspended in methanol, and transferred to flasks. After another drying under vacuum, the extract was resuspended in 200 µL of HPLC-grade acetonitrile and derivatized with 50 µL of heptafluorobutyric anhydride, sealed, and placed in a 55° C oven for 1.5 h. The extracts were then cooled and evaporated under a gentle stream of nitrogen prior to resuspension in 100 µL of isooctane that contained hexachlorobenzene (400 µg/L) as an internal standard.

#### *3.2.2.2 Method for Acidic Drugs*

Acidic drugs were extracted by using ENVI-18 SPE resin followed by derivatization and GC/MS/MS. The surrogate standard fluriprofen was spiked into the filtered samples at a concentration of 500 ng/L. Acidic drugs were then extracted by pumping the filtrate (10 mL/min) via a peristaltic pump through the extraction columns containing preconditioned ENVI-18 SPE resin. The ENVI-18 cartridges were then dried for 10 min by pumping air through the resins. To remove polar organic matter from the extraction cartridges, the ENVI-18 resin was washed with 10 mL of methanol solution. The eluent was then dried under vacuum, resuspended in methanol, and transferred to 4-mL glass vials. After being dried under a gentle stream of high-purity nitrogen, the extract was derivatized with 250 µL of diazomethane/diethylether mixture. The extracts were allowed to react for 2 min prior to quenching of the excess diazomethane with 10 mL of a 1:10 acetic acid/acetone mixture. The derivatized samples were again blown to near-dryness under a stream of high-purity nitrogen and resuspended in 200 µL of isooctane with 500 mg of hexachlorobenzene/L as an internal standard.

### 3.2.3 LC/MS-MS (SNWA)

Analytes were extracted by using 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 by using preconditioned 500-mg hydrophilic-lipophilic balance cartridges. All extractions were performed by using an automated SPE system. The sample was then loaded (15 mL/min) onto the cartridges, after which the cartridges were rinsed with 5 mL of reagent water and were then dried with a stream of nitrogen for 60 min. 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. 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 by using methanol. The final concentration of the internal standards was 50 µg/L.

## 3.3 INTERLABORATORY COMPARISON (ROUND ROBIN)

As of today, none of the methods to quantify trace organics at the nanograms-per-liter level are standardized and analytical protocols currently employed vary widely among laboratories. While interlaboratory (Round Robin) studies to assess the ruggedness of analytical methods for regulated compounds such as pesticides have been performed multiple times (Gonzalez et

al., 2004), little is known about how accurate, precise, and reproducible current analytical methods are in quantifying unregulated trace organics at the nanograms-per-liter level in different water matrices. Sengl and Krezmer (2003) reported findings from two proficiency tests among 20 laboratories in Germany (employing GC and LC methods) for 11 different groups of pharmaceuticals in surface and wastewater samples. While the recovery of spiked compounds to these samples varied between 50 and 140%, reported concentrations varied between 35 and 70% for surface and wastewater samples, respectively. Ternes et al. (2002) reported findings from an interlaboratory comparison among three laboratories employing GC/MS for groundwater and surface water samples. The mean recovery of spiked samples for five analytes exceeded 70% with relative standard deviations (RSDs) among the three laboratories of less than 25%.

This section represents the results of Round Robin tests among five different laboratories (three research, one water utility, and one commercial laboratories) employing GC/MS, GC/MS-MS, and LC/MS-MS methodologies to evaluate their proficiency in detecting trace organics at concentrations of very few nanograms per liter in water samples.

## 3.3.1 Experimental Approach

### *3.3.1.1 Analytical Methods*

The five participating laboratories participating in these Round Robin events adopted or slightly modified analytical protocols that had been previously published (Kolpin et al., 2002; Vanderford et al., 2003; Reddersen and Heberer, 2003; Kolodziej et al., 2004). These protocols are multicomponent methods targeting a wide range of different organic micropollutants in aqueous samples.

In general, analytes were extracted by using SPE followed by either LC/MS-MS or derivatization followed by GC/MS or GC/MS-MS (Table 3.2). The LC/MS-MS methods employed positive and negative ion mode with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). Surrogate standards were spiked into the samples prior to extraction at concentrations between 50 and 100 ng/L. Analytes were eluted and quantified with methods as outlined in the above-mentioned references. The experience among the five laboratories applying the aforementioned methods varied between one and 10 years.

**Table 3.2. Group of Compounds Used in Round Robin Tests and Analytical Techniques Used by Various Laboratories**

| | Analytical Methods | | | | |
|---|---|---|---|---|---|
| **Compound Group** | **GC/MS** | **GC/MS-MS** | **LC/MS-MS ESI Positive** | **LC/MS-MS APCI Positive** | **LC/MS-MS ESI Negative** |
| *Analgesics* | | | | | |
| Acetaminophen | | | 2 | | |
| Diclofenac | 1 | | | | 1 |
| Ibuprofen | 1 | | | | 2 |
| Naproxen | 1 | | | | 1 |
| *Antibiotics* | | | | | |
| Sulfamethoxazole | | | 2 | | |
| Trimethoprim | | | 2 | | |
| *Antimicrobial* | | | | | |
| Triclosan | | 1 | | | 2 |
| *Antiepileptics* | | | | | |
| Carbamazepine | 1 | | 1 | | |
| Fluoxetine | | | 2 | | |
| *Fire retardants* | | | | | |
| TCEP | 1 | 1 | 1 | | |
| TDCPP | 1 | 1 | 1 | | |
| *Insect repellent* | | | | | |
| DEET | | 1 | 1 | | |
| *Lipid-lowering agent* | | | | | |
| Gemfibrozil | 1 | | | | 2 |
| *Plasticizers* | | | | | |
| Bisphenol A | 1 | 1 | | | |
| *Steroid hormones* | | | | | |
| Estradiol | | 1 | 1 | 1 | |
| Estrone | | 1 | | 1 | |
| Ethynylestradiol | | | | 1 | |
| Estriol | | 1 | | 1 | |
| Progesterone | | 1 | 1 | 1 | |
| Androstenedione | | 1 | | 1 | |
| Testosterone | | 1 | 1 | 1 | |
| *Stimulant* | | | | | |
| Caffeine | 1 | 1 | 2 | | |
| *X-ray contrast agent* | | | | | |
| Iopromide | | | | | 2 |

#### *3.3.1.2 Round Robin Samples*

For the Round Robin events, a primary stock solution in methanol/acetone was prepared by an independent third party containing a mixture of pharmaceutical residues, personal care products, and steroid hormones. The selected target compounds and their concentrations in the primary stock solution were unknown to all participating laboratories. The concentration range of the spiked compounds was 140 to 440 ng/L and 55 ng/L for estradiol. The primary standard solution was spiked to 60 L of a filtered (nominal 0.7-mm glass fiber filter) secondary-treated wastewater effluent sample, which was collected in a stainless steel container. The same sample was used to provide a filtered unspiked sample consisting of the same water matrix used for the spike. The unspiked and spiked samples were filled into precleaned 1-L amber glass bottles, and five replicates of each sample were preserved (i.e., 50 mg of ascorbic acid/L; 1 g of sodium azide/L) and shipped on ice overnight to each of the participating laboratories. Each laboratory also received a blank sample (type I water), which was analyzed as triplicate. One laboratory reported triclosan exceeding 300 ng/L in one of the blank samples, which was attributed to laboratory contamination. Another laboratory reported the presence of both estradiol (2 ng/L) and progesterone (10 ng/L) in blank samples. Since similar concentrations were reported by this laboratory for the unspiked wastewater sample, the reported concentrations of these two hormones were corrected to the detection limit (i.e., < 1.0 ng/L).

Each laboratory was asked to analyze each replicate independently. Extraction of the samples occurred within 2 weeks. Two proficiency tests were conducted. Three laboratories participated in the first event; five participated in the second. In addition, samples from various water treatment processes collected during field monitoring efforts were split among three laboratories employing GC/MS, GC/MS-MS, and LC/MS-MS methods. These samples represent raw sewage, tertiary-treated wastewater, and groundwater matrices.

### 3.3.2 Results and Discussion

#### *3.3.2.1 Recovery*

During the first Round Robin test conducted among three laboratories employing GC and LC methods, five compounds were spiked at nominal concentrations between 500 and 700 ng/L to a secondary-treated wastewater effluent sample. Recovery was estimated by calculating the difference between spiked and the unspiked samples. The RSD and average recovery for the unspiked and spiked samples varied between 6 and 30% and 60 and 91%, respectively (Table 3.3). These results are consistent with previous studies (Ternes et al., 2002; Sengl and Krezmer, 2003) and point to a high level of confidence among these laboratories in measuring these five target analytes.

Of the compounds covered by the six different analytical methods employed among the five different laboratories during the second Round Robin test, 14 compounds were spiked at various concentrations to secondary-treated effluent samples. The nominal spiked concentrations are summarized in Table 3.4. Compounds selected in this assessment were quantified by at least two laboratories. Reported recoveries for the spiked samples are summarized in Table 3.4. High recoveries of compounds (i.e., 84 to 142%) during both the first and second Round Robin tests (i.e., caffeine and ibuprofen) were confirmed among the laboratories participating in both proficiency tests (Labs III, IV, and V) but varied between 34 and 49% for laboratories that more recently established their analytical methods (Lab I and II). For compounds for which the nominal spike concentration was less than 20% of the

unspiked average concentration (e.g., gemfibrozil and TCEP), only one out of three laboratories was capable of quantifying the spiked amount with recoveries varying between 54 and 68%. For compounds spiked at a nominal concentration of 60% or higher as the average concentration observed in the unspiked sample, recoveries for analytes with the exception of iopromide and steroid hormones varied between 13 and 157%. The lowest recoveries were reported for acetaminophen (i.e, 14 to 29%), a highly polar compound that has been observed to usually exhibit poor recoveries during SPE, which might explain the low recoveries observed during the proficiency test. The X-ray contrast agent iopromide was either not recovered or recovered at only 22% by two laboratories that have established their methods more recently. The largest variation in recoveries was observed for the steroid hormone estradiol, varying from 34 to 166%, while progesterone was recovered by two laboratories at 100% and two laboratories at 18 and 23%, respectively. It is noteworthy that all methods employed in this study utilized surrogate standards for quality control but that the observed recovery range of the standards (data not shown) did not point to any significant recovery issues while analysis was being conducted. These findings suggest that the recovery of compounds occurring at the nanograms-per-liter level can be quite variable regardless of the method or instrument employed.

**Table 3.3. Average Concentrations, RSDs, and Recoveries Reported among Three Laboratories (First Round Robin) for an Unspiked and Spiked Wastewater Effluent Sample**

| Analyte | Unspiked Wastewater | | | Spiked Wastewater | | | |
|---|---|---|---|---|---|---|---|
| | N[a] | Avg. (ng/L) | RSD (%) | N | Avg. (ng/L) | RSD (%) | Recovery[b] (%) |
| Caffeine | 2 | <100 | — | 2 | 454 | 16 | 91 |
| Carbamazepine | 2 | 444 | 26 | 2 | 760 | 6 | 63 |
| Diclofenac | 3 | 56 | 13 | 3 | 482 | 30 | 62 |
| Ibuprofen | 3 | 64 | 11 | 3 | 646 | 28 | 87 |
| Naproxen | 3 | 208 | 26 | 3 | 600 | 30 | 60 |

[a]N, number of laboratories (each sample analyzed as triplicate).
[b]Average recovery among laboratories.

**Table 3.4. Reported Recovery (in Percent) for Spiked Samples among Five Different Laboratories (Second Round Robin)[a]**

| Compound | Avg. Unspiked Concn (ng/L) | Nominal Spike Concn (ng/L) | Lab Ia (LC/MS-MS) | Lab Ib (GC/MS-MS) | Lab II (LC/MS-MS) | Lab III (LC/MS-MS) | Lab IV (GC/MS) | Lab V (GC/MS-MS) |
|---|---|---|---|---|---|---|---|---|
| Acetaminophen | <10–38 | 270 | 14 | — | — | 29 | — | — |
| Bisphenol A | 567 | 335 | — | 53 | 41 | — | — | — |
| Caffeine | 13 | 335 | 38 | 34 | — | 84 | — | — |
| DEET | 15 | 83 | — | 47 | — | 74 | — | — |
| Estradiol | 0.8 | 55 | 58 | — | 34 | 166 | — | 40 |
| Fluoxetine | 15 | 330 | 107 | — | 13 | 35 | — | — |
| Gemfibrozil | 3294 | 280 | 0 | — | — | 68 | 0 | — |
| Ibuprofen | 417 | 274 | 49 | — | — | 108 | 142 | — |
| Iopromide | 159 | 440 | 22 | — | 0 | 74 | — | — |
| Progesterone | <1.0 | 385 | 100 | — | 23 | 100 | — | 18 |
| Sulfamethoxazole | 220 | 250 | 157 | — | 20 | 67 | — | — |
| TCEP | 445 | 83 | — | 0 | — | 54 | 0 | — |
| Triclosan | 33 | 140 | 93 | 82 | 45 | 94 | — | — |
| Trimethoprim | 465 | 290 | 53 | — | — | 74 | — | — |

[a]Dash denotes that compound was not analyzed.

#### *3.3.2.2 Precision*

During the second Round Robin test, each laboratory analyzed five replicates of an unspiked and spiked sample. The RSD of each sample among three laboratories employing their methods for several years (Labs III, IV, and V) was less than 20% (Table 3.5). The RSD of sample results reported by laboratories that established their methods more recently (Labs I and II) varied between 5 and 56%. Of the compounds presented in Tables 3.4 and 3.5, not a single analyte exhibited both high recoveries and low RSDs across all analytical methods employed in this study. Since all methods are designed for multicomponent analyses (with different analytes targeted by each method), this finding was not expected. Recoveries and RSDs of these analytical protocols will always vary in a certain range, and both are subject to—among others—variable SPE extraction efficiencies, compound amenability for GC or LC, and stability of a compound during the analytical procedure.

All methods designed to quantify estradiol and progesterone consistently reported no detect concentrations (i.e., less than 1.0 ng/L) of both analytes in the unspiked sample. The spiked sample for estradiol, however, exhibited significant RSDs exceeding 70%. Three laboratories attempted to analyze for the X-ray contrast agent iopromide, but only two were able to quantify the analyte, with RSDs varying between 13 and 56%.

#### *3.3.2.3 Field Monitoring*

Samples from various water treatment processes collected during field monitoring efforts of this study were split among three laboratories employing GC/MS, GC/MS-MS, and LC/MS-MS methods. The results of these monitoring efforts, representing raw sewage, tertiary-treated effluents, and groundwater matrices, are presented in Table 3.6. While all three methods agreed well regarding the determination of "no detects" with the exception of ibuprofen in a tertiary-treated effluent, the RSDs among the three laboratories for most samples varied between 16 and 30%, with some excursion of 85 to 125%. It is noteworthy that, when the results are used to assess removal efficiencies of different processes, the reported removal percentages among the three laboratories are highly consistent. Findings from this comparison, using a limited data set, support that RSDs of 30% or more in multicomponent analysis are common and achievable, while absolute concentrations are associated with a degree of uncertainty.

**Table 3.5. Average Concentrations and RSDs (in Percent) among Five Laboratories for Wastewater Matrix (Second Round Robin)[a]**

| Compound | Nominal Spike | Avg. among All Laboratories | | Lab Ia (LC/MS-MS) | | Lab Ib (GC/MS-MS) | | Lab II (LC/MS-MS) | | Lab III (LC/MS-MS) | | Lab IV (GC/MS) | | Lab V (GC/MS-MS) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Avg.[b] | RSD | Avg. | RSD | Avg. | RSD | Avg. | RSD | Avg. | RSD | Avg. | RSD | Avg. | RSD |
| Acetaminophen | — | <10–38[2] | — | 38 | 52 | — | — | — | — | <10 | — | — | — | — | — |
| Acetaminophen, spiked | 270 | 78[2] | 3 | 76 | 16 | — | — | — | — | 79 | 9 | — | — | — | — |
| Bisphenol A | — | 567[2] | 24 | — | — | 661 | 25 | 472 | 4 | — | — | — | — | — | — |
| Bisphenol A, spiked | 335 | 723[2] | 23 | — | — | 838 | 11 | 607 | 15 | — | — | — | — | — | — |
| Caffeine | — | 13[3] | 6 | 13 | 27 | 125 | 7 | — | — | <100 | — | <100 | — | — | — |
| Caffeine, spiked | 335 | 181[3] | 48 | 138 | 5 | 125 | 9 | — | — | 280 | 12 | <100 | — | — | — |
| Carbamazepine | — | 172[2] | 64 | — | — | — | — | 77 | 12 | 266 | 9 | — | — | — | — |
| DEET | — | 15[2] | 8 | — | — | <2 | — | — | — | 15 | 8 | — | — | — | — |
| DEET, spiked | 83 | 58[2] | 46 | — | — | 39 | 8 | — | — | 76 | 15 | — | — | — | — |
| Diclofenac | — | 75[2] | 21 | — | — | — | — | — | — | 62 | 10 | 80 | 6 | — | — |
| Estradiol | — | 0.8[4] | 19 | <1.0 | — | — | — | <10 | — | <1.0 | — | — | — | 0.8 | 19 |
| Estradiol, spiked | 55 | 55[4] | 77 | 32 | 40 | — | — | 18.4 | 20 | 91 | 12 | — | — | 23 | 3 |
| Estrone | — | 13[8] | 63 | — | — | — | — | 12 | 7 | 13 | 18 | — | — | 3 | 4 |
| Fluoxetine | — | 15[3] | 72 | 27 | 10 | — | — | 6 | 9 | 12 | 11 | — | — | — | — |
| Fluoxetine, spiked | 330 | 184[3] | 86 | 377 | 10 | — | — | 47 | 16 | 127 | 13 | — | — | — | — |
| Gemfibrozil | — | 3294[3] | 13 | 3762 | 12 | — | — | — | — | 3214 | 8 | 2906 | 7 | — | — |
| Gemfibrozil, spiked | 280 | 3270[3] | 47 | | | | | | | | | | | | |
| Ibuprofen | — | 417[3] | 65 | 145 | 32 | — | — | — | — | 420 | 10 | 685 | 7 | — | — |
| Ibuprofen, spiked | 275 | 690[3] | 56 | 280 | 14 | — | — | — | — | 717 | 11 | 1074 | 5 | — | — |
| Iopromide | — | 159[2] | 59 | 225 | 17 | — | — | <1.0 | — | 92 | 14 | — | — | — | — |
| Iopromide, spiked | 440 | 371[2] | 17 | 323 | 56 | — | — | <1.0 | — | 418 | 13 | — | — | — | — |
| Naproxen | — | 365[2] | 15 | — | — | — | — | — | — | 326 | 12 | 410 | 8 | — | — |

*(Continued)*

**Table 3.5.** ***Continued***

| Compound | Nominal Spike | Avg. among All Laboratories | | Lab Ia (LC/MS-MS) | | Lab Ib (GC/MS-MS) | | Lab II (LC/MS-MS) | | Lab III (LC/MS-MS) | | Lab IV (GC/MS) | | Lab V (GC/MS-MS) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Avg.[b] | RSD | Avg. | RSD | Avg. | RSD | Avg. | Avg.[b] | RSD | Avg. | RSD | Avg. | RSD | Avg. |
| Progesterone | — | <1.0 | — | <1.0 | — | — | — | <1.0 | — | <1.0 | — | — | — | <1.0 | — |
| Progesterone, spiked | 385 | 383[4] | 38 | 387 | 28 | — | — | 90 | 25 | 383 | 10 | — | — | 71 | 4 |
| Sulfamethoxazole | — | 220[3] | 76 | 217 | 12 | — | — | 54 | 5 | 389 | 10 | — | — | — | — |
| Sulfamethoxazole, spiked | 250 | 421[3] | 65 | 604 | 14 | — | — | 104 | 6 | 554 | 12 | — | — | — | — |
| Testosterone | — | <1–27[3] | 30 | 23 | 50 | — | — | — | — | — | <1.0 | — | — | <1.0 | — |
| TCEP | — | 445[3] | 57 | ND[c] | — | 320 | 28 | — | — | — | — | 735 | 9 | — | — |
| TCEP, spike | 83 | 443[3] | 55 | — | — | 281 | 16 | — | — | — | — | 724 | 3 | — | — |
| Triclosan | 33 | <1–119[4] | — | ND | — | — | — | 119 | 45 | 13 | 9 | — | — | — | — |
| Triclosan, spike | — | 143[4] | 20 | 130 | 54 | 115 | 7 | 182 | 40 | 144 | 13 | — | — | — | — |
| Trimethoprim | 465 | 465[4] | 26 | 550 | 10 | — | — | — | — | 379 | 8 | — | — | — | — |
| Trimethoprim, spike | — | 649[4] | 12 | 704 | 13 | — | — | — | — | 594 | 9 | — | — | — | — |

[a]All concentrations are in nanograms per liter.

[b]Superscripted number respresents number of laboratories analyzing each sample (each sample was analyzed five times).

[c]ND, not determined.

**Table 3.6. Target Compound Concentrations (ng/L) during Field Monitoring Efforts**

| Compound | Laboratory | MBR Influent | MBR Effluent | Removal (%) | Tertiary effluent | Groundwater after SAT | Removal (%) |
|---|---|---|---|---|---|---|---|
| Ibuprofen | A | — | — | — | <10 | <10 | — |
| | B | — | — | — | <10 | <10 | — |
| | C | — | — | — | 115 | <1.0 | 100 |
| Gemfibrozil | A | 2459 | 571 | 77 | 189 | <10 | 100 |
| | B | — | — | — | 46 | <10 | 100 |
| | C | 3810 | 839 | 78 | 378 | <1.0 | 100 |
| Naproxen | A | 13,873 | 266 | 98 | 30 | <10 | 100 |
| | B | — | — | — | — | — | — |
| | C | 22,700 | 337 | 99 | — | — | — |
| Estrone | A | — | — | — | — | — | — |
| | B | — | — | — | 0.8 | <0.6 | 100 |
| | C | — | — | — | 15 | <1.0 | 100 |

### 3.3.3 Conclusions

During low-nanograms-per-liter-level analysis, many factors can affect the precision of a measurement. Interlaboratory comparisons can provide only some insight into possible causes of these variations. This study considered a very limited data set during the interlaboratory comparison, but results of this effort point to the need to conduct more comprehensive Round Robin experiments considering various analytical methods and water matrices. A standardization of analytical techniques was clearly beyond the scope of this project. Findings from both Round Robin experiments and field monitoring efforts indicated that the methods employed during this study seem to be comparable and that the results are more dependent upon the skill and level of experience of each laboratory. The high variations in RSDs observed among laboratories that recently established methods for the compounds of interest indicate that it takes a fair amount of time to establish and optimize a method for nanograms-per-liter-level analysis and that a top-shelf analytical instrument is no guarantee of precise and reproducible measurements. Findings suggest that RSDs of less than 30% are achievable by an experienced laboratory. All methods targeted for multicomponent analysis exhibited high variations of recovery, indicating the degree of uncertainty that is still associated with reported low-nanograms-per-liter-level results. There are clear limitations on the ability of sound laboratory practice to improve recovery, and it appeared that consistently high recoveries could be ensured only by method modifications. Vanderford and Snyder (2006) recently proposed isotope dilution for each target analyte during multicomponent LC/MS-MS analysis to correct for matrix suppression, SPE losses, and instrument variability.

# CHAPTER 4

# OCCURRENCE OF WASTEWATER-DERIVED CONTAMINANTS IN TREATED EFFLUENTS

## 4.1 OCCURRENCE OF INDIVIDUAL COMPOUNDS IN CONVENTIONAL TREATED WASTEWATER EFFLUENTS BASED UPON PUBLISHED DATA

In order to compile information on viable indicator compounds, only articles that reported concentrations of xenobiotic organic contaminants in effluents of conventional wastewater treatment facilities (i.e., secondary- or tertiary-treated effluents) were considered in this survey. Over 1000 references reporting occurrence of trace organics in studies across the globe were screened. This comprehensive review considered only articles that were reported in peer-reviewed publications and listed both analytical methods employed and detailed experimental conditions. Papers reporting occurrence in surface water or estimated sewage-treatment-plant effluent concentrations from surface water sources ("surface water under the impact of wastewater discharge") were not considered due to the possibility of undefined dilution. Furthermore, only peer-reviewed papers reporting a sufficient description of the analytical methods were accepted for inclusion. All of the included papers reported the method detection limit (MDL or LOD), limit of quantification (LOQ), or a reporting level (RL) for all of the identified compounds. Several authors have previously conducted literature reviews on the presence of such compounds in environmental samples and in wastewater (Daughton and Ternes, 1999; Halling-Sorensen et al., 1998; Snyder et al., 2003a). However, review criteria applied in these surveys were less stringent than for the review conducted for this study.

From the references screened, over 100 papers published in 15 separate journals from 70 authors were identified as meeting the review criteria of this study. Based upon this survey, the team identified 239 unique wastewater-derived organic micropollutants in treated municipal wastewater effluents. These compounds were classified into 24 categories (i.e., antibacterial, antibiotic). For a full list, see Table 8.1, Appendix. It is noteworthy that the number of compounds detected in each category does not necessarily reflect a real occurrence distribution but is biased through the selection of compounds targeted in studies currently published in the peer-reviewed literature. Based upon the findings of this survey, pharmaceutical residues, antibiotics, steroid hormones, and fragrances were the trace organic compounds most commonly reported as currently occurring in secondary- and tertiary-treated municipal effluents. The majority of studies on EDC and PPCP occurrence in treated wastewater published in the peer-reviewed literature today have been conducted in Europe and North America, followed by Asia, South America, and Australia. The following sections will focus on occurrence of EDCs and PPCPs only in Europe and North America.

### 4.1.1 Detection Frequency in Secondary/Tertiary Effluents

In order to determine regional variability within the data set, a comparison was developed between average detected concentrations in Europe and North America for compounds that had significant reporting and occurrence in studies reported from both continents. The

detection frequencies of select pharmaceutical residues and steroid hormones in secondary/tertiary-treated wastewater effluents reported in studies from North America and Europe are presented in Figures 4.1 and 4.2. The targeted pharmaceutical residues exhibited a detection frequency of 70% in Europe for all compounds selected, whereas a lower detection frequency was observed in effluent samples collected in North America. In contrast, the detection frequency of steroid hormones exceeding 60% was very similar between Europe and North America. Of the four estrogens, 17α-ethynylestradiol exhibited the lowest detection frequency. From the detected compounds in both regions (Europe and North America), some had a notable number of nondetects, which could indicate that these compounds do not always occur in a secondary/tertiary-treated effluent (Table 8.2, Appendix). For both Europe and North America, a high number of nondetects was observed for 17α-ethynylestradiol (EE2), norfloxacin, erythromycin, clofibric acid, and salicylic acid. For Europe, frequent nondetects were observed for roxithromycin, sulfamethoxazole, musk ketone, musk xylene, bisphenol A (BPA), nonylphenol, and octylphenol. For North America, frequent nondetects were observed for carbamazepine, diclofenac, gemfibrozil, ibuprofen, ketoprofen, and naproxen. It is noteworthy that this observation might also be affected by the limited number of studies reported for each region.

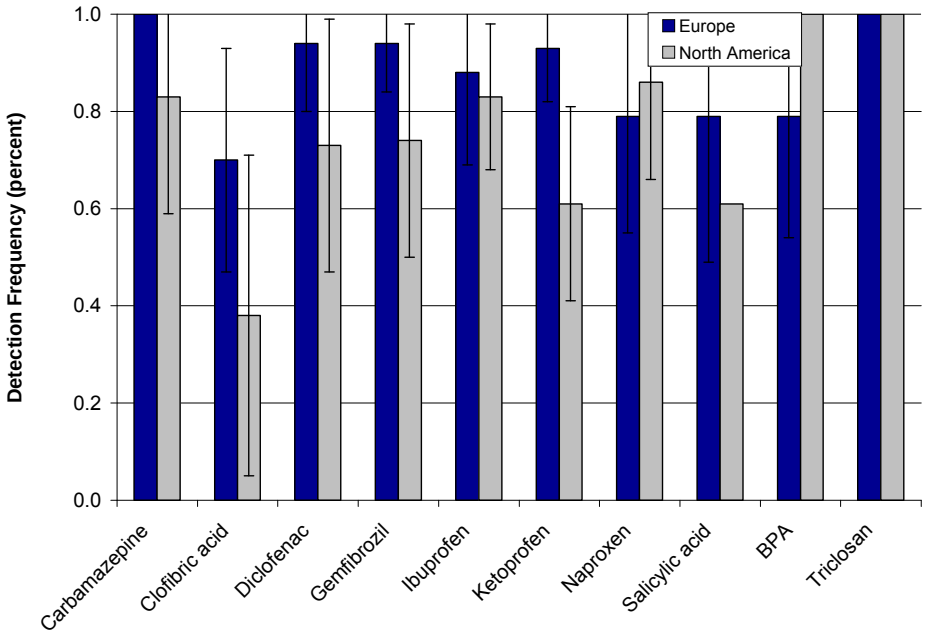



**Figure 4.1. Detection frequencies of select pharmaceutical residues in secondary/tertiary effluents in Europe and North America (error bars represent 1σ standard deviation).**

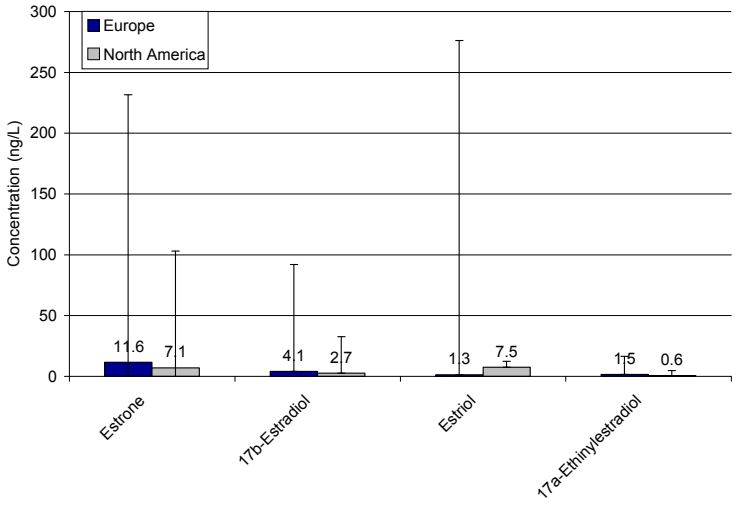



**Figure 4.2. Detection frequencies of select steroid hormones in secondary/tertiary effluents in Europe and North America (error bars represent 1σ standard deviation).**

### 4.1.2 Average Concentrations in Secondary/Treated Effluents

Average concentrations, maximum and minimum concentrations of select compounds representing pharmaceutical residues, steroid hormones, and household chemicals reported to occur in secondary/tertiary-treated effluents both in Europe and North America are presented in Figures 4.3 to 4.6. This comparison revealed that concentrations of a significant number of these commonly occurring compounds are generally higher in Europe than in North America. Notable exceptions to this trend are the antibacterial triclosan, the fragrances HHCB and methyl salicylate, and the surfactant degradation by-product octylphenol, all of which have higher average detected concentrations in North America. Triclosan is a key ingredient in antimicrobial solutions that are widely used in North America but less popular in Europe, resulting in 10-fold-higher effluent concentrations in North America (Figure 4.3). Rather similar concentrations were observed for certain antibiotics (e.g., sulfamethoxazole) and fragrances (e.g., acetyl cedrene, AHTN, benzyl acetate, isobornyl acetate, methyl salicylate, musk xylene, and *p*-*t*-bucinal) (Figure 4.3).

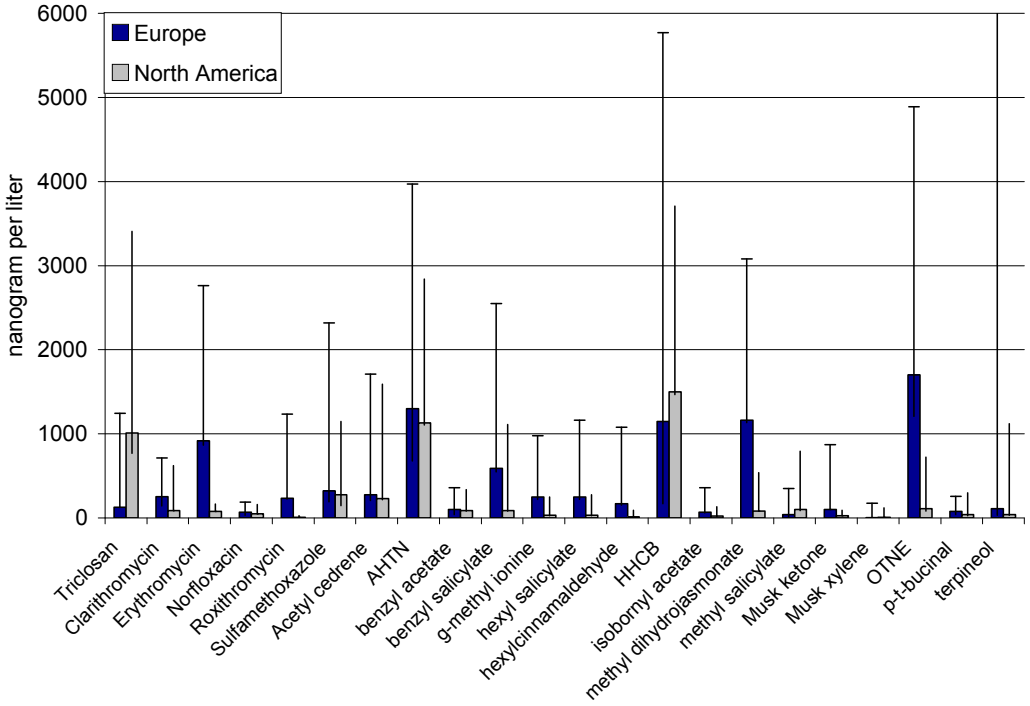



**Figure 4.3. Concentration of select household chemicals in secondary/tertiary effluents in Europe and North America (error bars represent maximum and minimum concentrations reported).**

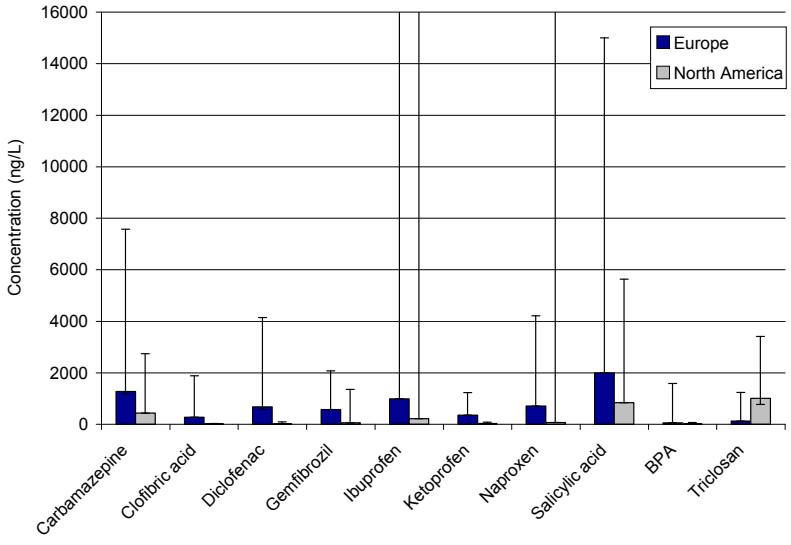



**Figure 4.4. Concentration of select pharmaceutical residues in secondary/tertiary effluents in Europe and North America (error bars represent maximum and minimum concentrations reported).**

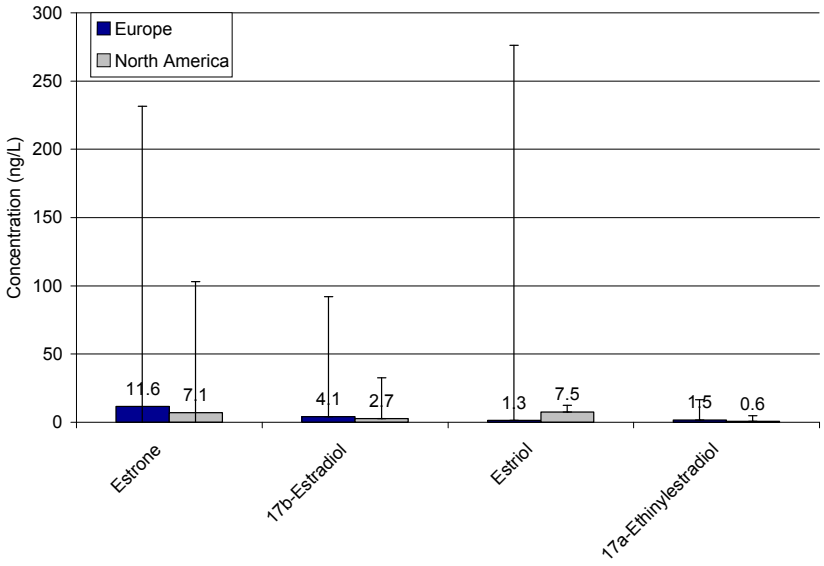



**Figure 4.5. Concentration of select steroid hormones in secondary/tertiary effluents in Europe and North America (error bars represent maximum and minimum concentrations reported).**

Steroid hormones (Figure 4.5) exhibited similar concentrations in treated wastewater effluents in Europe and North America with median concentrations of less than 12 ng/L. Estriol concentrations quantified in treated wastewater effluents were slightly higher in North America than in Europe. The similar occurrence of steroids in Europe and North America is likely due to the occurrence level of hormones in treated wastewater generally being lower than that of pharmaceutical residues and personal care products and a rather efficient removal during conventional wastewater treatment (Drewes et al., 2005a). It is noteworthy that the level of occurrence of pharmaceutical residues and household chemicals was in general higher in European studies than in studies conducted in North America (Figures 4.4 and 4.6).

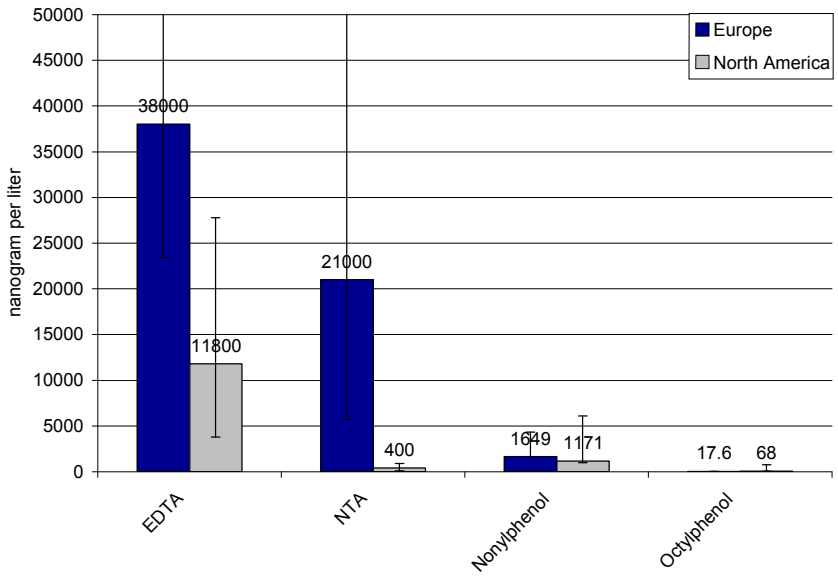



**Figure 4.6. Concentration of select surfactant chemicals in secondary/tertiary effluents in Europe and North America (error bars represent maximum and minimum concentrations reported).**

The occurrence of these target compounds can vary from region to region due to various factors as stated earlier, but two reasons are likely the cause for the difference in occurrence pattern: prescription and consumption practice and per capita water consumption. The prescription practice for pharmaceuticals as well as the usage pattern for certain personal care products can differ between regions and certainly deviates between different countries. For example, clofibric acid, a breakdown product of a blood lipid regulator, is widely administered in central Europe but rarely used in the United States. As a consequence, clofibric acid concentrations in treated wastewater in Europe were approximately 50 times higher (Figure 4.4). A similar ratio was observed for the anti-inflammatory drug diclofenac, its concentrations also being approximately 50 times higher in Europe. Unique prescription practices might also be reflected in the occurrence pattern of gemfibrozil, ketoprofen, and naproxen, which all exhibited significantly higher concentrations in European wastewater effluents.

Another important factor to consider in the occurrence pattern of wastewater-derived contaminants in treated wastewater is the strength of the wastewater produced. The per capita water consumption is usually a factor of 2 to 3 lower in Europe than in the United States, resulting in more highly concentrated wastewater in Europe (AWWA, 2007; BGW, 2007). For pharmaceutical drugs, e.g., ibuprofen, carbamazepine, or salicylic acid (the breakdown product of aspirin) or household chemicals (e.g., EDTA) that are popular in Europe and North America, this pattern would result in a lower occurrence level in North America. Indeed, concentrations of ibuprofen, carbamazepine, salicylic acid, and EDTA are by a factor of 2 to 4 higher in European wastewater effluents than those observed in North American effluents (Figures 4.4 and 4.6).

These findings reveal that the occurrence pattern of wastewater-derived contaminants in treated municipal wastewater effluent is region or country specific and that findings from occurrence studies conducted in one country are not necessarily applicable to other regions of

the world. This regional variability is an important consideration for the selection of trace organics for monitoring purposes.

### 4.1.3 Average Concentrations in North American Secondary/Treated Effluents

In addition to compounds that have been reported to occur both in Europe and North America, Figure 4.7 summarizes reported compounds with average detected concentrations that have been reported only in North America.

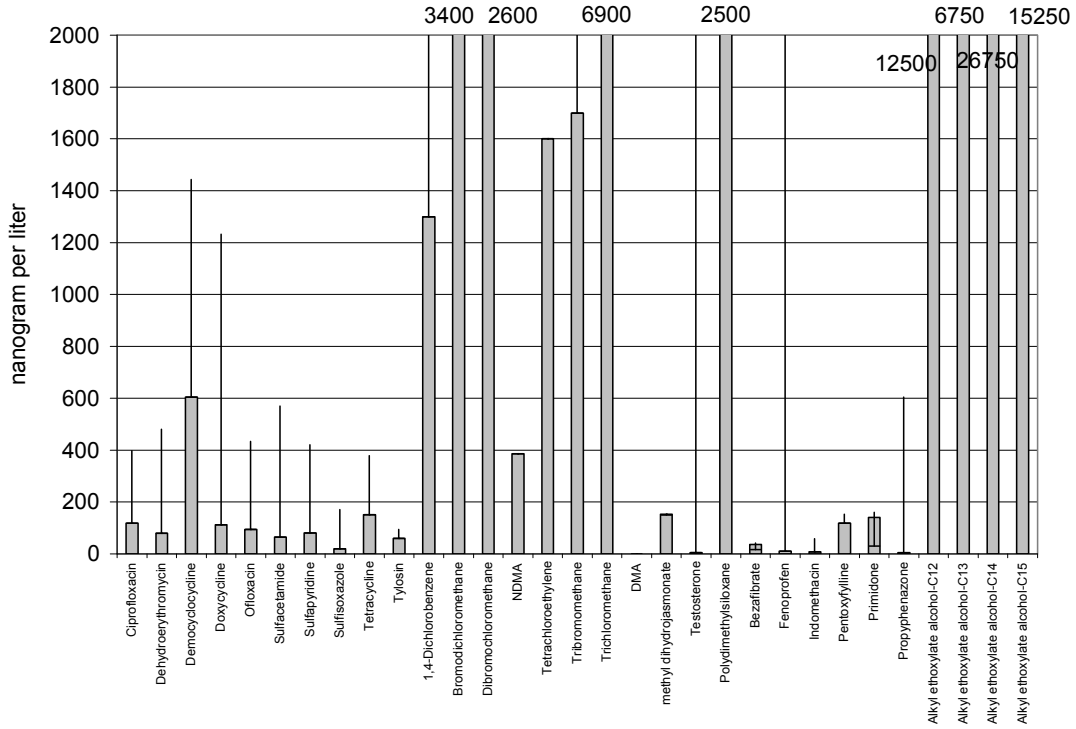



**Figure 4.7. Occurrence of additional trace chemicals in secondary/tertiary effluents in North America only (error bars represent maximum and minimum concentrations reported).**

### 4.1.4 DR of Target Compounds Occurring in Secondary/Treated Effluents

The occurrence database compiled during this survey was used to compare the reported concentrations of organic compounds with the particular analytical MDL, adopting an approach proposed by Sedlak et al. (2005). This detection ratio (DR) is defined as the ratio between median concentration and LOQ (equation 1).

$$DR_{median} = \frac{[Secondary\_Effluent]_{median}}{[LOQ]} \quad (1)$$

Compounds that occur at a ratio of >5 were considered for further evaluation. The research team was aware of the limitations of this approach since MDLs can change or are likely

different among various analytical methods employed. However, this process eliminates those compounds that are not ubiquitously occurring or those for which adequately sensitive analytical techniques that permit monitoring during subsequent advanced treatment processes do not exist.

The most frequently reported analytical methods for reported compounds from studies in Europe and North America along with the MDL and LOQ are summarized in Table 8.2 (Appendix). However, these methods are by no means considered standardized and still deviate regarding SPE, elution practices, derivatization agents, mass ionization, etc. (see related discussion in Chapter 3). The average detected concentration (Figure 4.3) and the LOQ reported in these studies were used to calculate the DRs for each compound, which are presented in Figures 4.8 and 4.9.

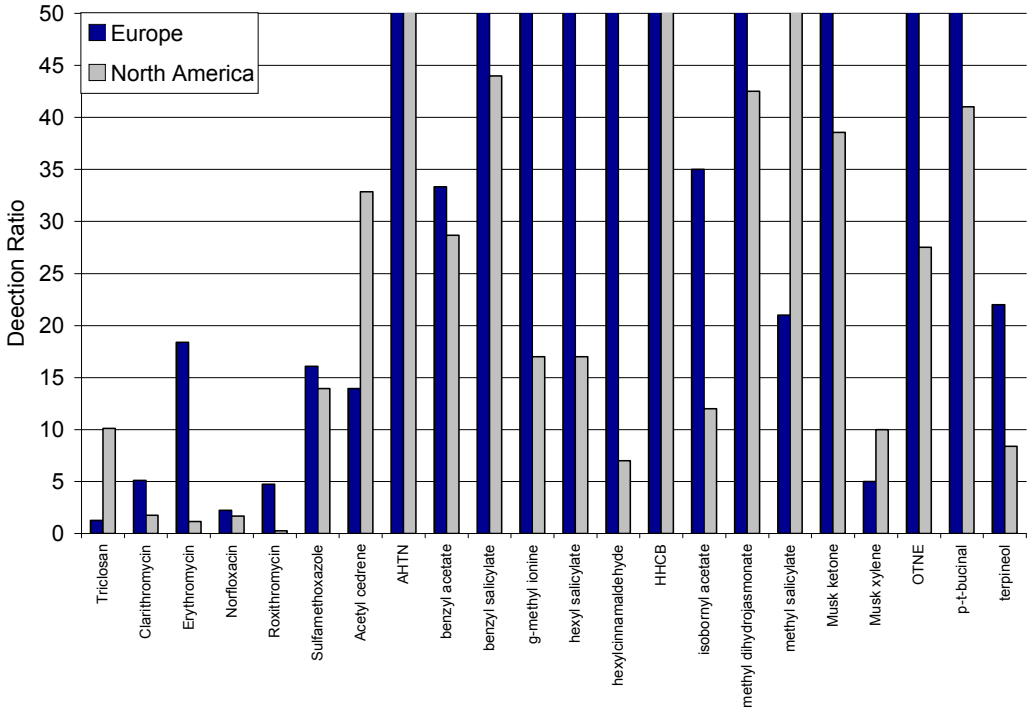



**Figure 4.8. DR of select household chemicals in secondary/tertiary effluents in Europe and North America.**

With a few exceptions, such as triclosan, acetyl credence, methyl salicylate, and musk xylene, DRs of compounds identified in European wastewater effluents are significantly higher than in North American effluents.

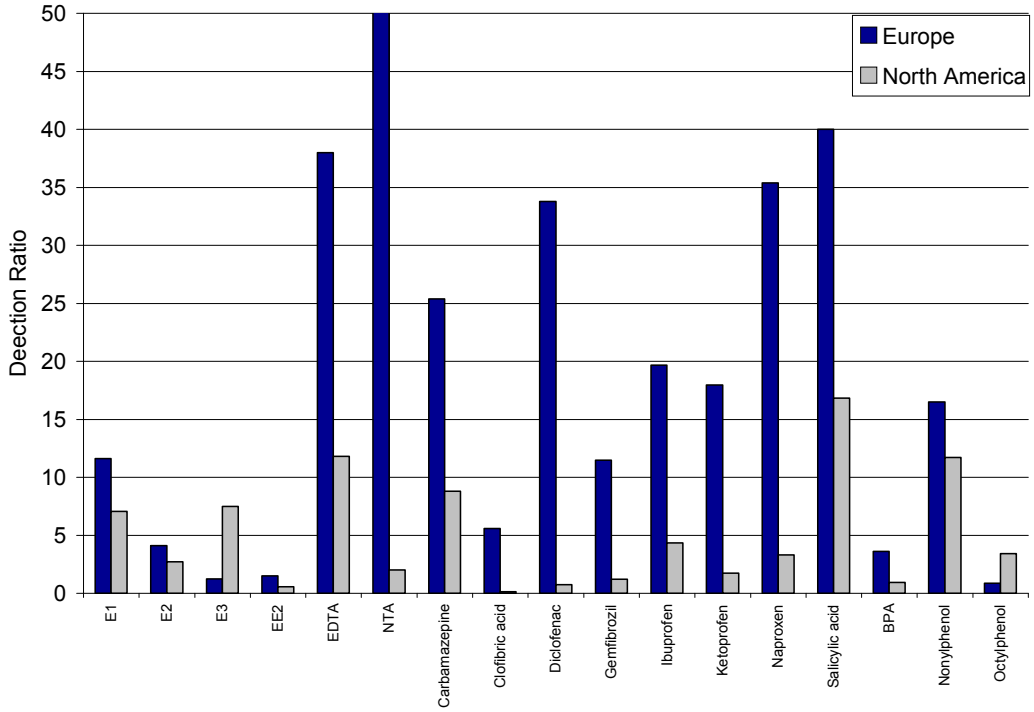



**Figure 4.9. DR of select steroid hormones and PPCPs in secondary/tertiary effluents in Europe and North America.**

In this research project, a DR of larger than 5 served as the threshold to select viable individual constituents as indicator compounds considering the analytical methods reported in the studies. Table 4.1 presents indicator compounds with a DR larger than 5 for compounds reported to occur in secondary/tertiary-treated effluents both in Europe and North America.

**Table 4.1. Indicator Compounds with a DR Larger than 5 for Compounds Reported to Occur Both in Europe and North America**

| Compound | Finding for: | |
|---|---|---|
| | Europe | North America |
| Triclosan | | √ |
| Clarithromycin | √ | |
| Erythromycin | √ | |
| Sulfamethoxazole | √ | √ |
| Acetyl cedrene | √ | √ |
| AHTN | √ | √ |
| Benzyl acetate | √ | √ |
| Benzyl salicylate | √ | √ |
| *g*-Methyl ionine | √ | √ |
| Hexyl salicylate | √ | √ |
| Hexylcinnamaldehyde | √ | √ |
| HHCB | √ | √ |
| Isobornyl acetate | √ | √ |
| Methyl dihydrojasmonate | √ | √ |
| Methyl salicylate | √ | √ |
| Musk ketone | √ | √ |
| Musk xylene | | √ |
| OTNE | √ | √ |
| *p*-*t*-Bucinal | √ | √ |
| Terpineol | √ | √ |
| Estrone (E1) | √ | √ |
| Estriol (E3) | | √ |
| EDTA | √ | √ |
| NTA | √ | |
| Carbamazepine | √ | √ |
| Clofibric acid | √ | |
| Diclofenac | √ | |
| Gemfibrozil | √ | |
| Ibuprofen | √ | |
| Ketoprofen | √ | |
| Naproxen | √ | |
| Salicylic acid | √ | √ |
| Nonylphenol | √ | √ |

For compounds that have been reported to occur in North America only (Figure 4.7), the DRs are summarized in Figure 4.10.

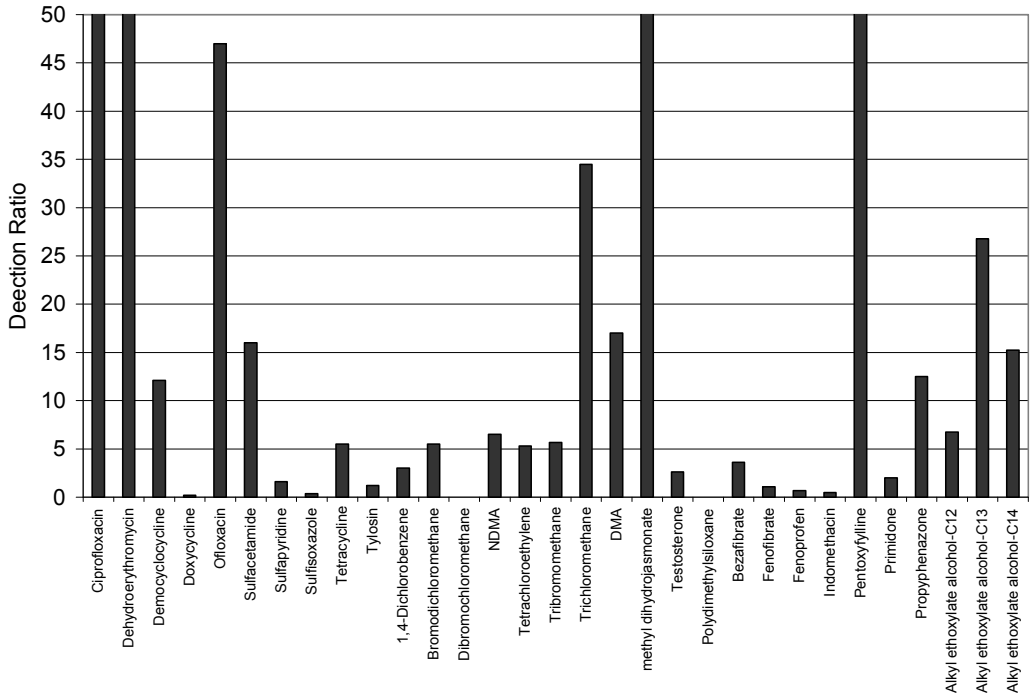



**Figure 4.10. DR of additional trace chemicals in secondary/tertiary effluents in North America only.**

## 4.2 OCCURRENCE OF INDIVIDUAL COMPOUNDS IN CONVENTIONAL TREATED WASTEWATER EFFLUENTS BASED UPON AN INTERNAL OCCURRENCE SURVEY AMONG TEAM MEMBERS

In addition to the indicator compound survey that was based on peer-reviewed journal articles, an "internal" occurrence survey was performed among members of the research team. This survey of trace organic occurrence in secondary- or tertiary-treated wastewater effluents has drawn upon the yet-to-be published findings and ongoing projects among the three principal investigators. Additional occurrence data generated by CSM, UC, and SNWA are summarized in Tables 8.3 to 8.5 (see Appendix).

## 4.3 FINAL LIST OF VIABLE INDICATOR COMPOUNDS OCCURRING IN CONVENTIONAL TREATED WASTEWATER EFFLUENTS

The DR approach (median effluent concentration divided by the LOQ) has been used to further evaluate organic compounds reported in the literature and "internal" surveys. The DR was calculated for each compound, and a DR larger than 5 served as the threshold to select viable individual constituents as indicator compounds considering the analytical methods reported in the studies. Table 4.2 presents the final list of viable indicator compounds with a DR larger than 5 for compounds reported to occur in North America based upon the comprehensive literature review and the internal occurrence survey. The second column

highlights those indicator compounds for which analytical methods were available among the team members. The physicochemical properties of the selected indicator compounds are summarized in Table 8.6 (Appendix).

**Table 4.2. Indicator Compounds with a DR Larger than 5 for Compounds Reported to Occur in North America for Both the Comprehensive Literature Review and Internal Occurrence Survey**

| Indicator Compound | Analytical Methods Available within Project |
|---|---|
| Acetaminophen | ✓ |
| Acetyl cedrene | |
| Atenolol | ✓ |
| Atorvastatin | ✓ |
| Atorvastatin (*o*-hydroxy) | ✓ |
| Atorvastatin (*p*-hydroxy) | ✓ |
| Benzyl acetate | |
| Benzyl salicylate | |
| Bisphenol A | ✓ |
| Bucinal | |
| Butylated hydroxyanisole | |
| Caffeine | ✓ |
| Carbamazepine | ✓ |
| Chloroform | ✓ |
| Ciprofloxacin | |
| DEET | ✓ |
| Dichlorprop | ✓ |
| Diclofenac | ✓ |
| Dilantin | ✓ |
| EDTA | ✓ |
| Erythromycin–$H_2O$ | ✓ |
| Estriol (E3) | ✓ |
| Estrone (E1) | ✓ |
| Fluoxetine | ✓ |
| Galaxolide | |
| Gemfibrozil | ✓ |
| Hexyl salicylate | |
| Hexylcinnamaldehyde | |
| Hydrocodone | ✓ |
| Ibuprofen | ✓ |
| Indolebutyric acid | |
| Iopromide | ✓ |

*Continued*

| Indicator Compound | Analytical Methods Available within Project |
|---|---|
| Isobornyl acetate | |
| Isobutylparaben | |
| Ketoprofen | ✓ |
| Mecoprop | ✓ |
| Meprobamate | ✓ |
| Methyl dihydrojasmonate | |
| Methyl ionine | |
| Methyl salicylate | |
| Metoprolol | ✓ |
| Musk ketone | |
| Musk xylene | |
| Naproxen | ✓ |
| NDMA | ✓ |
| Nonylphenol | |
| Norfluoxetine | ✓ |
| Ofloxacin | |
| OTNE | |
| Phenylphenol | |
| Primidone | ✓ |
| Propranolol | ✓ |
| Propylparaben | |
| Salicylic acid | ✓ |
| Simvastatin hydroxy acid | ✓ |
| Sulfamethoxazole | ✓ |
| TCEP | ✓ |
| TCPP | ✓ |
| TDCPP | ✓ |
| Terpineol | |
| Tonalide | |
| Triclocarban | |
| Triclosan | ✓ |
| Trimethoprim | ✓ |

# CHAPTER 5

# SURROGATE AND INDICATOR FRAMEWORK TO ASSESS PERFORMANCE OF WATER RECLAMATION PROCESSES

## 5.1 INTRODUCTION

Building upon the previously compiled list of selected surrogate parameters and indicator compounds (see Chapters 3 and 4) and by considering their (1) median DR, (2) physicochemical properties, and (3) reported treatability and fate in the environment, as well as (4) analytical detection methods, we classified indicators and surrogates into categories of different treatability. These treatment categories include conventional and advanced water treatment processes commonly employed in indirect potable reuse applications. The treatment processes are characterized by key removal mechanisms, such as biodegradation (i.e., SAT and MBR), chemical oxidation (i.e., ozonation, advanced oxidation, chlorination, and chloramination), photolysis (i.e., low- and medium-pressure UV radiation), adsorption (i.e, GAC), or physical separation (i.e., NF and RO). Physicochemical properties (e.g., molecular size, $pK_a$, log $K_{ow}$, volatility, and dipole moment) often determine the fate and transport of a compound in various treatment processes (Chang et al., 2002; Snyder et al., 2003a; Drewes et al., 2003b; Bellona et al., 2004). Thus, selecting multiple indicators representing a broad range of properties will allow accounting for compounds currently not identified and new compounds synthesized and entering the environment in the future (i.e., new pharmaceuticals) provided they fall within the range of properties covered by the selected indicator compounds. Relevant characteristics of the individual compounds (i.e., MW, $pK_a$, and log $K_{ow}$) were compiled (Table 8.6, Appendix) and considered while removal efficiencies were assessed. To monitor system performance at a given facility, the selection of appropriate indicator compounds will depend upon the treatment processes comprising an overall treatment train and the geographic and temporal variations in the occurrence pattern of certain wastewater-derived contaminants. Therefore, the determination of appropriate indicator compounds and surrogate parameters for a given treatment train can vary from site to site.

In each treatment category, indicator compounds were given a removal rating and were classified as follows: “good removal (> 90%),” “intermediate removal (25% < x < 50% and 50% < x < 90%),” or “poor removal (< 25%).” This classification of indicators into removal categories for individual unit processes is dependent upon the physicochemical and biodegradable properties of the compounds, whereas the degree of removal usually depends upon operational conditions of the treatment process (e.g., oxidant dose concentration, type of activated carbon, water matrix, and CT). Along with this classification, relevant operational boundary conditions were defined for each type of treatment. For each treatment process, a master list of indicator compounds is provided by recruiting compounds from the final list of viable indicator compounds for which peer-reviewed analytical methods existed (Table 4.2).

A similar treatment classification scheme for surrogate parameters was developed. Surrogate parameters considered for each of the key removal mechanisms of interest are summarized in Table 5.1. The suitability of each surrogate parameter to assess performance of a treatment process is discussed for each treatment category.

**Table 5.1. Selected Surrogate Parameters for Treatment Categories**

| Mechanism | Surrogate for Performance Assessment |
|---|---|
| Biodegradation | BDOC |
| | TOC |
| | COD |
| | Inorganic anions and cations (e.g., $NH_4$-N, $NO_3$-N) |
| | Fluorescence |
| | UVA |
| Chemical oxidation | TOC |
| | UVA |
| | Color |
| | Fluorescence |
| | Oxidant CT |
| UV disinfection | — |
| Adsorption | Hydrophobic/hydrophilic DOC |
| | Adsorption analysis |
| | TOC |
| | UVA |
| | Color |
| | Fluorescence |
| Physical separation | TOC |
| | UVA |
| | Conductivity |
| | TDS |
| | Hardness |
| | Boron |
| | Inorganic anions and cations (e.g., $NH_4$-N, $NO_3$-N, and calcium) |

Within the gamut of organic chemicals present in recycled water, individual compounds and bulk parameters selected as indicators and surrogates also have to fulfill the criteria of practicability and regulatory compliance. The practicability of selected surrogates and indicators (i.e., the ease with which the compound can be monitored and its predictive ability) was assessed through pilot- and full-scale monitoring efforts, and key findings are documented in this chapter. Recommendations on how the surrogate and indicator framework can be applied to performance and compliance monitoring are provided in Chapter 7.

## 5.2 TREATMENT CATEGORIES FOR INDIVIDUAL PROCESSES

Water treatment processes discussed in this chapter represent conventional and advanced unit processes commonly employed in planned indirect potable reuse applications. The focus of this study was directed to processes beyond conventional secondary and tertiary wastewater treatment.

### 5.2.1 Biodegradation

Biodegradation is the predominant removal mechanism of naturally based treatment systems such as SAT, riverbank filtration, and aquifer recharge and recovery, as well as of engineered systems such as BAC filters or MBRs. This section highlights what surrogate parameters and indicator compounds could be used to assess treatment systems employing, for example, SAT or MBR.

#### *5.2.1.1 SAT*

Recycled water applied to spreading basins leading to SAT usually has previously received secondary or tertiary treatment and disinfection. Most SAT operations are characterized by percolation of water through a vadose zone followed by additional attenuation processes occurring in the saturated zone of the underlying aquifer. The primary removal mechanisms during SAT for target contaminants include adsorption to soil grains or soil organic matter and/or biodegradation under oxic and/or anoxic redox conditions. A significant amount of research has been conducted to understand the performance of SAT systems in removing pathogens, TOC, nutrients, and select trace organics (Drewes and Fox, 1999; Drewes and Fox, 2000; Leenheer et al., 2001; Fox et al., 2001; Drewes et al., 2003b; Drewes et al., 2006).

Building upon this knowledge base, results revealed from laboratory-scale experiments during this study, and findings from supplemental studies conducted by members of the research team, we developed universal treatment removal categories for indicator compounds of SAT systems (Table 5.2). This master list has been augmented with compounds that had a DR of >5 but were not monitored during this study. Estimates of their removal during SAT were accomplished by using structural property relationships (i.e., log $K_{ow}$ and biodegradability based on EPA BioWin calculations). The operational boundary conditions of this master list are a TOC concentration of less than 10 mg/L in the recycled water prior to spreading, a travel time in the subsurface of approximately 4 weeks, redox regimens that transition from oxic to anoxic between the point of spreading and abstraction, low organic carbon soil, and no dilution with native groundwater during the 4-week travel time.

**Table 5.2. Treatment Removal Categories for Indicator Compounds of SAT Systems**[a]

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

[a]Recycled water quality: TOC concentration < 10 mg/L; subsurface conditions: travel time ≥4 weeks; predominant redox conditions: oxic followed by anoxic; dilution with native groundwater: 0%. Removal of compounds with no footnote was verified through peer-reviewed data or experimental data generated during this study.

[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.

As demonstrated by previous studies, indicator compounds that exhibit removal exceeding 90% during SAT are acidic drugs (e.g., ibuprofen, ketoprofen, naproxen, diclofenac, gemfibrozil, and salicylic acid) (Drewes et al., 2002; Drewes et al., 2003b), trimethoprim (Snyder et al., 2007a), pesticides (e.g., mecoprop and dicloprop), caffeine (Drewes et al.,

2003b), EDTA and nonylphenol (Montgomery-Brown et al., 2003), steroid hormones (Mansell and Drewes, 2004), NDMA (Drewes et al., 2006), and iopromide (Putschew and Jekel, 2001; Schittko et al., 2004). Indicator compounds that exhibit more hydrophobic properties (i.e., exceeding a log $K_{ow}$ of 3) can also potentially adsorb to soil and/or organic matter. Of the well-removed compounds listed in Table 5.2 and measured during experiments in this study, only the antimicrobial triclosan exhibited a hydrophobic character (log $K_{ow}$ of 5.8), which likely resulted in some adsorptive losses during SAT (Heidler and Halden, 2007) in addition to biotransformation. Considering these easily removable indicator compounds in SAT, a partial performance failure of an SAT system due to a loss of biological activity would be displayed by a shift of these compounds into intermediate- or poor-removal categories.

Six compounds exhibited conservative behavior during SAT, namely, chlorinated flame retardants (i.e., TCEP, TCPP, and TDCPP) and antiepileptic drugs (i.e., primidone, carbamazepine, and dilantin). The recalcitrant character of these compounds is consistent with findings published previously (Drewes et al., 2003b; Amy and Drewes, 2006; Snyder et al., 2007a). None of these compounds exhibits hydrophobic properties resulting in a significant retardation or adsorption to porous media. If indeed removal of these compounds is observed in groundwater recharge projects, likely dilution with unimpaired water occurred.

In order to validate the master indicator list for SAT systems, three full-scale SAT sites were selected for performance monitoring. All three SAT sites received either secondary- or tertiary-treated wastewater effluents and were in operation for many years. All sites were well instrumented with multiple monitoring wells, and the hydrogeology had been characterized in previous studies, allowing an estimation of travel times to monitoring wells utilized during the sampling campaigns (Fox et al., 2001). For all three sites, the research team had access to historic water quality data generated during previous research efforts. Samples were analyzed for most of the indicator compounds listed in Table 5.2 and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of DR being > 5 (see Table 4.2).

**SAT Operation No. 1**

SAT operation no. 1 (Facility 7) is characterized by an extensive vadose zone approximately 120 ft (40 m) in depth. Two sampling campaigns were conducted at this site. Samples were collected from the spreading basin, a shallow lysimeter well (5 ft or 1.5 m below ground surface), and a monitoring well (130 ft or 43 m below ground surface) representing the underlying groundwater quality. The spreading basin received secondary-treated, nonnitrified effluent. Synoptic samples were collected after approximately 5 days from the shallow lysimeter well and after approximately 2 weeks from the groundwater well. The observed removal percentage ranges of indicator compounds quantified at this site exhibiting a DR of >5 in the secondary-treated effluent are summarized in Table 5.3. The absolute concentrations for samples collected at this site are reported in Table 8.7 (Appendix).

Several compounds classified as “good removal (>90%)” during SAT (Table 5.2) were already removed after a travel time of 5 days, but some acidic drugs (i.e., diclofenac, gemfibrozil, ibuprofen, and naproxen), NDMA, EDTA, meprobamate, trimethoprim, and sulfamethoxazole required a longer retention time to achieve a similar degree of removal. The recalcitrant indicator compounds (i.e., antiepileptic drugs and chlorinated flame retardants) were, as expected, not removed after 5 days of SAT; however, these compounds shifted to higher removal categories after 2 weeks of travel. This shift is likely due to the combination of a slight degree of dilution with native groundwater, potential errors associated with the

measurement of low nanograms-per-liter levels, and an unrepresentative presentation of the slug of water sampled after 2 weeks although synoptic sampling was attempted. It is noteworthy that all of the additional compounds analyzed for were efficiently removed during SAT after 2 weeks of travel time (see Table 8.7, Appendix).

**SAT Operation No. 2**

SAT operation no. 2 (Facility 1) is characterized by spreading into a short vadose zone followed by saturated flow conditions. One sampling campaign was conducted at this site. Synoptic samples were collected from the spreading basin and from downgradient monitoring wells, each representing travel times of approximately 2 weeks. The recharge basin received nitrified or denitrified tertiary-treated effluent during the time of spreading. The observed removal percentage ranges of indicator compounds quantified at a DR of >5 are summarized in Table 5.4 for the monitoring well representing 2 weeks' travel time. Absolute concentrations for samples collected at the spreading basin and one of the monitoring wells are summarized in Table 8.8 (Appendix).

After 2 weeks of SAT, indicator compounds classified in the category "good removal" were also well removed at this site with the exception of sulfamethoxazole, which might require more time to achieve a high degree of removal. The shift of several recalcitrant indicator compounds to the "intermediate removal" category indicated that some degree of dilution with native groundwater was occurring at this site.

**Table 5.3. Removal of Indicator Compounds of SAT Operation No. 1**[a]

*Removal after 5 Days*

| Good Removal (>90%) | Intermediate Removal | | Poor Removal (<25%) |
|---|---|---|---|
| | 90–50% | 50–25% | |
| 17β-Estradiol | Diclofenac | | Carbamazepine |
| Atenolol | Gemfibrozil | | Dilantin |
| Atorvastatin | Ibuprofen | | Primidone |
| Caffeine | Naproxen | | TCEP |
| Estrone | NDMA | | TCPP |
| Fluoxetine | Trimethoprim | | TDCPP |
| Norfluoxetine | | | Meprobamate |
| *o*-Hydroxy atorvastatin | | | Sulfamethoxazole |
| *p*-Hydroxy atorvastatin | | | EDTA |
| Salicylic acid | | | |
| Simvastatin hydroxy acid | | | |
| Triclosan | | | |

*Removal after 2 Wks*

| Good Removal (>90%) | Intermediate Removal | | Poor Removal (<25%) |
|---|---|---|---|
| | 90–50% | 50–25% | |
| 17β-Estradiol | Dilantin | Primidone | Carbamazepine |
| Atenolol | | TCEP | |
| Atorvastatin | | TCPP | |
| Caffeine | | TDCPP | |
| Diclofenac | | | |
| EDTA | | | |
| Estrone | | | |
| Fluoxetine | | | |
| Gemfibrozil | | | |
| Ibuprofen | | | |
| Meprobamate | | | |
| Naproxen | | | |
| NDMA | | | |
| Norfluoxetine | | | |
| *o*-Hydroxy atorvastatin | | | |
| *p*-Hydroxy atorvastatin | | | |
| Salicylic acid | | | |
| Simvastatin hydroxy acid | | | |
| Sulfamethoxazole | | | |
| Triclosan | | | |
| Trimethoprim | | | |

[a]Recycled water quality: TOC, 9.9 mg/L; subsurface conditions: travel time in subsurface, 5 to 14 days; predominant redox conditions: oxic to anoxic.

**Table 5.4. Removal of Indicator Compounds of SAT Operation No. 2**[a]

| *Removal after 2 Wks* | | | |
|---|---|---|---|
| **Good Removal (>90%)** | **Intermediate Removal** | | **Poor Removal (<25%)** |
| | **90–50%** | **50–25%** | |
| Acetaminophen | Dilantin | Carbamazepine | |
| Androstenedione | Sulfamethoxazole | | |
| Caffeine | Primidone | | |
| DEET | TCEP | | |
| Diclofenac | TCPP | | |
| EDTA | TDCPP | | |
| Erythromycin–$H_2O$ | | | |
| Estrone | | | |
| Gemfibrozil | | | |
| Hydrocodone | | | |
| Ibuprofen | | | |
| Iopromide | | | |
| Meprobamate | | | |
| Metoprolol | | | |
| Naproxen | | | |
| Salicylic acid | | | |
| Trimethoprim | | | |

[a]Recycled water quality: TOC, 6.57 mg/L; subsurface conditions: travel time, 14 days; predominant redox conditions: anoxic.

### SAT Operation No. 3

SAT operation no. 3 (Facility 1) is also characterized by spreading into a short vadose zone followed by saturated flow conditions. One sampling campaign was conducted at this site. Synoptic samples were collected from the spreading basin, a downgradient monitoring well representing a travel time of approximately 1 month, and a monitoring well representing a travel time of approximately 3 months. The recharge basin received nitrified/denitrified tertiary-treated effluent during the time of spreading. The observed removal percentages of indicator compounds quantified at a DR of >5 for samples collected from the two monitoring wells are summarized in Table 5.5. Absolute concentrations for samples collected at this site are reported in Table 8.9 (Appendix).

Indicator compounds classified in the category "good removal" were also removed at this site, confirming previous observations. While the antiepileptic drugs primidone and carbamazepine exhibited poor removal after 1 month of SAT, these compounds along with polar chlorinated flame retardants tended to shift to higher removal categories with increasing travel time. These findings suggest that dilution with native groundwater became more important with increasing distance from the spreading basin.

**Table 5.5. Removal of Indicator Compounds of SAT Operation No. 3**[a]

| *Removal after 1 Mo.* | | | |
|---|---|---|---|
| **Good Removal (>90%)** | **Intermediate Removal** | | **Poor Removal (<25%)** |
| | **90–50%** | **50–25%** | |
| 17β-Estradiol<br>Estrone<br>Gemfibrozil<br>Mecoprop<br>Naproxen<br>NDMA | TCEP<br>TDCPP | TCPP | Carbamazepine<br>Primidone |
| *Removal after 3 Mo.* | | | |
| **Good Removal (>90%)** | **Intermediate Removal** | | **Poor Removal (<25%)** |
| | **90–50%** | **50–25%** | |
| 17β-Estradiol<br>Estrone<br>Gemfibrozil<br>Mecoprop<br>Naproxen<br>NDMA | TCEP<br>TCPP<br>TDCPP | Carbamazepine<br>Primidone | |

[a]Recycled water quality: TOC, 4.1 mg/L; subsurface conditions: travel times, 1 and 3 months; predominant redox conditions: anoxic.

The surrogate parameters measured during the sampling campaigns at the three SAT operations are summarized in Table 5.6. Significant changes of several bulk measurements support previous observations that SAT is a highly biologically active process and that many water quality changes already occur in the initial phase of SAT. Within 2 weeks of SAT, TOC, SUVA, COD, TOI, and UVA were reduced to concentrations that represent the recalcitrant nature of the remaining organic matter. These surrogates are limited in reflecting additional transformations of the organic matter during subsequent travel in the subsurface. The surrogate parameter BDOC was determined in controlled laboratory experiments under both oxic and anoxic conditions for a groundwater sample after 2 weeks of SAT. The sample did not exhibit any measurable DOC (Figure 5.1), confirming that the site is biologically active and that ample time was provided to remove the BDOC in the recycled water during 2 weeks of SAT.

**Table 5.6. Surrogate Parameters Quantified during Sampling of the Three Full-Scale SAT Facilities**

| | Approximate Travel Time | TOC (mg/L) | SUVA (L/mg m) | COD (mg/L) | TOX (μg/L) | TOI (μg/L) | UVA (1/cm) | Protein Fluor (AU) | Humic Fluor (AU) | $NH_3$-N (mg/L) | $NO_3$-N (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SAT operation no. 1 | | 9.92 | 3.12 | 70 | 152 | 11.0 | 0.31 | 1.9 | 3.6 | 31 | 0.4 |
| Lysimeter | 5 days | 5.91 | 3.89 | 33 | 134 | 9.3 | 0.23 | 0.89 | 2.3 | 1.5 | 19 |
| Monitoring well | 2 wks | 1.40 | 6.71 | <10 | 58 | 5.6 | 0.094 | 0.28 | 0.48 | <0.05 | 10 |
| SAT operation no. 2 | | 6.57 | 1.98 | — | — | 3.7 | 0.13 | 0.67 | 2.9 | 0.99 | 2.8 |
| Monitoring well | 2 wks | 1.58 | 2.21 | — | — | 2.8 | 0.035 | 0.13 | 0.95 | 0.04 | 1.7 |
| Monitoring well | 2 wks | 1.55 | 1.87 | — | — | 2.6 | 0.029 | 0.14 | 0.72 | ND | 1.6 |
| SAT operation no. 3 | | 4.11 | 2.06 | — | 58 | 6.6 | 0.085 | — | — | 0.27 | 1.0 |
| Monitoring well | 1 mo. | 1.65 | 2.18 | — | 68 | 6.1 | 0.036 | — | — | 0.10 | 1.1 |
| Monitoring well | 3 mos. | 1.71 | 2.1 | — | <20 | 7.8 | 0.036 | — | — | <0.1 | 1.2 |

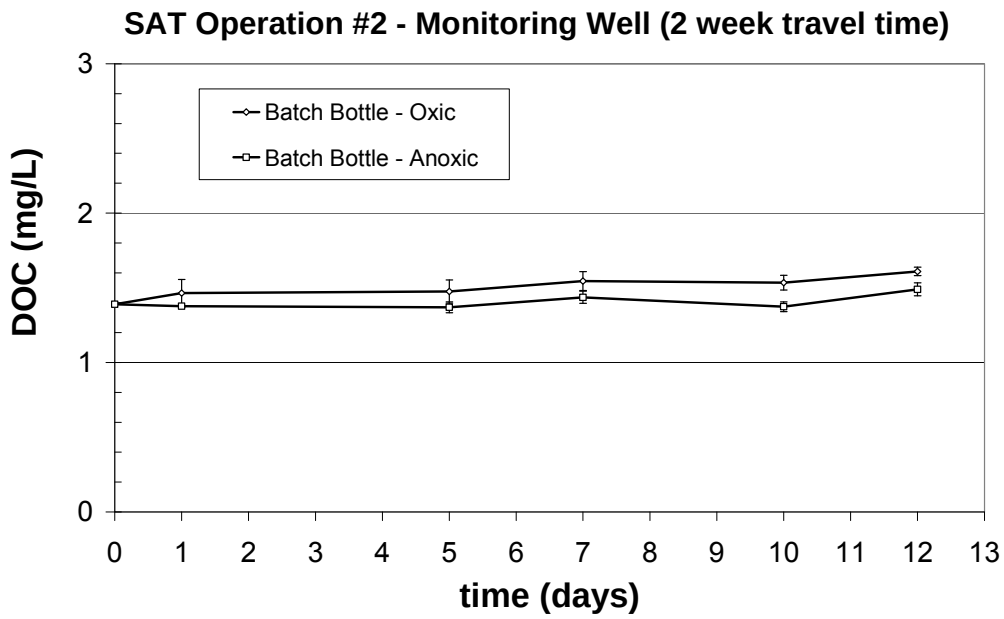



**Figure 5.1. BDOC measured as DOC in groundwater sample after 2 weeks of SAT.**

Ammonia concentrations were also quickly reduced to levels close to the detection limit after short-term SAT (Figure 5.2). At sites where nitrate concentrations are elevated and providing denitrifying conditions exist, the change of nitrate nitrogen could be tracked to represent additional water quality changes during long-term SAT. The removal of phosphate during SAT was rather small and is less suitable as a performance measure of SAT.

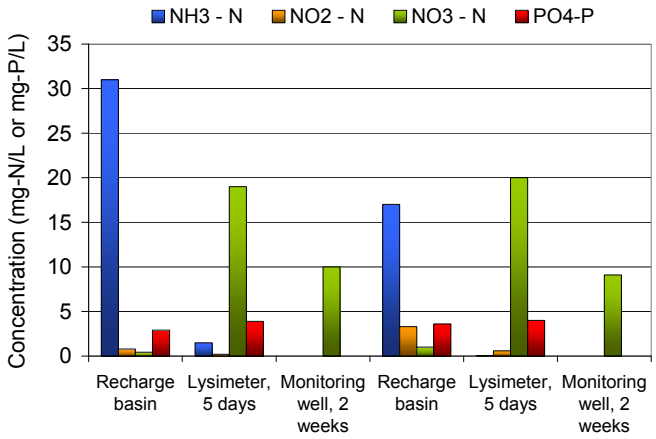



**Figure 5.2. Change of nitrogen and phosphorus concentrations during full-scale SAT.**

Slightly more sensitive at registering additional changes of organic matter during longer subsurface travel times were the surrogate parameters SUVA and SFLUOR. The latter is a measurement at a given excitation/emission wavelength normalized to DOC. The

fluorescence emissions are compound specific, and 3-D excitation/emission spectral analysis permits distinguishing protein-like from humus-like organic matter (McKnight et al., 2001; Amy and Drewes, 2006). For SAT operation no. 1, the SUVA significantly increased between 5 days and 2 weeks of SAT, suggesting a preferable removal of nonaromatic organic carbon structures in the initial phase of SAT. SFLUOR provides additional insight into the transformations of organic matter. The SFLUOR-protein index does not change in the infiltration phase of SAT, whereas the SFLUOR–humic acid index increased in a manner similar to that of SUVA. At a later phase in SAT, the SFLUOR-protein index increased significantly because non-protein-like organic matter is degraded.

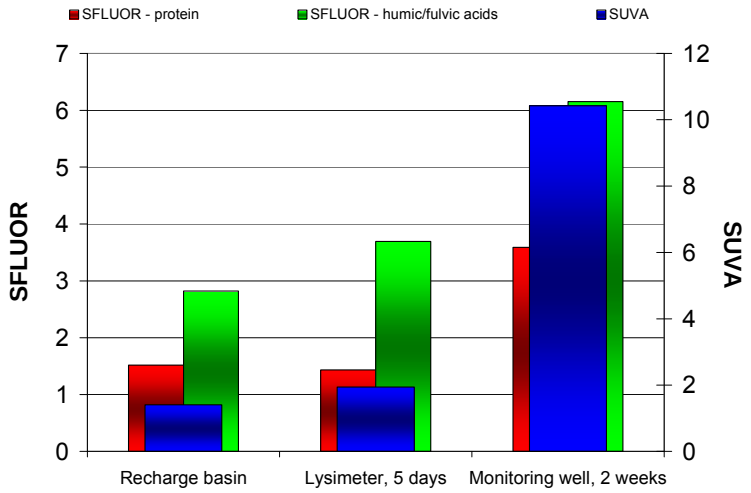



**Figure 5.3. Change of surrogate parameters SFLUOR and SUVA during full-scale SAT.**

The 3-D fluorescence spectra for the spreading basin as well as for the lysimeter and groundwater monitoring samples collected at SAT operation no. 1 are illustrated in Figure 5.4. 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. Therefore, sensitive surrogate parameters exist to describe the biological activity and biological performance of an SAT process.

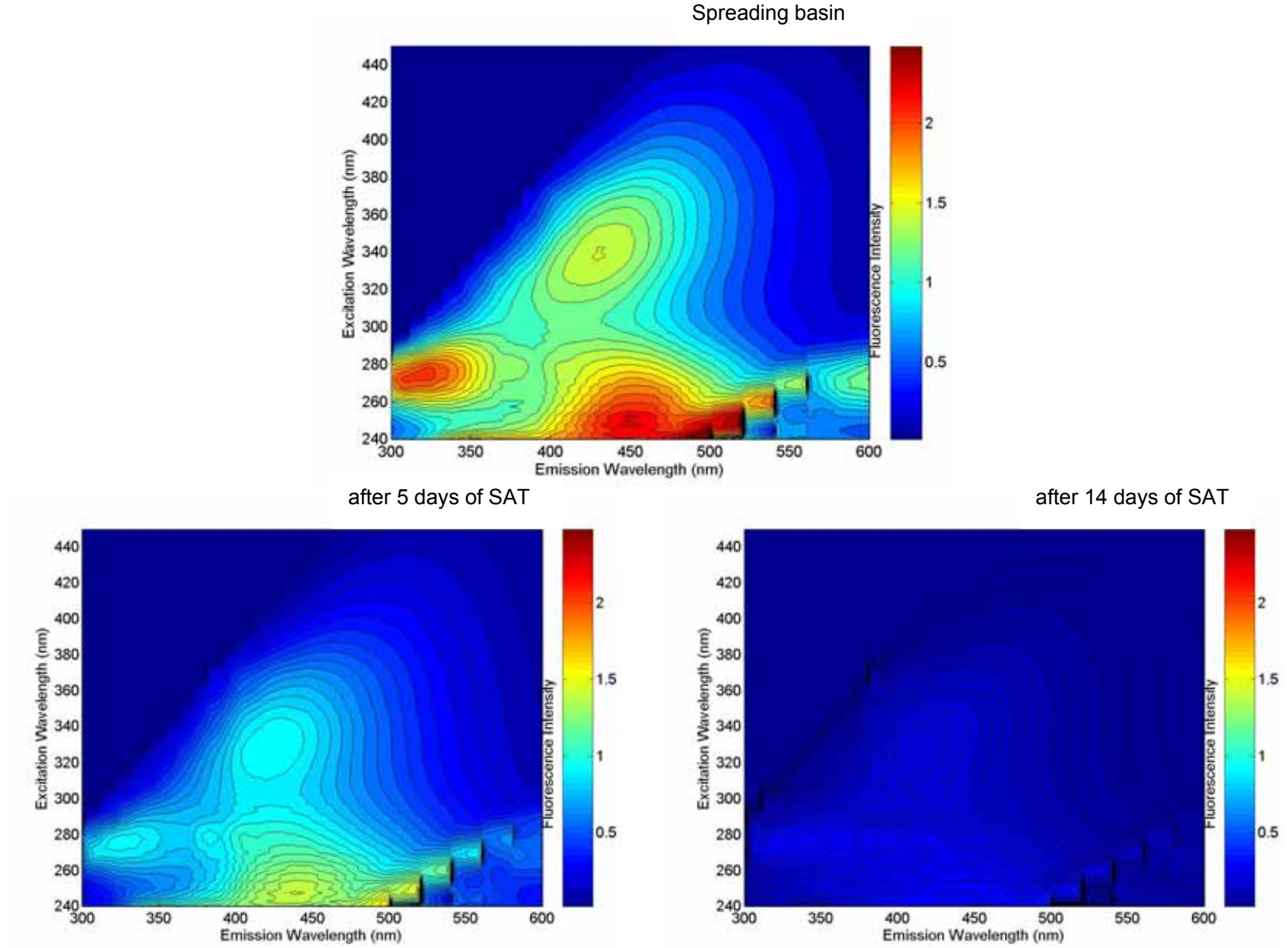



**Figure 5.4. Change of the surrogate parameter fluorescence during full-scale SAT.**

#### *5.2.1.2 MBR*

Four sampling campaigns were conducted to monitor the performance of a full-scale MBR (Facility 10) and a pilot-scale MBR receiving primary effluent from Facility 1. At Facilities 1 and 10, primary effluent and raw wastewater, respectively, and MBR permeate samples were collected. The average mixed liquor aeration time of the full- and pilot-scale MBRs varied between 5 and 8 h, and the solid retention time (SRT) varied between 10 and 15 days. The pilot- and full-scale MBRs operated at a mixed liquor suspended-solid concentration of approximately 7500 to 8500 mg/L and 14,000 mg/L, respectively. Samples were analyzed for select indicator compounds and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2). Because the database generated during these experiments was limited, no master list of indicator compounds for MBR treatment was developed. However, to illustrate the fate of indicator compounds during MBR treatment, the observed removal percentages at both MBR operations are summarized in Table 5.7. Absolute concentrations for compounds listed in Table 5.7 are summarized in Tables 8.10 and 8.11 (Appendix). The observed removal during MBR treatment is consistent with previous studies (Clara et al., 2005; Drewes et al., 2005a; Snyder et al., 2007a). With some exceptions, compounds classified in the "good removal" category were efficiently removed (>90%) during MBR treatment and were similar to those in SAT operations (Table 5.2). However, EDTA, meprobamate, or sulfamethoxazole exhibited a removal of less than 50%. Although monitoring efforts and previous studies of SAT operations demonstrated that these compounds are amenable to biotransformation, likely the lack of a more diverse or adopted biocommunity and sufficient retention time resulted in rather poor removal during MBR treatment. Since the primary effluent at Facility 1 was fed not only to the pilot-scale MBR but also to a full-scale nitrifying/denitrifying activated sludge system (10 million gallons per day [mgd] or 37,800 $m^3$/day), a direct comparison of indicator compound removal by activated sludge and MBR treatment was possible (Figure 8.1 [Appendix]). Findings from this study revealed a similar degree of removal of select indicator compounds by both treatment systems.

The observed removal percentages of select indicator compounds and surrogate parameters during MBR treatment are compared in Figure 5.5. The surrogate parameter BOD was entirely removed (<2 mg/L) during treatment and thus lacked the sensitivity to properly represent MBR system performance. The surrogate parameters TOC and UVA exhibited removals of 86 and 81%, respectively, and might serve as conservative parameters to monitor the removal of indicator compounds classified in the "good removal" category and to represent proper operating conditions.

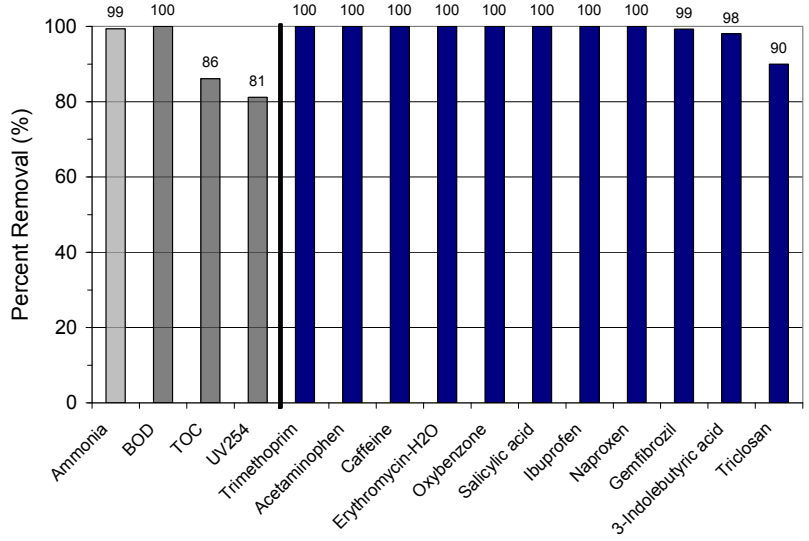



**Figure 5.5. Removal of select surrogate parameters and indicator compounds during MBR treatment.**

**Table 5.7. Removal of Indicator Compounds during MBR Treatment**[a]

| Good Removal (>90%) | | Intermediate Removal | | Poor Removal (<25%) |
|---|---|---|---|---|
| | | 90–50% | 50–25% | |
| Bisphenol A | Menthol | Atenolol | EDTA (total) | Carbamazepine |
| Acetaminophen | Naproxen | Atorvastatin | Fluoxetine | Dilantin |
| Benzophenone | Norfluoxetine | Atorvastatin (*o*-hydroxy) | Sulfamethoxazole | Meprobamate |
| Butylated hydroxyanisole | Oxybenzone | Atorvastatin (*p*-hydroxy) | TCEP | |
| Caffeine | Phenacetine | DEET | TCPP | |
| Enalapril | Phenoxyethanol | NDMA | | |
| Erythromycin–$H_2O$ | Phenylphenol (*o*-) | Simvastatin hydroxy acid | | |
| Gemfibrozil | Propylparaben | Trimethoprim | | |
| Ibuprofen | Salicylic acid | | | |
| Indolebutyric acid | Simvastatin | | | |
| Isobutylparaben | Triclosan | | | |
| Mecoprop | Vanillin | | | |

[a]Primary effluent quality: TOC concentration, 40 to 60 mg/L; SRT, 15 days; MLSS, ~3500 mg/L.

### 5.2.2 Chemical Oxidation

Chemical oxidation is the predominant removal mechanism of oxidation processes, such as ozone ($O_3$) and advanced (i.e., UV/$H_2O_2$, ozone/$H_2O_2$, and ozone/UV) oxidation, as well as of disinfection processes (i.e., chlorination and chloramination). This section highlights how the proposed surrogate and indicator framework can be applied to assess the performance of treatment systems employing, for example, ozone, AOPs, chloramination, and chlorination.

#### *5.2.2.1 Ozonation*

A significant amount of research has been conducted to understand the performance of ozonation systems in removing select wastewater-derived contaminants (Hoigne and Bader, 1983; Adams et al., 2002; Andreozzi et al., 2002; Huber et al., 2003; Ternes et al., 2003; Lenz et al., 2004; Westerhoff et al., 2005; Huber et al., 2005; McDowell et al., 2005; Yang et al., 2005; Hua et al., 2006; Vieno et al., 2007; Lei and Snyder, 2007; Lee et al., 2007; Drewes et al., 2008). Building upon this knowledge base, results revealed from laboratory-scale experiments during this study, and findings from supplemental studies conducted by members of the research team, we developed universal treatment removal categories for indicator compounds of ozonation systems (Table 5.8).

**Table 5.8. Treatment Removal Categories for Indicator Compounds of Systems Using Ozone[a]**

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

[a]Conditions: wastewater, tertiary treated; TOC, <10 mg/L; ozone exposure: >26 mg min/L. Removal of compounds with no footnote was verified through peer-reviewed literature data or experimental data generated during this study.

[b]Hydroxy aromatic (activating).

[c]Amino aromatic (activating).

[d]Acylamino aromatic (activating).

[e]Alkoxy aromatic (activating).

[f]Alkyl aromatic (activating).

[g]Aliphatic (halogens).

[h]Aliphatic ketone/hydroxyl/ester.

[i]Cycloalkane/cycloalkene.

[j]Aromatic with heterocyclic ring (nitrogen containing).

This master list has been augmented with compounds that had a DR of >5 but for which removal through oxidation was not estimated during this study. Estimates were accomplished by examining the compounds' structural properties. The operational boundary conditions of this master list are a TOC concentration of less than 10 mg/L in the recycled water, a contact time of 20 min, and an ozone dosage of 7 mg/L. Ozone exposure conditions represent an upper margin of typical recycled water ozonation. Thus, the reported removal efficiencies of trace organics might be lower at less favorable conditions.

Ozone reacts with organic compounds through either the direct reaction with molecular ozone or through the formation of free radicals, including the hydroxyl radical (HO•). Oxidation reactions through ozone or hydroxyl radicals usually do not result in mineralization; therefore, oxidation products should be expected. Molecular ozone is a selective electrophile that reacts quickly with double bonds, activated aromatic systems, and nonprotonated amines. These preferred reaction pathways allow an assessment of the likelihood of ozone reacting with trace organic compounds:

- In general, electron-donating groups (e.g., hydroxyl, amine, conjugated double bond, and sulfide) enhance reactivity with ozone, whereas electron-withdrawing groups (e.g., iodine, chlorine, fluorine, and nitro) reduce the reaction rate.
- Electron-donating groups enhance the reactivity of aromatic compounds toward ozone, while electron-withdrawing groups inhibit the reactivity.
- Phenolic compounds are highly amenable to an attack by ozone, whereas ketone groups decrease the reactivity of ozone with adjacent carbons on aromatic structures.
- Hydroxyl and ketone groups have an activating effect on the adjacent methylene groups of an aliphatic chain, though the oxidation rates are lower than those of corresponding aromatic structures.

Alkalinity, pH, and NOM, as well as certain inorganic compounds, affect the concentrations of ozone available for reactions with trace organic compounds. NOM and elevated pH (i.e., presence of hydroxide ions) can promote the formation of HO• radicals.

In order to validate the master indicator list for ozone systems, one full-scale ozone facility was monitored and additional experiments were conducted by using a laboratory-scale ozone system under controlled conditions. For the full-scale site, the research team had access to historic water quality data generated during previous research efforts. Samples were analyzed for many of the indicator compounds listed in Table 5.8 and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2).

**Full-Scale Ozone Operation**

Facility 5 employs ozonation disinfection for tertiary- and activated carbon–treated wastewater. A relatively low ozone dose of 1 mg/L with an estimated contact time of less than 1 min is applied at this facility. Indicator compounds classified in the categories "good removal (>90%)" and "intermediate removal (90–50%)" were efficiently removed as predicted (Table 5.9). With the exception of compounds not amenable to oxidation with ozone (i.e., chlorinated flame retardants), only atrazine exhibited a partial removal of 32%. However, it is important that the concentration of atrazine in the recycled water was already less than 6 ng/L and that the rather low removal efficieny for atrazine might simply be the result of a lack of analytical sensitivity. Absolute concentrations for compounds listed in Table 5. 9 are summarized in Table 8.12 (Appendix).

**Table 5.9. Removal of Indicator Compounds during Full-Scale Ozone Operation**

| Good Removal (>90%) | Intermediate Removal | | Poor Removal (<25%) |
|---|---|---|---|
| | 90–50% | 50–25% | |
| Atenolol | Meprobamate | Atrazine | TCEP |
| Carbamazepine | Dilantin | | TCPP |
| Gemfibrozil | Bisphenol A | | TDCPP |
| Sulfamethoxazole | | | EDTA |
| Trimethoprim | | | |

[a]Conditions: tertiary-treated wastewater; 1 mg of ozone/L; <1-min contact time.

### Laboratory-Scale Ozone Operation

A tertiary-treated effluent sample was collected at Facility 2 and delivered to the SNWA Laboratories. A 55-gal. (200-L) stainless steel drum was used to feed the tertiary-treated wastewater effluent sample to a laboratory-scale ozone skid at a design flow rate of 1 L/min. The experimental setup is described in section 2.4.2; the ozone conditions are summarized in Table 2.3. Three ozone dosages were applied (2, 3.6, and 7 mg/L as $O_3$) with contact times varying between 2 and 18 min. The observed removal efficiencies for indicator compounds are summarized in Figure 5.6, for which it should be noted that removal of ibuprofen in excess of 90% was not achievable because the feed concentration was already close to the detection limit. Absolute concentrations for indicator compounds before and after ozonation are are summarized in Table 8.13 (Appendix).

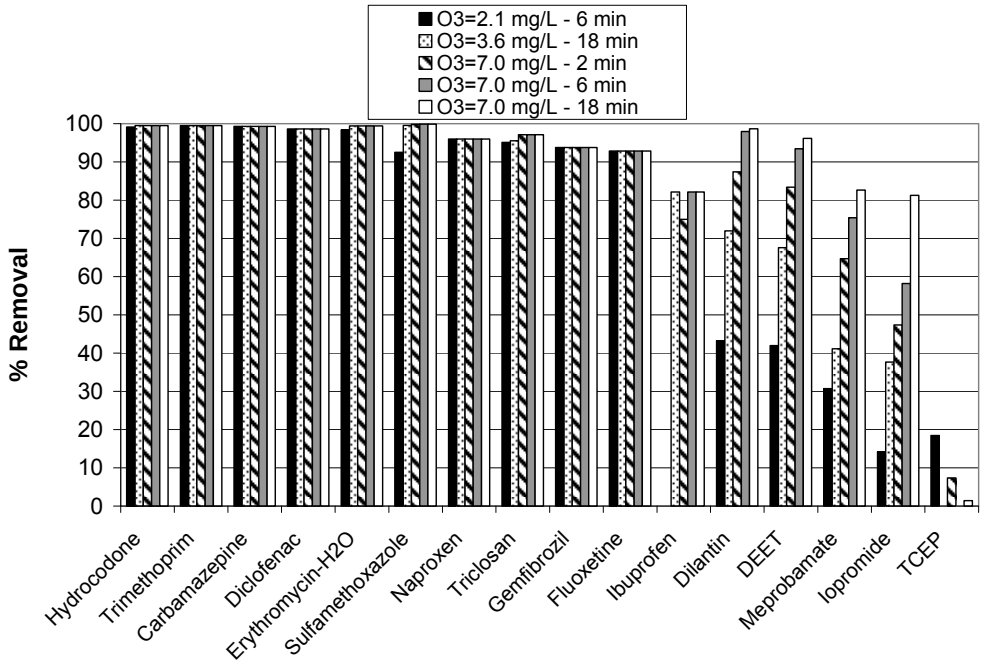



**Figure 5.6. Removal of indicator compounds during laboratory-scale ozone experiments.**

Findings from these controlled studies confirm that low ozone dosages and short exposure times are sufficient to achieve a high removal (>90%) of indicator compounds classified in the category "good removal" (Table 5.8). For indicator compounds classified as "intermediate removal" (e.g., dilantin, DEET, meprobamate, and iopromide), a higher ozone dose resulted in higher removal. For these compounds (e.g., meprobamate and iopromide), longer ozone exposure also resulted in higher removals, indicating that the direct oxidation reaction with ozone might be kinetically hindered. The indicator compounds present in tertiary-treated wastewater fed to the laboratory-scale ozone skid for an ozone dose of 7 mg/L and a contact time of 18 min are classified by observed removal percentages in Table 5.10. The removal of indicator compounds observed under these conditions agrees well with the indicator compound master list for ozone systems (Table 5.8).

The observed changes of surrogate parameters during ozonation both at laboratory and full scale are summarized in Table 5.11. Of the surrogate compounds examined, UVA removal exhibited the highest degree of sensitivity to increasing ozone dosages and correlated well with greater removal of indicator compounds (Figure 5.7).

**Table 5.10. Removal of Indicator Compounds during Laboratory-Scale Ozone Operation**

| Good Removal (>90%) | Intermediate Removal | | Poor Removal (<25%) |
|---|---|---|---|
| | 90–50% | 50–25% | |
| Butylated hydroxyanisole | Bisphenol A | Vanillin | TCEP |
| Carbamazepine | Ibuprofen | | |
| DEET | Indolebutyric acid | | |
| Diclofenac | Iopromide | | |
| Dilantin | Meprobamate | | |
| Erythromycin–$H_2O$ | | | |
| Estrone | | | |
| Fluoxetine | | | |
| Gemfibrozil | | | |
| Hydrocodone | | | |
| Naproxen | | | |
| Sulfamethoxazole | | | |
| Triclocarban | | | |
| Triclosan | | | |
| Trimethoprim | | | |

[a]Conditions: tertiary-treated wastewater; 7 mg of ozone/L; 18-min contact time.

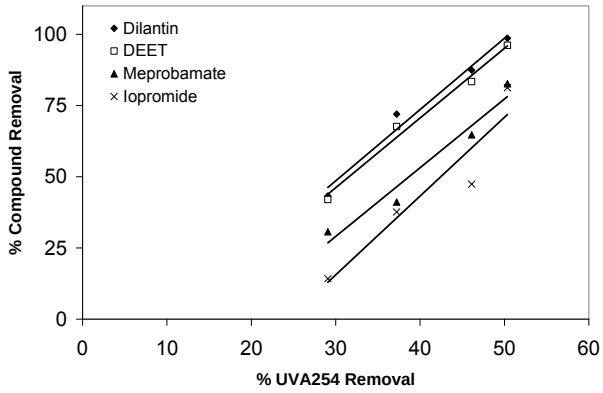



**Figure 5.7. Correlation between removal of UVA and that of indicator compounds.**

For the full-scale ozone treatment facility (Facility 5), measurements of the 3-D fluorescence spectra prior to and after ozonation indicate that significant changes of the organic matter structure had occurred during ozonation (Figure 5.8).

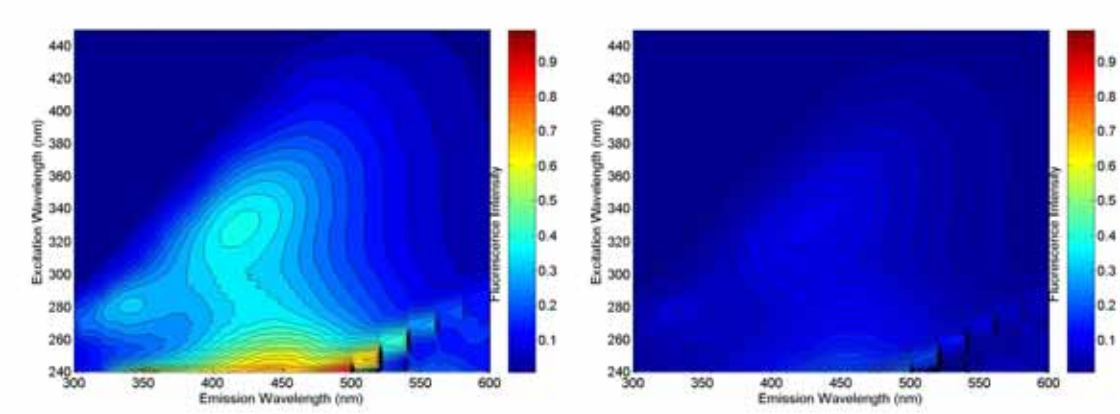



**Figure 5.8. 3-D fluorescence spectra prior to and after ozonation.**

Of the by-products formed during ozonation, formate and assimilable organic carbon (AOC) might also serve as surrogate parameters to assess the efficiency of ozonation. However, UVA is much easier and faster to quantify than formate or AOC. In addition, certain operational parameters can be considered to assess the efficiency of an ozonation process. The oxidant exposure time or integral contact time (CT) is also highly correlated with removal of more problematic indicator compounds (classified as "intermediate removal") (Figure 5.9) and can be easily tracked or integrated into the supervisory control and data acquisition system of an ozonation facility.

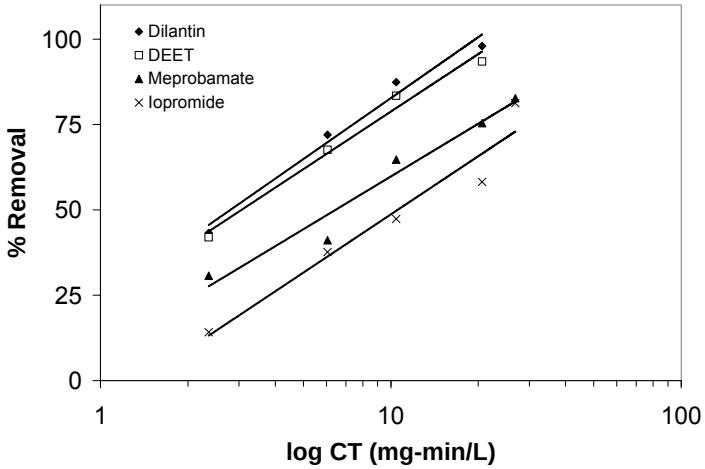



**Figure 5.9. Correlation between CT and removal of select indicator compounds.**

**Table 5.11. Surrogate Parameters Quantified during Sampling of Laboratory- and Full-Scale Ozone Operations**

| Scale of Operation | Ozone Dose (mg/L) | Contact time (min) | Concn or value of: CT (mg-min/L) | TOC (mg/L) | TOX (μg/L) | TOI (μg/L) | UVA (1/cm) | Bromate (μg/L) | Formate (μg/L) | Oxalate (μg/L) | Aldehydes (μg/L) | AOC (μg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab-scale operation | 0 | 0 | 0 | 6.84 | 499 | 12.2 | 0.123 | <1 | <20 | 45 | 22 | 320 |
| | 2.1 | 6 | 2.4 | 6.84 | — | — | 0.087 | <1 | 209 | 84 | — | — |
| | 3.6 | 10 | 6.1 | 6.99 | 384 | 7.8 | 0.077 | 2.8 | 377 | 116 | 114 | 971 |
| | 7 | 2 | 10.4 | — | — | 8.8 | 0.066 | 8.7 | — | — | — | — |
| | 7 | 6 | 20.6 | — | — | — | — | 20 | — | — | — | — |
| | 7 | 18 | 26.8 | 6.91 | 424 | 8.1 | 0.061 | 23 | 526 | 274 | 149 | 1149 |
| Full-scale operation | 0 | 0 | 0 | 5.6 | — | 7.2 | 0.075 | — | — | — | — | — |
| | 1 | <1 | — | 5.6 | — | 2.6 | 0.045 | — | — | — | — | — |

#### *5.2.2.2 AOPs*

AOPs can form hydroxyl radicals, which can nonselectively attack and transform organic compounds. Examples of AOPs include ozone/hydrogen peroxide, UV/hydrogen peroxide, and UV/ozone. Hydroxyl radicals usually exhibit higher reaction rates than does ozone and therefore can play an important role in the oxidation of compounds reacting slowly with ozone. NOM can initiate the formation of hydroxyl radicals, whereas humic substances and bicarbonate can scavenge radicals.

Significant research has been conducted in the recent past to understand the performance of AOPs in removing select wastewater-derived contaminants. Zwiener and Frimmel (2000) reported removal efficiencies exceeding 90% for diclofenac, ibuprofen, and clofibric acid at ozone and hydrogen peroxide doses greater than 3.7 and 1.4 mg/L, respectively ($O_3$:$H_2O_2$ = 2.5 mg/mg; 10-min CT). For a UV/$H_2O_2$ process, Rosenfeldt and Linden (2004) observed removal exceeding 90% of bisphenol A, 17β-estradiol, and 17α-ethynylestradiol at a UV dose of 1000 mJ/cm$^2$ and a hydrogen peroxide dose of 15 mg/L. Huber et al. (2003) observed that the ozone/hydrogen peroxide AOP considerably increased the removal of ibuprofen from 40 to 80% as compared to ozone alone. Similar observations were made by Westerhoff et al. (2005), who reported the addition of a small amount of $H_2O_2$ (i.e., 0.025 mg of $H_2O_2$/mg of $O_3$) prior to ozonation generally improved the extent of trace organic compound oxidation by 5 to 15% as compared to ozone alone. AOPs are very effective treatment processes for oxidizing wastewater-derived contaminants; however, compared to ozone, AOPs provide little additional benefit in removal efficiency for the majority of compounds of interest.

Building upon this knowledge base, results revealed from laboratory-scale experiments during this study, and findings from supplemental studies conducted by members of the research team, we developed universal treatment removal categories for indicator compounds of AOP systems (Table 5.12). The operational boundary conditions of this master list are a feedwater quality equivalent to that of RO-treated recycled water, an ozone dose of 7 mg/L, a hydrogen peroxide dose of 3.5 mg/L, and a 2-min contact time.

As compared to similar oxidation conditions using ozone alone (Table 5.8), compounds classified as “intermediate removal” and “poor removal” shifted to compounds classified as “good removal” in the master list of ozone indicator compounds. This shift is likely driven by higher oxidation reaction rates in the presence of hydroxyl radicals. Chloroform and chlorinated flame retardants, however, were not amenable to oxidation using either ozone or AOPs.

It is noteworthy that removal efficiencies similar to those reported in Table 5.12 for ozone/$H_2O_2$ were observed for UV/$H_2O_2$ AOPs using low-pressure high-output and medium-pressure UV radiation (1000 mJ/cm$^2$) in the presence of hydrogen peroxide (10 mg of $H_2O_2$ per L) (Pereira et al., 2007a; Pereira et al., 2007b; Rosenfeldt and Linden, 2004). However, NDMA is better removed by UV/$H_2O_2$ AOP systems (Sharpless and Linden, 2003).

**Table 5.12. Treatment Removal Categories for Indicator Compounds of AOP Systems**[a]

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

[a]Conditions: RO-treated feedwater; 7 mg of ozone per L, 3.5 mg of $H_2O_2$ per L; 2-min contact time.

In order to validate the master indicator list for AOP systems, experiments were conducted with a laboratory-scale ozone/$H_2O_2$ system under controlled conditions. In addition, performance monitoring of a full-scale UV/AOP using RO-treated recycled water was conducted. For the full-scale site, the research team had access to historic water quality data generated during previous research efforts. Samples were analyzed for most of the indicator compounds listed in Table 5.12 and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2).

**Laboratory-Scale AOP Operation**

A tertiary-treated effluent sample was collected at Facility 2 and delivered to the SNWA laboratories. A 55-gallon (200 L) stainless steel drum was used to feed the tertiary-treated wastewater effluent sample to a laboratory-scale ozone/hydrogen peroxide skid at a design flow rate of 1 L/min. The experimental setup is described in section 2.4.2; the ozone conditions are summarized in Table 2.3. Three ozone dosages were applied (2, 3.6, and 7 mg/L as $O_3$) with contact times varying between 2 and 10 min. Alongside ozone, hydrogen peroxide was applied at dosages of 1, 2, and 3.5 mg/L. The observed removal efficiencies by ozone/$H_2O_2$ for indicator compounds are summarized in Figure 5.10. Absolute concentrations for indicator compounds before and after advanced oxidation are are summarized in Table 8.13 (Appendix).

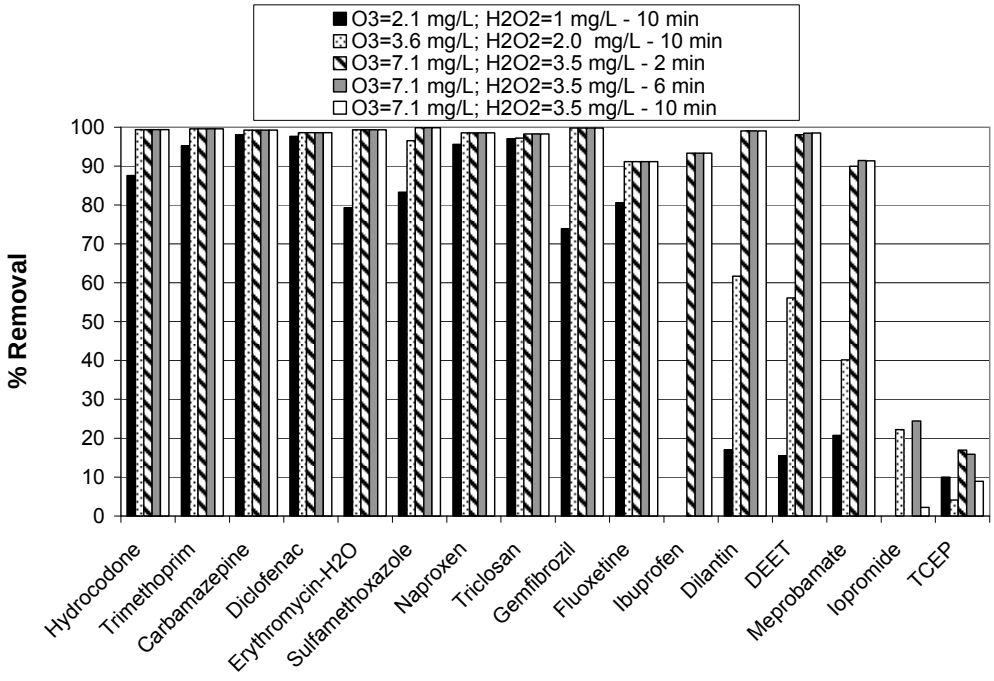



**Figure 5.10. Removal of indicator compounds during laboratory-scale AOP experiments.**

Findings of these controlled experiments confirm the high efficiency of AOP at oxidizing the majority of wastewater-derived organic compounds even in the presence of organic matter (i.e., tertiary-treated effluent). Higher dosages of ozone were necessary to achieve a more complete oxidation of ibuprofen, dilantin, DEET, and meprobamate. A direct comparison of the oxidation efficiencies of ozone/$H_2O_2$ and ozone alone is illustrated in Figure 5.11. When the same ozone dose was used, similar degrees of removal were achieved by ozone and ozone/$H_2O_2$ with a significantly shorter exposure time for treatment by AOP. The lower removal of iopromide, an X-ray contrast agent, during AOP was unexpected, but Snyder et al. (2007a) observed the same or slightly better removal of iopromide in the presence of hydrogen peroxide with the same initial ozone concentration. The removal efficiencies of indicator compounds during controlled laboratory-scale ozone/$H_2O_2$ conditions are summarized in Table 5.13.

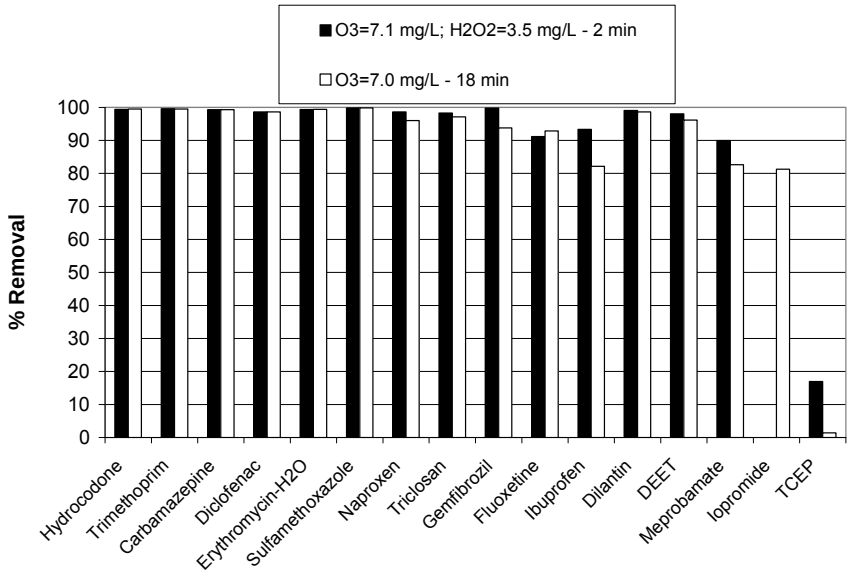



**Figure 5.11. Removal of indicator compounds during laboratory-scale AOP and ozone experiments.**

**Table 5.13. Removal of Indicator Compounds during Laboratory-Scale AOP Operation**[a]

| Good Removal (>90%) | Intermediate Removal (90–50%) | Intermediate Removal (50–25%) | Poor Removal (<25%) |
|---|---|---|---|
| 3-Indolebutyric acid | Vanillin | | TCEP |
| Bisphenol A | | | Iopromide |
| Butylated hydroxyanisole | | | |
| Carbamazepine | | | |
| DEET | | | |
| Diclofenac | | | |
| Dilantin | | | |
| Erythromycin–$H_2O$ | | | |
| Estrone | | | |
| Fluoxetine | | | |
| Gemfibrozil | | | |
| Hydrocodone | | | |
| Ibuprofen | | | |
| Meprobamate | | | |
| Naproxen | | | |
| Sulfamethoxazole | | | |
| Triclocarban | | | |
| Triclosan | | | |
| Trimethoprim | | | |

[a]Conditions: tertiary-treated watewater; 7 mg of ozone/L, 3.5 mg of $H_2O_2$/L; 2-min contact time.

### Full-Scale AOP Operation

Two sampling campaigns were conducted at a full-scale facility (Facility 4) employing an $UV/H_2O_2$ AOP using RO-treated recycled water. The facility is utilizing a low-pressure high-output UV system (i.e., 50 to 100 $mJ/cm^2$) and a hydrogen peroxide dose of 3 mg/L. Given the extensive pretreatment (i.e., activated sludge, ultrafiltration, and RO), only a few indicator compounds were detected in the recycled water feeding the AOP system (Table 5.14). None of the indicator compounds present in the feedwater exceeded a concentration of 30 ng/L. Of the indicator compounds detected in the feedwater, concentrations were further reduced by the $UV/H_2O_2$ treatment either to undetectable levels or traces at the lowest nanograms-per-liter range. Considering the observed removal efficiencies, indicator compounds detected in the AOP feedwater were classified into categories of different removal efficiencies (Table 5.15).

**Table 5.14. Concentrations of Indicator Compounds before and after Full-Scale AOP Treatment**[a]

| Indicator Compound | After RO (ng/L) | After AOP (ng/L) |
|---|---|---|
| Atenolol | 11 | 2.1 |
| Atorvastatin | <0.25 | <0.25 |
| Atrazine | <0.25 | <0.25 |
| Bisphenol A | <5.0 | <5.0 |
| Carbamazepine | 0.80 | <0.50 |
| Diclofenac | <0.25 | <0.25 |
| Dilantin | <1.0 | <1.0 |
| Estrone | <0.2 | <0.2 |
| Fluoxetine | <0.50 | <0.50 |
| Gemfibrozil | 4.5 | 0.53 |
| Ibuprofen | <4 | <4 |
| Ketoprofen | <2 | <2 |
| Meprobamate | 0.62 | 0.34 |
| Naproxen | <0.50 | <0.50 |
| Naproxen | <1 | <1 |
| NDMA | 27 | <2 |
| Norfluoxetine | <0.50 | <0.50 |
| *o*-Hydroxy atorvastatin | <0.50 | <0.50 |
| *p*-Hydroxy atorvastatin | <0.50 | <0.50 |
| Simvastatin hydroxy acid | <0.25 | <0.25 |
| Sulfamethoxazole | 2.0 | <0.25 |
| TCEP | <30 | <30 |
| TCPP | <30 | <30 |
| TDCPP | <30 | <30 |
| Triclosan | 24 | <1.0 |
| Trimethoprim | 2.1 | 0.50 |

[a]Conditions: RO-treated feedwater; 50 to 100 mJ of low-pressure high-output UV per $cm^2$; 3.0 mg of $H_2O_2$ per L.

**Table 5.15. Removal of Indicator Compounds during Full-Scale AOP Operation**[a]

| Good Removal (>90%) | Intermediate Removal | | Poor Removal (<25%) |
|---|---|---|---|
| | 90–50% | 50–25% | |
| Triclosan | Atenolol | Meprobamate | |
| | Gemfibrozil | | |
| | Trimethoprim | | |
| | NDMA | | |

[a]Conditions: RO-treated feedwater; 50 to 100 mJ of low-pressure high-output UV/cm$^2$; 3.0 mg of $H_2O_2$ per L.

Observed changes of surrogate parameters during ozonation both at laboratory and full scale are summarized in Table 5.16. Of the surrogate compounds examined, removal of UVA exhibited the highest degree of sensitivity to increasing AOP dosages and correlated with higher removals of indicator compounds (Figure 5.12).

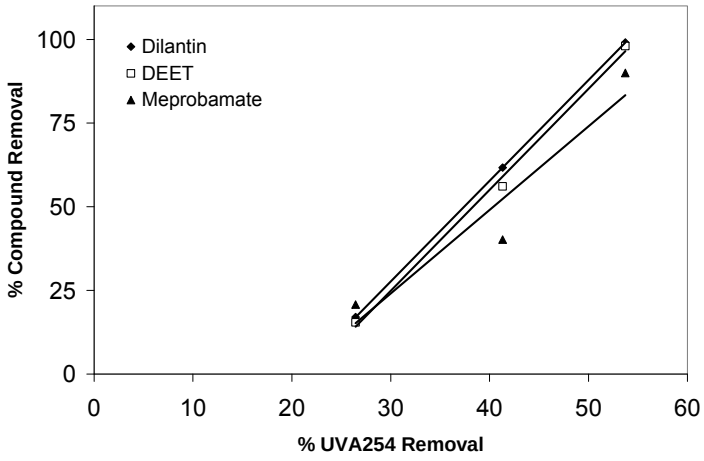



**Figure 5.12. Correlation between removal of UVA and that of select indicator compounds.**

Of the by-products formed during ozonation, formate, oxalate, aldehyde, and AOC might also serve as viable surrogate parameters to assess the efficiency of ozonation. However, UVA is much easier and faster to quantify than formate, oxalate, aldehyde, or AOC.

**Table 5.16. Surrogate Parameters Quantified during Sampling of Laboratory- and Full-Scale AOP Operations**

| Scale | Ozone or UV Dose (mg of $O_3$/L or mJ/cm$^2$) | Hydrogen Peroxide Concn (mg/L) | Contact Time (min) | Concn or value of: | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | TOC (mg/L) | TOX (μg/L) | TOI (μg/L) | $UVA_{254}$ (1/cm) | Bromate (μg/L) | Formate (μg/L) | Oxalate (μg/L) | Aldehydes (μg/L) | AOC (μg/L) |
| Lab scale ($O_3/H_2O_2$) | 0 | 0 | 0 | 7.11 | 330 | 18.9 | 0.121 | <1 | <20 | 27 | 31 | 343 |
| | 2.1 | 1.0 | 10 | 7.16 | 270 | 12.4 | 0.089 | <1 | 239 | 89 | — | — |
| | 3.6 | 2.0 | 10 | 6.91 | 230 | — | 0.071 | <1 | 417 | 160 | 149 | 1019 |
| | 7.1 | 3.5 | 2 | 7.33 | — | 8.6 | 0.056 | 13.3 | — | — | — | — |
| | 7.1 | 3.5 | 6 | — | — | — | — | 13.1 | — | — | — | — |
| | 7.1 | 3.5 | 10 | 7.23 | 244 | 8.6 | 0.071 | 15.7 | 779 | 311 | 310 | 1752 |
| Full scale ($UV/H_2O_2$) | 0 | 0 | 0 | 0.22 | — | <0.1 | 0.022 | — | — | — | — | — |
| | 50–100 | 3.0 | — | 0.22 | — | <0.1 | 0.002 | — | — | — | — | — |

#### *5.2.2.3 Chloramination*

Sampling campaigns were conducted at three full-scale facilities practicing chloramination. Samples were collected prior to formation of chloramines and approximately after 1 h of CT. Samples were analyzed for select indicator compounds and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2).

The removal efficiencies of indicator compounds observed at the three full-scale facilities were classified into removal categories (Table 5.17). The operating conditions among the three facilities were found to be similar after the use of secondary/tertiary-treated wastewater with a CT between 0.75 and 1 h and residual chloramine concentrations of 2.5 to 4.5 mg/L. Absolute concentrations of indicator compounds listed in Table 5.17 are summarized in Tables 8.14 to 8.16 (Appendix).

**Table 5.17. Removal of Indicator Compounds during Chloramination Operations**[a]

| Good Removal (>90%) | Intermediate Removal | | Poor Removal (<25%) |
|---|---|---|---|
| | 90–50% | 50–25% | |
| Butylated hydroxyanisole | Vanillin | Bisphenol A | Benzophenone |
| | Triclosan | | Caffeine |
| | | | DEET |
| | | | Diclofenac |
| | | | EDTA |
| | | | Gemfibrozil |
| | | | Ibuprofen |
| | | | Indolebutyric acid |
| | | | Naproxen |
| | | | NDMA |
| | | | Primidone |
| | | | Salicylic acid |
| | | | TCEP |
| | | | TCPP |
| | | | TDCPP |
| | | | Triclocarban |

[a]Operating conditions: secondary/tertiary-treated wastewater; 0.75 to 1 h of contact time; 2.5 to 4.5 mg of residual chloramine/L. Based on sampling campaigns at three full-scale facilities practicing chloramination.

As compared to ozone and AOP, chloramines are a relatively weak oxidant. As a consequence, the removal efficiency of chloramines for wastewater-derived trace organic compounds is rather poor. The majority of the targeted compounds exhibited a removal of less than 25%. Only one compound, butylated hydroxyanisole, was removed in excess of 90%, followed by triclosan (81%), vanillin (66%), and bisphenol A (29%). Therefore,

chloramination is not considered a viable barrier in removing wastewater-derived trace organic compounds in indirect potable reuse applications.

#### *5.2.2.4 Chlorination*

Recent studies have examined the removal of select wastewater-derived organic contaminants by chlorination (Westerhoff et al., 2005; Snyder et al., 2007a; Carlile et al., 1996; Dodd and Huang, 2004; Gallard et al., 2004; Alum et al., 2004; Deborde et al., 2004; Gibs et al., 2007; Bedner and MacCrehan, 2006; Dodd and Huang, 2007; Pinkston and Sedlak, 2004; Dodd et al., 2005). Building upon these findings, treatment removal categories for indicator compounds in chlorine operations were developed (Table 5.18). In general, oxidation and substitution are the main reaction mechanisms observed during chlorination of trace organic compounds. Activated aromatic ring structures are usually well removed, such as phenolics (Westerhoff et al., 2005; Gallard and von Gunten, 2002) as well as aromatics with amine groups (i.e., sulfamethoxazole, triclocarban, diclofenac, and trimethoprim). Compounds experiencing high to intermediate removal are chacterized by doubly activated aromatics (i.e., activating group in meta position, such as alkyl and/or alkoxy groups). Meta-substituted aromatics result in ortho and para positions having added electron density from both substituents, and these sites with higher electron density are presumably more susceptible to electrophilic attack by chlorine (i.e., naproxen, propanolol, gemfibrozil, and galaxolide). Compounds experiencing intermediate to poor removal are alkoxy/alkyl aromatics (i.e., atenolol; metoprolol, DEET, ibuprofen, and ketoprofen), aliphatics (i.e., TCEP and meprobamate), cycloalkane/alkene compounds, and heterocyclic nitrogen-containing compounds (i.e., caffeine, carbamazepine, and dilantin).

Acidic drugs (i.e., gemfibrozil and naproxen) usually exhibit higher removals with decreasing pH due to an increase in hypochlorous acid (Westerhoff et al., 2005; Pinkston and Sedlak, 2004), which is the dominant species when pH < 7.5. Hypochlorite ions do not react at a significant rate with substituted phenols. However, the phenolate form of substituted phenols occurs at higher pH, is a stronger nucleophile, adds more electron density to the aromatic ring (e.g., acetaminophen), and thus is more reactive than the protonated form (Gallard and von Gunten, 2002). Primary and secondary amine-containing compounds are susceptible to chlorination at higher chlorine doses, resulting in chloraminated compounds. Bedner and MacCrehan (2006) reported that secondary amine compounds (e.g., flouxetine and metoprolol) can be removed by chlorination (chlorine in excess). Other compounds containing secondary amines are carbamazepine, dilantin, indolebutyric acid, and primidone, which potentially could be removed by chlorine at high doses. In principle, compounds can be reduced back to their parent compounds in the presence of sulfite and thiosulfate reducing agents (Bedner and MacCrehan, 2006; Pinkston and Sedlak, 2004); however, the reduction reaction is slow in regard to full-scale dechlorination CTs (Bedner and MacCrehan, 2006). In general, trace organic compounds are not degraded substantially during chlorination and are transformed into chlorinated and/or slightly oxidized by-products.

The operational boundary conditions for the selection of indicator compounds of chlorination systems are a dose of 1 mg of Cl/mg of C, a contact time of 24 h, and pH of 7 to 8. For some compounds, removal during chlorination was not reported in the literature. For these compounds, removal percentages were estimated by examining the compound's structural properties and comparing these properties with compounds with known removals.

**Table 5.18. Treatment Removal Categories for Indicator Compounds of Chlorine Systems**[a]

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

[a]Conditions: 1 mg of Cl/mg of C; 24-h contact time; pH 8. Removal of compounds with no footnote was verified through peer-reviewed literature data or experimental data generated during this study.

[b]Hydroxy aromatic (activating).

[c]Amino aromatic (activating).

[d]Acylamino aromatic (activating).

[e]Alkoxy aromatic (activating).

[f]Alkyl aromatic (activating).

[g]Aliphatic (halogens).

[h]Aliphatic ketone/hydroxyl/ester.

[i]Cycloalkane/cycloalkene.

[j]Aromatic with heterocyclic ring (nitrogen containing).

[k]Activating group in meta position.

**Laboratory-Scale Chlorination Experiments**

Controlled chlorination experiments were conducted at the bench-scale with a chlorine dose of 2 and 3 mg/L, a pH of 8, and a contact time of 24 h. For these experiments a suite of trace organic compounds was spiked at the nanograms-per-liter level into a natural surface water with a TOC of 2.6 mg/L. Samples were collected prior to and after chlorination. Samples were analyzed for select indicator compounds and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2).

The efficiency of chlorine, similar to that of other oxidants, will depend upon the applied dose. Higher dosages at similar contact time usually result in more efficient oxidation (Figure 5.13). Therefore, increasing the chlorination dose beyond disinfection requirements can be a strategy to improve removal of wastewater-derived organic contaminants. Figure 5.13 reflects a 24-h contact time and a pH of 8.

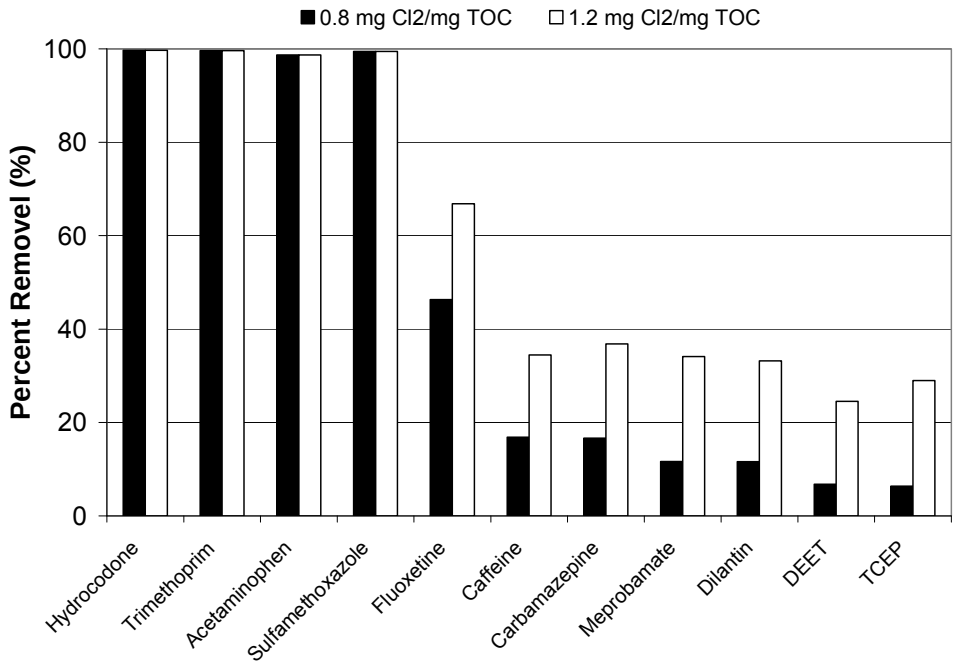



**Figure 5.13. Effect of chlorine dose on the removal of indicator compounds during chlorination.**

The removal efficiencies of indicator compounds observed during bench-scale chlorination were classified into removal categories (Table 5.19). Absolute concentrations for compounds listed in Table 5.19 are summarized in Table 8.17 (Appendix). With the exception of fluoxetine exhibiting a better removal than predicted, the observed removal of indicator compounds under similar chlorination conditions confirms the classification of the proposed master list (Table 5.18).

**Table 5.19. Removal of Indicator Compounds during Bench-Scale Chlorination**[a]

| Good Removal (>90%) | Intermediate Removal (90 < x < 50%) | Intermediate Removal (50 < x < 25%) | Poor Removal (<25%) |
|---|---|---|---|
| Hydrocodone | | Fluoxetine | Caffeine |
| Trimethoprim | | | Pentoxifylline |
| Acetaminophen | | | Meprobamate |
| Sulfamethoxazole | | | Dilantin |
| Oxybenzone | | | TCEP |
| | | | Carbamazepine |
| | | | DEET |
| | | | Atrazine |
| | | | Diazepam |

[a]Conditions: $Cl_2$ = 2 mg/L, 0.8 mg of Cl/mg of C; 24-h contact time; pH = 7.

Surrogate parameters quantified during bench-scale experiments are summarized in Table 5.20. UVA at 272 nm did not change significantly, because bonds within aromatic structures may not necessarily break under the selected chlorination conditions. Similar to ozone, the integral CT might serve as a good surrogate parameter to assess the proper performance of a chlorination system. With increasing exposure time (CT), the removal of indicator compounds classified in the "poor removal" category increased.

**Table 5.20. Removal of Surrogate Parameters during Bench-Scale Chlorination**[a]

| Chlorine (mg/L) | Chlorine:TOC (mg/mg) | Integral CT (mg-min/L) | TOC (mg/L) | $UVA_{272}$ (1/cm) |
|---|---|---|---|---|
| 0 | 0 | 0 | 2.63 | 0.034 |
| 2 | 0.8 | 1862 | 2.48 | 0.028 |
| 3 | 1.2 | 2883 | 2.57 | 0.029 |

[a]Conditions: 24-h contact time; pH = 7. $UVA_{254}$ is not listed because of interference caused by the quenching agent sodium thiosulfate.

### 5.2.3 UV Radiation

Sampling campaigns were conducted at two full-scale facilities practicing disinfection with low-pressure UV radiation. The UV systems employed operated in the dose range of 30 to 40 $mJ/cm^2$. Samples were collected prior to and after the UV systems. Samples were analyzed for select indicator compounds and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2). Absolute concentrations of indicator compounds observed at the two facilities are summarized in Tables 8.18 and 8.19 (Appendix).

The removal efficiencies of indicator compounds observed at the two full-scale facilities were classified into removal categories (Table 5.21). Of the indicator compounds present in the tertiary effluent samples, only four compounds exhibited an intermediate removal in excess of 25%. These observations are consistent with previous studies reporting that diclofenac, fluoxetine, sulfamethoxazole, and carbamazepine are amenable to photolytic decay at low UV dosages (Boreen et al., 2004; Snyder et al., 2007a).

**Table 5.21. Removal of Indicator Compounds during Full-Scale UV Operation**[a]

| Good Removal (>90%) | Intermediate Removal (90–50%) | Intermediate Removal (50–25%) | Poor Removal (<25%) |
|---|---|---|---|
| | Diclofenac | Carbamazepine | Butylated hydroxyanisole |
| | | Fluoxetine | Bisphenol A |
| | | Sulfamethoxazole | Caffeine |
| | | | DEET |
| | | | Dilantin |
| | | | Erythromycin–$H_2O$ |
| | | | Gemfibrozil |
| | | | Hydrocodone |
| | | | Indolebutyric acid |
| | | | Meprobamate |
| | | | Naproxen |
| | | | Salicylic acid |
| | | | TCEP |
| | | | TCPP |
| | | | TDCPP |
| | | | Triclosan |
| | | | Trimethoprim |
| | | | Vanillin |
| | | | EDTA (total) |
| | | | Dichloroprop |
| | | | 17β-Estradiol |
| | | | Estrone |
| | | | Mecoprop |
| | | | Ibuprofen |
| | | | NDMA |

[a]Operating conditions: tertiary-treated wastewater; low-pressure UV at 30 to 40 mJ/cm$^2$. Based on sampling campaigns at two full-scale facilities practicing UV disinfection.

Given the low removal efficiency for the majority of indicator compounds, UV radiation applied at a disinfection dose is not considered a viable barrier in removing wastewater-derived trace organic compounds in indirect potable reuse applications.

### 5.2.4 Adsorption onto Activated Carbon

Removal of organic compounds by physical adsorption on porous adsorbents, such as activated carbon, involves several adsorption forces: coulombic-unlike charges, dipole-dipole interactions, van der Waals forces, covalent bonding, and hydrogen bonding (Sontheimer et al., 1988). The characteristics of the constituent that are of importance for adsorptive uptake include solubility, molecular structure, MW, polarity, and hydrocarbon saturation. NOM can compete for trace organic compounds and reduce the effectiveness of contaminant removal (Knappe et al., 1998; Li et al., 2005). Previous research has been conducted to understand the performance of PAC and GAC systems in removing select wastewater-derived trace organic compounds (Westerhoff et al., 2005; Snyder et al., 2006). This section highlights how surrogate parameters and indicator compounds can be applied to assess the performance of treatment systems employing PAC and GAC processes.

#### *5.2.4.1 PAC Adsorption*

Building upon the findings of Westerhoff et al. (2005) and Snyder et al. (2006), results revealed from full-scale monitoring during this study, and findings from supplemental studies conducted by members of the research team including quantitative structure property relationships, we developed universal treatment removal categories for indicator compounds of PAC systems (Table 5.22). The operational boundary conditions of this master list are a feedwater quality DOC concentration of less than 4 mg/L, 5 mg of PAC (Calgon WPM and Anticarb 800)/L, and 4 h of CT.

Removal percentages considered from the Westerhoff et al. (2005) study represent the average of four water matrices. Westerhoff et al. (2005) reported that higher PAC dosages (20 mg/L) led to only slight additional removal of trace organic compounds that were classified in the category of "good removal (>90%)" when PAC dosages of 5 mg/L were applied. For these compounds, the maximum calculated percentage removal was limited by the minimum reporting level. Westerhoff et al. (2005) observed that higher PAC dosages of 20 mg/L effectively removed 80% of all the compounds targeted in their study.

**Table 5.22. Treatment Removal Categories of Indicator Compounds of PAC Systems**[a]

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

[a]Conditions: DOC < 4 mg/L; 5 mg of PAC (Calgon WPM and Anticarb 800) per L; 4-h CT.
[b]Westerhoff et al., 2005.
[c]Removal estimate is based upon log D > 4 (pH 7); uncharged.
[d]Removal estimate is based upon log D = 0–4 (pH 7); uncharged.
[e]Removal estimate is based upon log D < 0 (pH 7); uncharged.
[f]Removal estimate is based upon log D = 0–1.5 (pH 7); protonated base.
[g]Removal estimate is based upon log D < 0 (pH 7); protonated base.
[h]Removal estimate is based upon log D = 0–2.5 (pH 7); deprotonated acid.
[i]Removal estimate is based upon log D < 0 (pH 7); deprotonated acid.

### *5.2.4.2 GAC Adsorption*

Building upon findings from Snyder et al. (2006, 2007b), results revealed from full-scale monitoring during this study, and findings from supplemental studies conducted by members of the research team including quantitative structure property relationships, we also developed universal treatment removal categories for indicator compounds of GAC systems (Table 5.23). The operational boundary conditions of the GAC master list are a DOC concentration of less than 3 mg/L, GAC Norit HD4000 (at bed volume (BV) = 55,000) and Norit Superdarco (at BV = 90,000), and an empty bed CT (EBCT) of 7.5 min.

**Table 5.23. Treatment Removal Categories of Indicator Compounds of GAC Systems**[a]

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

[a]DOC < 3 mg/L; Norit HD4000 at BV = 55,000 and Norit Superdarco at BV = 90,000; EBCT = 7.5 min.

[b]Snyder et al., 2007b.

[c]Removal estimate is based upon log D > 3 (pH 7); uncharged.

[d]Removal estimate is based upon log D = 2–3 (pH 7); uncharged.

[e]Removal estimate is based upon log D = 0–2 (pH 7); uncharged.

[f]Removal estimate is based upon log D < 0 (pH 7); uncharged or deprotonated acid.

[g]Removal estimate is based upon log D = 0–1.5 (pH 7); protonated base.

[h]Removal estimate is based upon log D < 0 (pH 7); protonated base.

[i] Removal estimate is based upon log D = 0–2.5 (pH 7); deprotonated acid.

Results reported by Snyder et al. (2007b) were derived only from rapid small-scale columns tests using one water matrix. It is noteworthy that the observed removal efficiency will depend upon the competitive adsorption of NOM makeup, which differs among water matrices. GAC systems in general have the benefit of CTs shorter than those of systems that apply PAC.

Quantitative-structure-property-relationship adsorption models consider relationships between the molar volume/hydrogen bonding affinity and the log $K_{ow}$ or log D values. Hydrophobic interactions for neutral compounds are usually well predicted by log $K_{ow}$. For ionseic compounds, it is more difficult to accurately predict log D and $pK_a$ values. In general, protonated bases appear to be well removed, whereas deprotonated acid functional groups seem the most difficult to remove. In general, quantitative-structure-property-relationship adsorption models require calibration for less volatile neutral compounds and protonated/deprotonated acids and bases.

### Full-Scale GAC Operation

In order to validate the master indicator list for GAC systems, two sampling campaigns at one full-scale GAC facility were conducted. For the full-scale site, the research team had access to historic water quality data generated during previous research efforts. Samples were analyzed for most of the indicator compounds listed in Table 5.23 and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2). Facility 5 employs GAC filtration (Norit GAC 820, EBCT of 15 min) for nitrified tertiary-treated wastewater. The observed removal percentage ranges of indicator compounds quantified at this site with a DR of >5 in the feedwater are summarized in Table 5.24. Absolute concentrations for compounds listed in Table 5.24 are reported in Table 8.20 (Appendix).

**Table 5.24. Removal of Indicator Compounds during Full-Scale GAC Operation**[a]

| Good Removal (>90%) | Intermediate Removal (90–50%) | Intermediate Removal (50–25%) | Poor Removal (<25%) |
|---|---|---|---|
| Atenolol | Carbamazepine | Dilantin | EDTA (total) |
| Diclofenac | Gemfibrozil | Sulfamethoxazole | Meprobamate |
| Fluoxetine | Mecoprop | TCEP | Atrazine |
| Naproxen | Salicylic acid | TCPP | |
| Triclosan | TDCPP | | |
| Trimethoprim | | | |

[a]Conditions: tertiary-treated wastewater; TOC = 3 to 7 mg/L, Norit GAC 820, EBCT = 15 min.

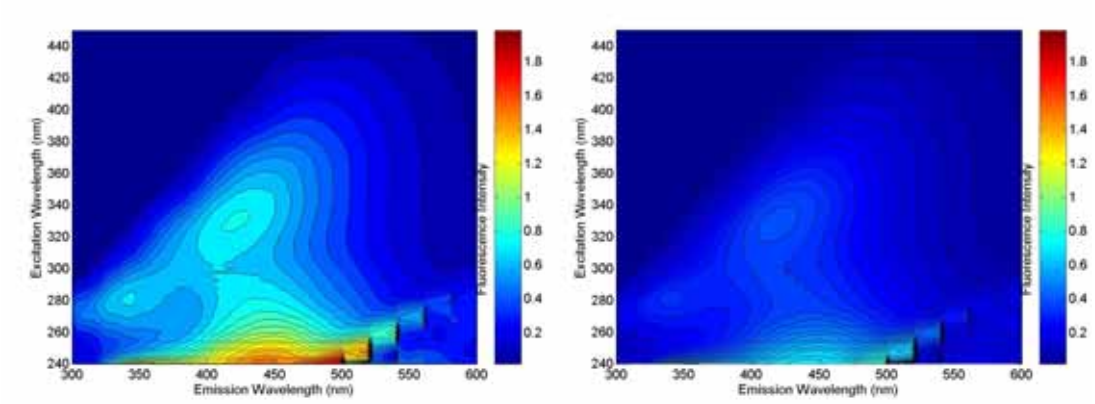
During the time of sampling, the GAC used at Facility 5 was exhausted, resulting in only a slight removal of organic matter represented by a small change of TOC (Table 5.25). However, the remaining capacity of the carbon resulted in removal of hydrophobic indicator compounds, such as carbamazepine and triclosan, among others. The activated carbon in this process arrangement was likely biologically active, which probably is the reason for the quite efficient removal of rather hydrophilic indicator compounds (i.e., atenolol, naproxen,

diclofenac, and salicylic acid), which usually do not adsorb that well. Surrogate parameter measurements during these sampling campaigns indicate an oxidation of ammonia during GAC treatment, further supporting biological transformations in the adsorber. Previous studies confirmed that regenerated GAC performs better than exhausted carbon in trace organic compound removal (Snyder et al., 2006). A more detailed study would be required to determine the rate and degree of contaminant breakthrough over time.

**Table 5.25. Surrogate Parameters Quantified during Full-Scale GAC Operation**

| | | Concn or value of: | | | | | |
|---|---|---|---|---|---|---|---|
| **Sampling Campaign** | **Location** | **$NH_4$-N (mg/L)** | **$NO_3$-N (mg/L)** | **TOC (mg/L)** | **COD (mg/L)** | **cBOD (mg/L)** | **$UVA_{254}$ (1/cm)** |
| Sampling campaign no. 1 | Before | 0.21 | 10.2 | 7.2 | 20 | 1.0 | 0.102 |
| | After | <0.05 | 12.4 | 5.6 | 15 | 0.7 | 0.075 |
| Sampling campaign no. 2 | Before | 0.08 | 5.6 | 2.9 | 14 | <0.2 | 0.093 |
| | After | <0.05 | 6.1 | 2.0 | 11 | <0.2 | 0.061 |

Beside the surrogate parameter UVA, which resulted in a significant change during GAC treatment indicating the selective removal of aromatic organic matter, fluorescence can serve as a viable parameter for GAC performance assessment. The 3-D fluorescence spectra of a full-scale sample prior to and after GAC treatment are illustrated in Figure 5.14. These spectra reveal significant changes in the organic matter during GAC treatment.




Before GAC After GAC

**Figure 5.14. 3-D fluorescence spectra of samples collected before and after GAC treatment.**

### 5.2.5 Physical Separation by Membranes

The majority of wastewater-derived contaminants occurring in the nanograms-per-liter concentration range represent a molecular size range of 100 to 800 g/mol. Thus, for effective rejection by physical separation processes, tight membranes are required and only treatment processes employing NF or RO membranes will be effective in removing these compounds. The primary removal mechanisms during membrane separation for wastewater-derived contaminants include size exclusion, electrostatic repulsion, and adsorption. The dominant mechanism depends upon 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 section highlights how the proposed surrogate and indicator framework can be applied to assess the performance of treatment systems employing RO or NF membranes.

#### *5.2.5.1 RO Membranes*

In drinking water augmentation projects in the United States, treatment of recycled water with an IMS consisting of MF or ultrafiltration followed by RO is considered the industry standard for direct injection projects. Recycled water applied to RO membranes usually has previously received secondary or tertiary treatment followed by disinfection. Significant research has been conducted to understand the performance of IMSs in removing TDS, TOC, nutrients, and select wastewater-derived contaminants (Lee and Leuptow, 2001; Drewes et al., 2003a; Schäfer et al., 2003; Drewes et al., 2005b; Nghiem et al., 2005; Snyder et al., 2006; Kim et al., 2007; Bellona and Drewes, 2007).

Building upon this knowledge base, findings from supplemental studies conducted by members of the research team, and results revealed from pilot- and full-scale experiments during this study, treatment removal categories for indicator compounds of RO systems were developed (Table 5.26). This master list has been augmented with compounds that had a DR of >5 but were not monitored during this study. Estimates of their removal during RO were accomplished by using structural property relationships (i.e., molecular size). The operational boundary conditions of this master list are a pretreatment of the recycled water with MF or ultrafiltration, pH adjustment to 6.5, a permeate flux of approximately 12 gfd (20 L per sq. m and 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., 2007b; Drewes et al., 2008). 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., 2007). 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., 2005b; Drewes et al., 2008). The highly efficient rejection of wastewater-derived contaminants by RO membranes limits the number of available indicator compounds representing intermediate removal to a few. None of the indicator compounds considered in this study 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 feedwater.

**Table 5.26. 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 | Propylparabe | | NDMA | |
| Acetyl cedrene[b] | Dilantin | Mecoprop | Salicylic acid | | | |
| 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] | Hexylcinnam-aldehyde[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. 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 upon MW being > 150 g/mol.

In order to validate the master indicator list for systems employing RO membranes, two full-scale RO facilities were selected for performance monitoring. The RO facilities utilized both nonnitrified and nitrified/denitrified microfiltered feedwater that was pH adjusted (6.5). Both systems were operated at a specific flux of 10 to 12 gfd (~20 LMH) and a recovery of 85%.

### RO Operation No. 1

RO operation no. 1 (Facility 4) utilized the RO membrane ESPA 2 (Hydranautics, Oceanside, CA) treating microfiltered nonnitrified feedwater. Two sampling campaigns were conducted at this site. Samples were collected from the microfiltered feedwater and the combined permeate. Samples were analyzed for select indicator compounds listed in Table 5.26 and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2). The observed removal percentage ranges of indicator compounds quantified at this site with a DR

of >5 in the feedwater are summarized in Table 5.27. Absolute concentrations of samples collected prior to and after RO treatment are reported in Table 8.21 (Appendix).

All of the indicator compounds classified in the category of "good removal" were removed at a level exceeding 90% and in most cases were below the detection limit in the combined RO permeate. Only NDMA exhibited a moderate rejection. These findings confirm the proposed selection of indicator compounds and proposed removal efficiencies for RO systems (Table 5.26).

**Table 5.27. Removal of Indicator Compounds during RO Operation at Facility 4**[a]

| Good Removal (>90%) | Intermediate Removal (90–50%) | Intermediate Removal (50–25%) | Poor Removal (<25%) |
|---|---|---|---|
| Atenolol | | NDMA | |
| Atorvastatin | | Chloroform | |
| Atorvastatin (*o*-hydroxy) | | | |
| Atorvastatin (*p*-hydroxy) | | | |
| Bisphenol A | | | |
| Carbamazepine | | | |
| Diclofenac | | | |
| Dilantin | | | |
| EDTA | | | |
| Estrone | | | |
| Fluoxetine | | | |
| Gemfibrozil | | | |
| Ibuprofen | | | |
| Meprobamate | | | |
| Naproxen | | | |
| Norfluoxetine | | | |
| Salicylic acid | | | |
| Simvastatin hydroxy acid | | | |
| Sulfamethoxazole | | | |
| TCEP | | | |
| TCPP | | | |
| TDCPP | | | |
| Triclosan | | | |
| Trimethoprim | | | |

[a]Operating conditions: membrane, ESPA 2 RO; recovery, 85%; permeate flux: ~12 gfd; pH = 6.5.

Feedwater and combined permeate samples were also analyzed for various surrogate parameters. Results of this analysis are summarized in Tables 5.29 and 5.30, and removal efficiencies for surrogate parameters are presented in Figure 5.15. With the exception of boron, all surrogate parameters were rejected by 93% or higher. Boron rejection, however,

was less than 30%, and given the low degree of rejection, a change in boron concentration is likely the surrogate parameter most sensitive to a system performance failure of RO membranes.

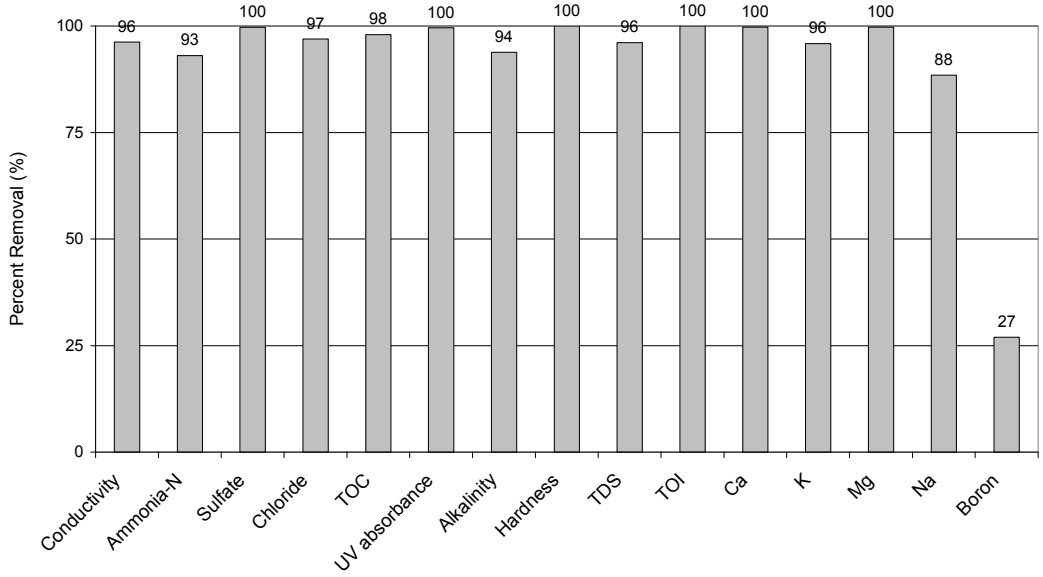



**Figure 5.15. Removal of surrogate parameters during full-scale RO treatment.**

### RO Operation No. 2

RO operation no. 2 (Facility 8) utilized the RO membrane TFC-HR (Koch Membrane Systems, San Diego, CA) treating microfiltered, nitrified/denitrified feedwater. One sampling campaign was conducted at this site. Samples were collected from the microfiltered feedwater and the combined permeate. Samples were analyzed for select indicator compounds listed in Table 5.26 and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion of a DR of >5 for indicator compounds (see Table 4.2). The observed removal percentage ranges of indicator compounds quantified prior to and after RO treatment with a DR of >5 are summarized in Table 5.28. Absolute concentrations of samples collected prior to and after RO treatment are reported in Table 8.22 (Appendix). It is noteworthy that many indicator compounds proposed for RO systems were not detectable in this denitrified, microfiltered feedwater.

All of the indicator compounds classified in the category of "good removal" were removed at a level exceeding 90% and in most cases were below the detection limit in the combined RO permeate. Only NDMA exhibited a moderate rejection. These findings confirm the proposed selection and classification of indicator compounds for RO systems (Table 5.26).

**Table 5.28. Removal of Indicator Compounds during RO Operation at Facility 8**[a]

| | Intermediate Removal | | Poor Removal |
|---|---|---|---|
| Good Removal(>90%) | 90–50% | 50–25% | (<25%) |
| EDTA | | NDMA | |
| Gemfibrozil | | Chloroform | |
| Metoprolol | | | |
| Naproxen | | | |
| Propranolol | | | |
| Salicylic acid | | | |
| TCEP | | | |
| TCPP | | | |
| TDCPP | | | |

[a]Operating conditions: membrane, TFC-HR RO; recovery, 85%; permeate flux, ~10 gfd; pH = 6.5.

Feedwater and combined permeate samples were also analyzed for various surrogate parameters. Results of this analysis are summarized in Tables 5.29 and 5.30, and removal efficiencies for surrogate parameters are presented in Figure 5.16. With the exception of boron and ammonia, all surrogate parameters were rejected by 90% or higher. Boron and ammonia rejections, however, were less than 35 and 60%, respectively. Given how small these molecules are and provided boron and ammonia are both present at quantifiable concentrations in the feed, monitoring the rejection of both surrogate parameters might allow researchers to detect a partial system failure.

Conductivity is currently the surrogate parameter of choice to assess membrane performance of RO installations. Conductivity measurements are quick, require little maintenance, are in most cases available as online instruments, and can be easily tied into the plant's supervisory control and data acquisition system. An earlier study demonstrated that conductivity measured in permeate samples is much more strongly correlated to the presence of low-MW and neutral wastewater-derived trace organic compounds than to that of TOC (Drewes et al., 2005b). The correlation between permeate conductivity and caffeine permeate concentrations is illustrated in Figure 5.17, which is derived from Drewes et al., 2005b. These results suggest that a rejection of conductivity exceeding 95% will indicate at least 90% removal of compounds with an MW exceeding 150 g/mol.

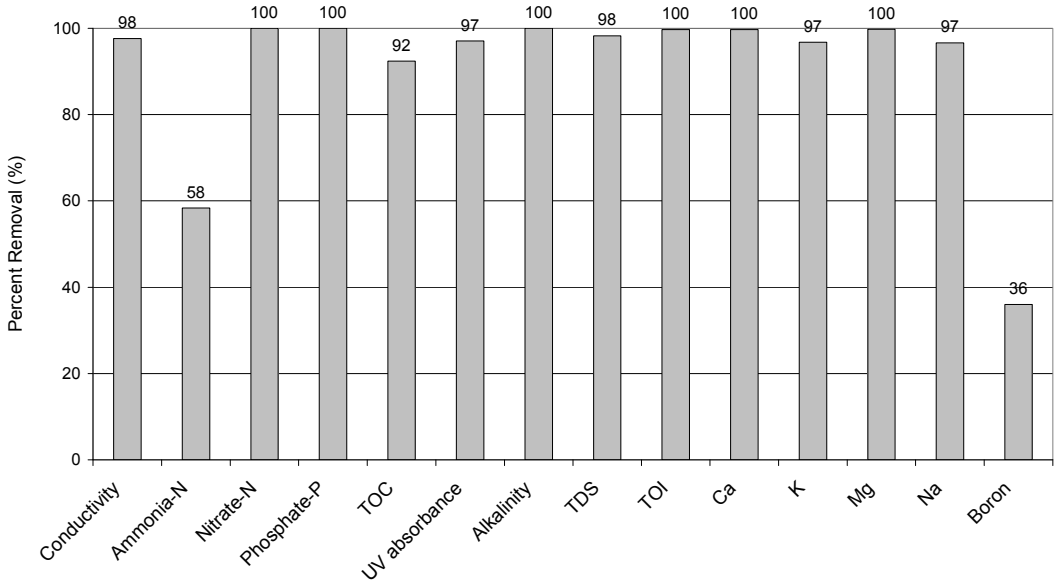



**Figure 5.16. Removal of surrogate parameters during full-scale RO treatment.**

**Table 5.29. Removal of Surrogate Parameters during Pilot- and Full-Scale RO Operations**

| | | Concn or value of: | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Location or scale | Stage | Conductivity (μS/cm) | TOC (mg/L) | UVA (1/cm) | Alkalinity (as $CaCO_3$) (mg/L) | Hardness (as $CaCO_3$) (mg/L) | TDS (mg/L) | TOI (μg/L) |
| Facility no. 4 | Before RO | 1600 | 11.4 | 0.188 | 263 | 273 | 882 | 18.4 |
| | After RO | 54 | 0.29 | 0.022 | 13.8 | <1 | 25.0 | <0.1 |
| Facility no. 8 | Before RO | 1900 | 5.76 | 0.085 | 98 | NA | 1000 | 22 |
| | After RO | 45 | 0.44 | 0.003 | <10 | NA | 17 | <0.1 |
| Pilot scale | Before NF | 1900 | 5.76 | 0.085 | 98 | NA | 1000 | 22 |
| | After NF | 1000 | 0.30 | 0.006 | 48 | NA | 510 | 1.8 |

**Table 5.29 Cont. Removal of Surrogate Parameters during Pilot- and Full-Scale RO Operation**

| Location or scale | Stage | Concn (mg/L) of: | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $SO_4$ | $NO_3$-N | Ca | Mg | K | Na | Cl | $NH_4$-N | B |
| Facility no. 4 | Before RO | 244 | <0.1 | 67 | 20 | 17.2 | 224 | 182 | 22.4 | 0.38 |
| | After RO | 0.66 | <0.1 | 0.17 | 0.05 | 0.70 | 26 | 4 | 1.6 | 0.27 |
| Facility no. 8 | Before RO | NA | 10 | 77 | 30 | 33 | 208 | NA | 1.2 | 0.47 |
| | After RO | NA | <1 | 0.21 | 0.07 | 1.0 | 7.1 | NA | 0.5 | 0.31 |
| Pilot scale | Before NF | NA | 10 | 77 | 30 | 33 | 208 | NA | 1.2 | 0.47 |
| | After NF | NA | 10 | 22 | 6.1 | 21 | 137 | NA | 0.8 | 0.51 |

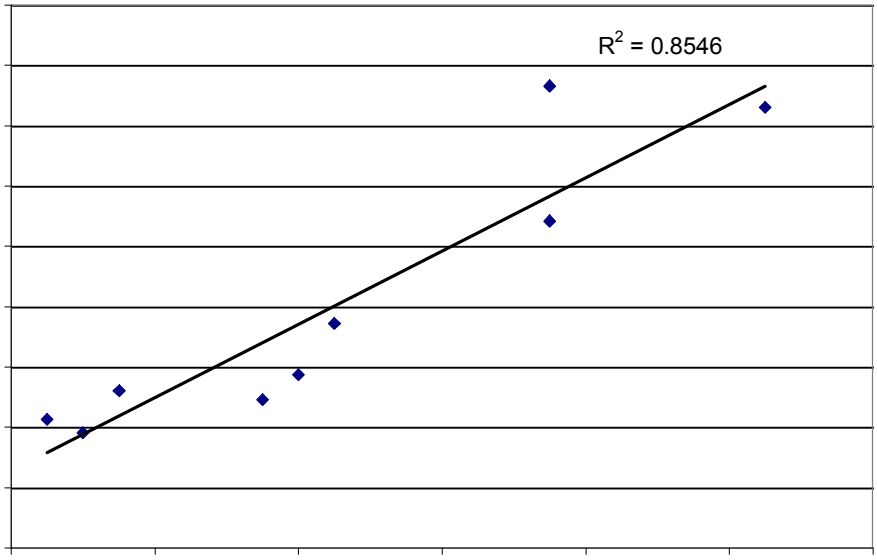



**Figure 5.17. Correlation between conductivity and caffeine in permeate samples.**

### *5.2.5.2 NF Membranes*

Newer-generation membranes, such as NF and to a lesser extent low-pressure RO (LPRO) membranes, may provide the opportunity to reduce feed pressures and operating costs associated with RO treatment while offering similar permeate water quality. Since NF membranes are supplied in the same configurations as RO membranes, utilities could replace RO with NF spiral-wound elements during a regularly scheduled membrane replacement program without the need for significant additional capital investment.

NF membranes are designed to provide limited rejection for monovalent cations while simultaneously removing divalent cations, TOC, and organic micropollutants such as pesticides. Previous studies demonstrated that NF membranes are quite effective in removing wastewater-derived contaminants (Xu et al., 2005; Bellona and Drewes, 2007). Because NF membranes are designed to be more porous, the MW cutoff of NF membranes is usually higher than that of conventional RO membranes, which becomes important especially for the rejection of small, neutral, wastewater-derived contaminants. The MW cutoff of a membrane is a continuum that is shifted to higher MWs the looser the membrane becomes. The removal efficiency for wastewater-derived contaminants using the NF membrane NF-4040 (Dow/Filmtec) is illustrated in Figure 5.18. The rejection behavior of this membrane would suggest an effective cutoff of approximately 200 g/mol.

Rejection of indicator compounds using the NF membrane NF-4040 (Dow/Filmtec) was tested at pilot scale at operating conditions similar to those commonly employed in full-scale installations (i.e., 82% recovery and permeate flux of 12 gfd or 20 LMH). A pilot-scale skid with a capacity of 18 gpm (68 L/min) was employed for 1400 h at Facility 8 receiving microfiltered, nitrified/denitrified wastewater effluent.

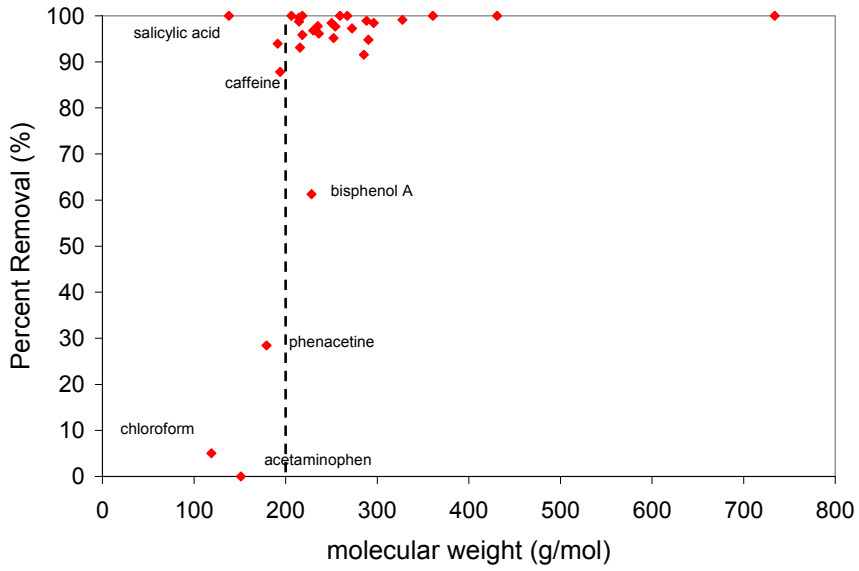



**Figure 5.18. Rejection of wastewater-derived organic contaminants by the NF-4040 membrane.**

The feedwater was spiked with indicator compounds of interest at levels 300 to 500% above the environmental concentrations usually observed in the tertiary-treated wastewater of the adjacent full-scale facility. Samples of the feedwater and corresponding combined permeate were collected. For this experiment, the observed removal percentages of indicator compounds quantified with a DR of >5 in the feedwater are summarized in Table 5.30.

**Table 5.30. Treatment Removal Categories of Indicator Compounds during NF Operation**[a]

| Good Removal (>90%) | | Intermediate Removal (90 < x < 50%) | Intermediate Removal (50 < x < 25%) | Poor Removal (<25%) |
|---|---|---|---|---|
| 17β-Estradiol | Ibuprofen | Bisphenol A | Phenacetine | $CHCl_3$ |
| Atrazine | Ketoprofen | Caffeine | | Acetaminophen |
| Carbamazepine | Mecoprop | | | |
| Clofibric acid | Meprobamate | | | |
| DEET | Naproxen | | | |
| Dichlorprop | Primidone | | | |
| Diclofenac | Salicylic acid | | | |
| Dilantin | Sulfamethoxazole | | | |
| Erythromycin–$H_2O$ | TCEP | | | |
| Estrone | TCPP | | | |
| Fenofibrate | TDCPP | | | |
| Gemfibrozil | Trimethoprim | | | |
| Hydrocodone | | | | |

[a]Conditions: membrane, NF-4040 membrane; recovery, 85%; permeate flux, ~12 gfd (~20 LMH); pH = 6.5.

While this NF membrane exhibited a conductivity rejection of less than 50%, the removal of indicator compounds was quite efficient. As expected, neutral indicator compounds that are close to or below the MW cutoff of this membrane (i.e., phenacetine, acetaminophen, and caffeine) exhibit only a partial removal. The removal percentages of the surrogate parameters are summarized in Figure 5.19, which reflects findings derived from using microfiltered tertiary-treated effluent from Facility 8. TOC was rejected in excess of 95%. Divalent cations exhibited a removal between 71 and 80%. As expected, monovalent ions, such as potassium, sodium or ammonium, exhibited only a partial rejection, whereas boron was not rejected by this membrane.

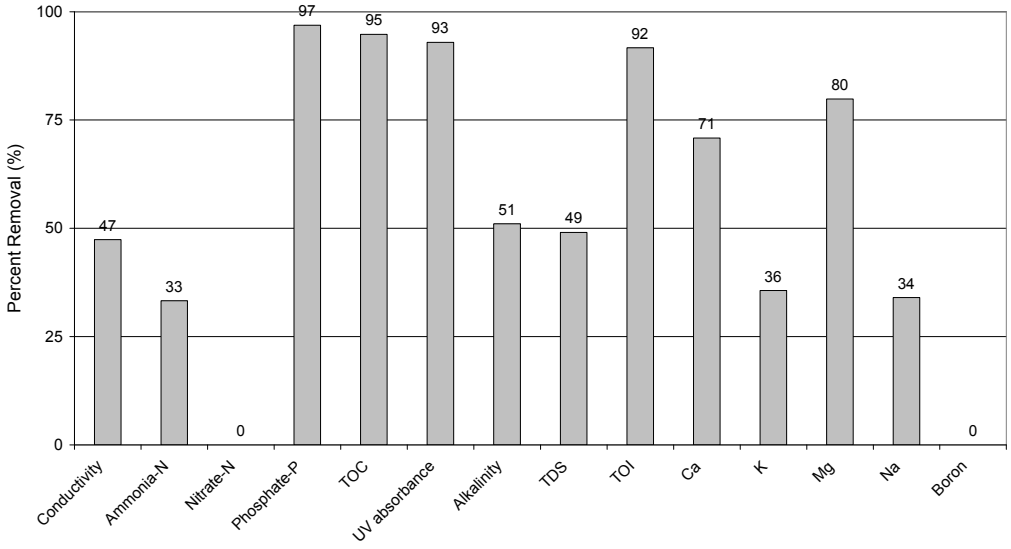



**Figure 5.19. Rejection of surrogate parameters during pilot-scale NF treatment.**

## 5.3 CONCLUSIONS

The evaluation of field-, pilot-, and laboratory-scale treatment processes validated the proposed indicator selection and removal categories. Selected indicators were frequently detected in reclaimed water receiving secondary or tertiary treatment, and observed percentage removals agreed well with the proposed removal ranking scheme of each treatment category. Appropriate surrogate parameters were identified for assessing the performance of a particular treatment process.

# CHAPTER 6

# SURROGATE AND INDICATOR FRAMEWORK TO ASSESS DISCHARGE TO RECEIVING STREAMS

## 6.1 INTRODUCTION

The potential use of the surrogate and indicator framework to assess the presence of wastewater-derived contaminants in systems in which unintentional potable water reuse is practiced was evaluated at two sites. Both sites are characterized by a degree of discharge of wastewater exceeding 80% to the receiving streams. While this degree of impact might not be representative for many sites under the impact of wastewater discharge, it provided good conditions to study the fate and transport of wastewater-derived organic compounds in the environment.

## 6.2 DISCHARGE TO RECEIVING STREAMS

Sampling campaigns were conducted at Facility 11 in May 2006 and Facility 7 in June 2006. The river sampled at Facility 11 received secondary-treated wastewater (nitrified) from a metropolitan area, which made up approximately 80% of the flow in the river during the time of sampling. The average flow on the day of sampling was 201 cfs (5.7 $m^3/s$). Sampling occurred at four locations downstream of a major wastewater treatment plant. These locations are representative of approximate travel times of 30 min, 5 h, 12 h, and 17 h downstream from the wastewater discharge, as determined by previous tracer studies performed on the river. The approximate travel distances of the water from the point of discharge are 0.5, 5, 12, and 17 mi (0.8, 8, 19, and 27 km), respectively. Samples were analyzed for select indicator compounds and for some additional compounds that were part of the analytical methods employed but did not meet the initial selection criterion for indicator compounds of a DR of >5 (see Table 4.2).

Concentrations of detectable indicator compounds at downstream locations are presented in Figure 6.1. The results suggest that with the exception of salicylic acid none of the detectable indicator compounds were removed within 17 h of travel. These findings are somewhat surprising since compounds such as ibuprofen, naproxen, and gemfibrozil have proven to be biodegradable both during MBR treatment and SAT (see Chapter 5). For a similar study on the Trinity River, TX, Fono et al. (2006) observed between a 60 and 90% decrease of gemfibrozil, ibuprofen, and naproxen over a travel time of 2 weeks. The researchers determined that biotransformation was more important than photolysis for the removal of gemfibrozil, ibuprofen, and naproxen. Thus, it is likely that the same compounds are also biotransformed in the river of Facility 11 after longer travel times on the order of weeks.

Samples were also analyzed for select surrogate parameters. Surrogate parameter measurements, such as conductivity, TOC, SUVA, hardness, ammonia, and anions (i.e., fluoride, chloride, and sulfate), remained relatively constant along the studied portion of the river of Facility 11. However, a decrease of EDTA from 123 μg/L (30 min downstream of discharge) to 69 μg/L (17 h downstream of discharge) was observed. This decrease is likely due to photolytic reactions. Other researchers have previously reported the photochemical degradation of EDTA in surface waters (Xue et al., 1995; Kari et al., 1996; Fono et al., 2006).

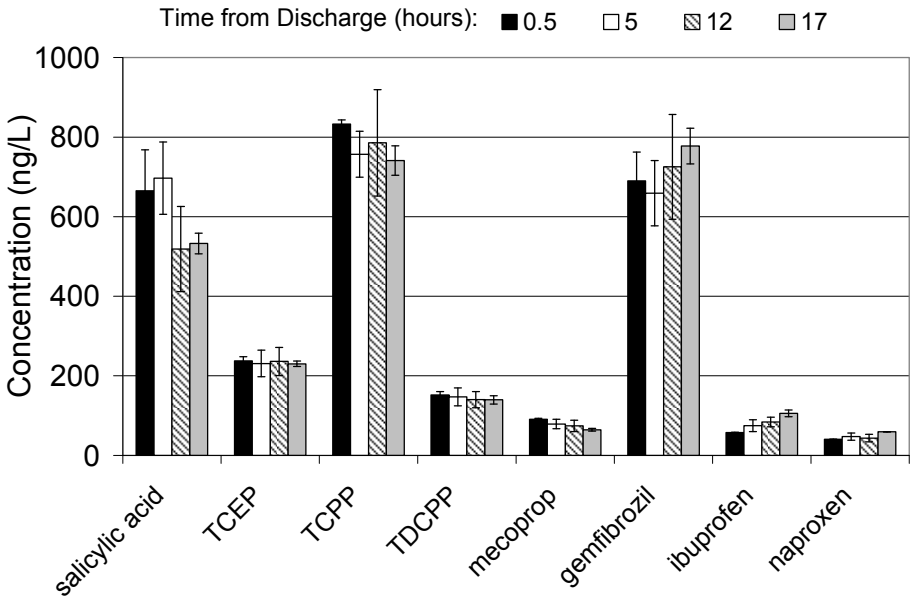



**Figure 6.1. Concentrations of detectable indicator compounds downstream of a wastewater plant in the receiving river of Facility 11.**

The river at Facility 7 received secondary-treated wastewater (not nitrified), which made up 100% of the flow in the river (no flow upstream of the discharge). Sampling occurred at 3 locations downstream of the discharge representing travel times of 2, 4, and 6 h. Similar to the findings of the study performed at Facility 11, most of the studied indicator compounds did not decrease in concentration after a travel time in the river of 6 h (Figure 6.2). Salicylic acid exhibited a reduction by approximately 50% after 6 h of travel, which likely was caused by biotransformation. Sulfamethoxazole and diclofenac concentrations also decreased by approximately 30% after 6 h of travel. Andreozzi et al. (2003) and Boreen et al. (2004) both reported that sulfamethoxazole and diclofenac undergo relatively fast degradation due to photolysis. EDTA concentrations also decreased from 283 μg/L (discharge) to 149 μg/L (after 6 h downstream of discharge). This decrease is also likely due to photolytic reactions and consistent with findings from previous studies (Xue et al., 1995; Kari et al., 1995; Fono et al., 2006).

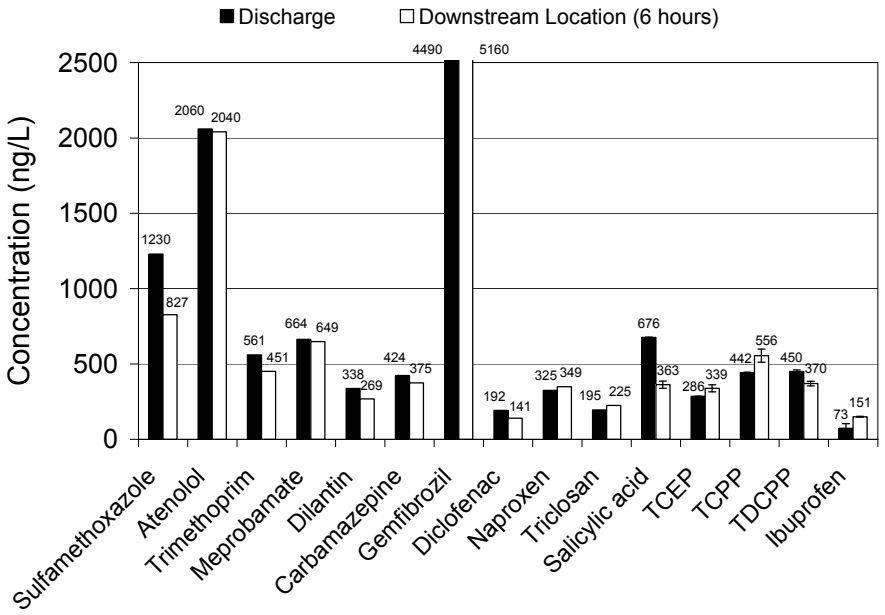



**Figure 6.2. Concentrations of detectable indicator compounds downstream of a wastewater plant.**

## 6.3 CONCLUSIONS

Removal of wastewater-derived contaminants in surface water is less favorable than in natural or engineered subsurface systems, such as SAT or riverbank filtration. Findings of this study supported by previously published reports reveal that there are only a few select compounds that will be attenuated by photolysis in receiving waters over short (i.e., 1 day) and long (i.e., weeks) travel times. Biotransformation mechanisms become more important with travel time but require several weeks of CT to be effective. Compounds that are recalcitrant, such as antiepileptic drug residues (i.e., primidone and carbamazepine) or chlorinated flame retardants (i.e., TCEP, TCPP, and TDCPP), are not attenuated during travel in wastewater-impacted surface water. These compounds are highly water soluble and could serve as indicators to assess the degree of wastewater impact to a stream.

# CHAPTER 7

# RECOMMENDATIONS AND CONCLUSIONS FOR MONITORING CHEMICAL CONTAMINANT REMOVAL

## 7.1 INDICATOR/SURROGATE FRAMEWORK—THE CONCEPT

The approach for monitoring wastewater-derived trace organic contaminants developed in this study is utilizing a combination of surrogate parameters and indicator compounds tailored to monitor the removal efficiency of individual unit processes comprising an overall treatment train. In the context of this study, an indicator compound 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 indirect potable reuse 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 viable 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 compound in various treatment processes. 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 compounds 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 compounds are limited and imprecise. Thus, this study focused on defining the operational boundary conditions for each treatment process under which removal is to be expected.

Indicator compounds and surrogate parameters identified were classified into categories of different treatability. These treatment categories include conventional and advanced water treatment processes commonly employed in indirect potable reuse applications. These treatment processes can be characterized by key removal mechanisms, such as biodegradation (i.e., SAT and MBR), chemical oxidation (i.e., ozonation, AOPs, chlorination, and chloramination), photolysis (i.e., low-pressure UV radiation), adsorption (i.e, PAC and GAC), or physical separation (i.e., NF and RO).

The properties and occurrence levels of organic micropollutants occurring at the nanograms-per-liter level in secondary- or tertiary-treated wastewater effluents vary widely, and different

analytical methods are required for their quantification. While multiple methods have been developed and employed during the last 10 years for the detection of these compounds, none of these methods currently is standardized. Interlaboratory comparisons among experienced analytical laboratories conducted during this study revealed that analytical methods targeted for multicomponent analysis exhibited significant variations of recovery and RSDs, indicating the degree of uncertainty that is still associated with reporting low nanograms-per-liter concentrations. Instead of relying on absolute numbers or threshold levels as a treatment goal or performance measure, we decided to group potential indicator compounds 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 upon the physicochemical and biodegradable properties of the compounds. Whether the proposed degree of removal is achieved will depend upon operational conditions of the treatment process (e.g., oxidant dose concentration, type of activated carbon, water matrix, and CT). 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 compounds classified in the categories "good removal (>90%)" and "intermediate removal (90% < x < 50%)," while normal operating conditions will be indicated by partial or complete indicator compound removal. As indicated earlier, along with these classifications, relevant operational boundary conditions were defined for each type of treatment.

For select treatment processes, a master list of indicator compounds was developed by recruiting compounds for which peer-reviewed analytical methods existed from the final list of viable indicator compounds present in secondary- or tertiary-treated wastewater effluents (Table 4.2). These master lists were compiled through a comprehensive literature review of over 100 peer-reviewed journal articles, internal occurrence surveys drawing upon yet-to-be-published findings and ongoing projects among the three principal investigators, and quantitative structure property relationships. Master lists of indicator compounds were provided for SAT (Table 5.2), ozonation (Table 5.8), AOPs (Table 5.12), chlorination (Table 5.18), PAC adsorption (Table 5.22), GAC adsorption (Table 5.23), and RO treatment (Table 5.26). Due to databases for other processes being less comprehensive, only indicator compound removal categories building upon specific case studies were proposed for MBR treatment, chloramination, low-pressure UV radiation, and NF. The developed treatment removal ratings for indicator compounds for each treatment process of interest (i.e., SAT, ozone, advanced oxidation, chlorination, carbon adsorption, and RO) were validated through laboratory- and pilot-scale experiments and full-scale monitoring efforts (Chapter 5). Findings of these studies confirmed the classification of indicator compounds into the different treatment categories and proposed removal rankings. As expected, results of these efforts also revealed that the majority of surrogate parameters are not strongly correlated with the removal of indicator compounds occurring at nanograms-per-liter concentrations. Partial or complete change of a surrogate parameter, however, can demonstrate the proper operation of a unit operation or treatment train. Enhanced removal of select surrogate parameters correlated with improved removal of indicator compounds. Thus, changes of certain surrogate or operational parameters summarized in Table 7.1 were identified as being sensitive in picking up performance deficiencies, which might or might not be resulting in a diminished removal of wastewater-derived contaminants in that treatment process. Thus, to ensure proper performance of unit operations regarding the removal of wastewater-derived contaminants, a combination of appropriate surrogate parameters and indicator compounds should be selected.

**Table 7.1. Sensitive Surrogate Parameters Identified for Different Treatment Categories**

| Mechanism | Treatment Process | Surrogate for Performance Assessment |
|---|---|---|
| Biodegradation | SAT | BDOC; ΔDOC; ΔUVA; ΔTOX; Δammonia; Δnitrate |
| | Riverbank filtration | SFLUOR; SUVA; 3-D fluorescence |
| | MBR | ΔTOC; ΔUVA |
| Chemical oxidation | Ozone | ΔUVA; Δcolor; 3-D fluorescence |
| | | Δformate; ΔAOC |
| | | Integral contact time |
| | AOP (ozone/$H_2O_2$; ozone/UV; UV/$H_2O_2$) | ΔUVA; Δcolor; 3-D fluorescence |
| | | Δformate; Δoxalate; Δaldehyde; ΔAOC |
| | Chlorination | Integral contact time |
| | Chloramination | Not a viable process to remove wastewater-derived organic contaminants |
| UV disinfection | Low-pressure UV | Not a viable process to remove wastewater-derived organic contaminants |
| Adsorption | PAC | ΔUVA; 3-D fluorescence |
| | GAC | ΔUVA; 3-D fluorescence; ΔTOC |
| Physical separation | RO | Δconductivity; Δboron |
| | NF | Δcalcium; Δmagnesium |

The proposed framework is a conservative approach designed to ensure proper removal of identified and unidentified wastewater-derived organic contaminants and to detect failures in system performance. Assessing system performance of individual unit processes comprising an overall treatment train is distinguished into two phases: piloting/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 their technical specifications. During a piloting/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 the presence of viable indicator compounds in the feedwater of each unit process. During piloting or start-up of a new treatment process, challenge or spiking tests can be conducted with select indicator compounds to determine the removal differential $\Delta Y$ under normal operating conditions. For these tests, 5 to 10 indicator compounds from the treatment category classified as "good removal" should be selected. For the full-scale operation, the operational boundary conditions and removal differential $\Delta X$ and $\Delta Y$ for selected surrogate and operational parameters and indicator compounds 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. While it is implied that proper performance of the full-scale treatment train will ensure appropriate removal of wastewater-derived organic contaminants, select indicator compounds (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 7.2.

**Table 7.2. Application of Surrogate/Indicator Framework to an Overall Treatment Train**

| | Surrogate Parameters | Indicator Compounds |
|---|---|---|
| **Piloting and/or Start-up** | | |
| Step 1 | Define operational boundary conditions for each unit process comprising the overall treatment train for proper operation according to technical specifications | |
| Step 2 | For each unit process, identify those surrogate or operational parameters that demonstrate a measurable removal under normal operating conditions and quantify their removal differential ($\Delta X = [X_{in} - X_{out}]/X_{in}$) | Conduct occurrence study to confirm presence of viable indicator compounds in the feedwater of each unit process |
| Step 3 | | Conduct challenge or spiking study with select indicator compounds (5 to 10) during pilot scale or start-up to determine the removal differentials under normal operating conditions ($\Delta Y = [Y_{in} - Y_{out}]/Y_{in}$) |
| Step 4 | Select viable 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 boundary conditions of full-scale operation and removal differential $\Delta X$ for selected surrogate and operational parameters | |
| Step 6 | Monitor differential $\Delta X$ of select surrogate and operational parameters for each unit process or/and the overall treatment train on a regular basis (daily, weekly) | Monitor differential $\Delta Y$ of selected indicator compounds for each unit process or/and the overall treatment train semiannually/annually |

Adopting the proposed treatment category framework can also assist in more properly tailoring multiple barriers of treatment processes with a demonstrated ability to remove wastewater-derived contaminants in indirect potable reuse applications. For wastewater-derived organic compounds, which are only moderately or poorly removed, an additional treatment barrier should be demonstrated. Since every proposed treatment scheme is likely unique, a monitoring strategy that covers all aspects needs to be developed for each site. While the "building blocks" for such a monitoring program are provided by the treatment removal categories for each treatment process, the selected indicator compounds and

surrogate parameters as well as the sampling frequencies might look different among different sites.

During this study, the developed surrogate and indicator framework was subject to multiple internal reviews and also to an external peer-review process during a 2-day Stakeholder Advisory Committee Workshop held in May 2006. The purpose of this workshop was to present the approach to practitioners in the field, to receive critiques for its improvement, and to develop recommendations for monitoring programs. Participants of this peer-review process are listed in Table 7.3.

**Table 7.3. Participants in Stakeholder Advisory Committee Workshop**

| Role | Name | Affiliation |
|---|---|---|
| Project team | Jörg E. Drewes | CSM |
| | David Sedlak | UC |
| | Shane Snyder | SNWA |
| | Eric Dickenson | CSM |
| SAC members | Anthony Andrade | Southwest Florida Water Management District, FL |
| | Rick Arber | Richard P. Arber and Associates, CO |
| | Steve Carr | County Sanitation Districts of Los Angeles County, CA |
| | Douglas Drury | Clark County Water Reclamation District, NV |
| | Andy Eaton | MWH Laboratories, CA |
| | John Kmiec | Tucson Water, AZ |
| | Sam Mowbray | Orange County Sanitation District, CA |
| | Mike Neher | City of Henderson, NV |
| | Margie Nellor | Nellor Environmental, TX |
| | Dave Rexing | Southern Nevada Water Authority, NV |
| | Rick Sakaji | East Bay Municipal Utility District, CA |
| | Martha Tremblay | County Sanitation Districts of Los Angeles County, CA |
| | Mike Wehner | Orange County Water District, CA |
| | David York | Florida Dept. of Environmental Protection, FL |
| TAC members | Rick Pleus | Intertox, Inc., WA |
| | Jim Crook | Crook Environmental, MA |
| Funding agency | Joshua Dickinson | WateReuse Foundation |

The subsequent chapter provides additional guidance on how the surrogate and indicator framework could be integrated into performance-monitoring programs and compliance monitoring for overall treatment trains leading to indirect potable reuse.

## 7.2 RECOMMENDATIONS FOR MONITORING DURING PILOT-SCALE STUDIES AND START-UP

To monitor system performance at a given facility, the selection of appropriate indicator compounds will depend upon the treatment processes employed comprising an overall treatment train and the geographic and temporal variations in the occurrence pattern of certain wastewater-derived contaminants. Therefore, the determination of an indicator/surrogate monitoring framework for a given treatment train will likely vary from site to site. The following sections provide some examples of how a monitoring program using the indicator/surrogate framework might look. These examples are provided for SAT, AOPs, and RO treatment.

### 7.2.1 Monitoring Framework for SAT

Following the steps outlined in Table 7.2, a viable 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 7.4). During a piloting 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 7.4 to be considered in performance-monitoring efforts.

**Table 7.4. 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 | | | |
| | ΔUVA | | | |
| | BDOC | | | |
| | ΔGemfibrozil | ΔMeprobamate | | ΔPrimidone |
| | ΔDiclofenac | | | |
| | ΔIopromide | | | |
| | ΔSulfamethoxazole | | | |
| 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 piloting or start-up, the expected removal differentials for these indicators need to be determined. Monitoring also 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.

### 7.2.2 Monitoring Framework for Advanced Oxidation

Following the steps outlined in Table 7.2, a viable surrogate parameter for an AOP operation could be the differential in UVA, color, AOC and formate measurements prior to and after oxidation (Table 7.5). During a piloting study or start-up of a full-scale facility, these measurement differentials will be determined. As an example, certain indicator compounds representing a different amenability to oxidation are suggested in Table 7.5 for consideration in performance-monitoring efforts.

**Table 7.5. Monitoring Framework for AOP Systems**[a]

| Monitoring Level | Good Removal (>90%) | Intermediate Removal (90 < x < 50%) | Intermediate Removal (50 < x < 25%) | Poor Removal (<25%) |
|---|---|---|---|---|
| Performance | ΔUVA | | | |
| | ΔColor | | | |
| | ΔAOC | | | |
| | ΔFormate | | | |
| | ΔDEET | ΔIopromide | | |
| | ΔDilantin | | | |
| | ΔMeprobamate | | | |
| | ΔIbuprofen | | | |
| Compliance monitoring | ΔColor | | | |
| | ΔFormate | | | |

[a]Dilution, 0%.

During piloting 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.

### 7.2.3 Monitoring Framework for High-Pressure Membrane Treatment

Following the steps outlined in Table 7.2, a viable surrogate parameter for an RO operation could be the differential in conductivity, TOC, and boron measurements prior to and after RO treatment (Table 7.6). During a piloting 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 7.6 for consideration in performance-monitoring efforts or RO operations.

**Table 7.6. Monitoring Framework for RO Systems**[a]

| | Good Removal | Intermediate Removal | | Poor Removal |
|---|---|---|---|---|
| **Monitoring Level** | **(>90%)** | **(90 < x < 50%)** | **(50 < x < 25%)** | **(<25%)** |
| Piloting/start-up: | ΔConductivity<br>ΔTOC<br>ΔBoron | | | |
| | ΔCaffeine<br>ΔButylated hydroxy anisole<br>ΔMeprobamate<br>ΔAcetaminophen | | ΔNDMA<br>ΔChloroform | |
| Compliance monitoring | ΔConductivity<br>ΔBoron | | | |

[a]Dilution, 0%.

During piloting 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.

## 7.3 RECOMMENDATIONS FOR MONITORING DURING FULL-SCALE OPERATION

### 7.3.1 Monitoring of RO/AOP Barriers

Utilities utilizing recycled water for direct injection in the State of California commonly employ an IMS (MF/RO treatment) followed by advanced oxidation (i.e., UV/$H_2O_2$) (Figure 7.1). A program adopting the surrogate/indicator framework is proposed that performs monitoring during an intial piloting or start-up followed by full-scale operation/compliance monitoring.

During the initial phase of start-up, select indicator compounds (i.e, sulfamethoxazole, NDMA, TCEP, and chloroform) and certain surrogate parameters (i.e., conductivity, TOC, and boron) will be tested for the MF/RO system (sampling locations nos. 4 and 3). The start-up of the UV/$H_2O_2$ system will be accompanied by measuring certain indicator compounds (i.e., DEET, dilantin, NDMA, and meprobomate) and the surrogate parameters formate and residual peroxide (at sampling locations nos. 3 and 2).

During full-scale compliance monitoring, only three surrogate parameters are suggested (at sampling locations nos. 4 and 2): conductivity, boron, and residual peroxide to demonstrate normal operating conditions. In addition, annual monitoring can occur for three key indicator compounds, namely, sulfamethoxazole, NDMA, and TCEP (at sampling locations nos. 4, 2, and 1).

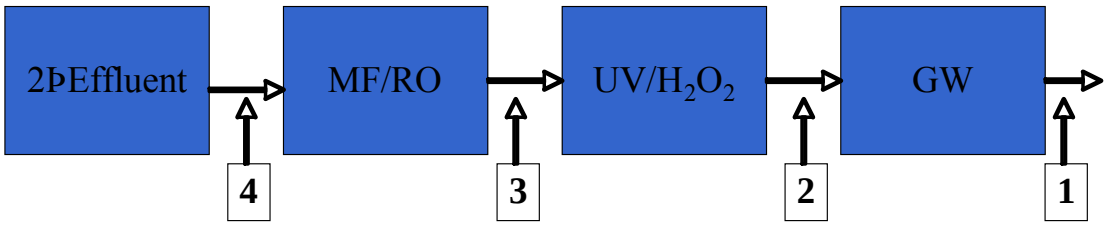



**Figure 7.1. Treatment schematic illustrating an advanced water treatment train.**

# CHAPTER 8

# APPENDIX

## 8.1 SUPPLEMENTAL INFORMATION

**Table 8.1. List of Compounds Considered during Indicator Compound Selection**

| Compound Class | Compounds Occurring in Secondary/Tertiary-Treated Effluents |
|---|---|
| Antibiotic | Acetyl-sulfamethoxazole, Amoxicillin, Azithromycin, Carbadox, Chloramphenicol, Chlorotetracycline, Ciproflaxacin, Clarithromycin, Cloxacillin, Dehydroerythromycin, Democyclocycline, Dicloxacillin, Doxycycline, Enrofloxacin, Erythromycin, N4-acetylsulfamethoxazole, Nafcillin, Norfloxacin, Ofloxacin, Olaquindox, Oxacillin, Oxolinic acid, Oxytetracycline, Penicillin G, Penicillin V, Pipemidic acid, Roxithromycin, Sulfacetamide, Sulfachloropyridazine, Sulfadiazine, Sulfadimethoxane, Sulfadimethoxine, Sulfaguanidine, Sulfamerazine, Sulfamethazine, Sulfamethizole, Sulfamethoxazole, Sulfamethoxypyridazine, Sulfamoxole, Sulfapyridine, Sulfaquinoxaline, Sulfasomidin, Sulfathiazole, Sulfisoxazole, Tetracycline, Methicillin, Trimethoprim, Tylosin |
| Antibacterial | Methyl Triclosan, Penta Chlorinated Triclosan, Tetra-II, Chlorinated Triclosan, Tetra-III, Chlorinated Triclosan, Triclosan |
| Benzothiazole | 2-Methylthiobenzothiazole, 2-Hydroxybenzothiazole, 2-Mercaptobenzothiazole, Benzothiazole, BTSA |
| DBPs | 1,4-Dichlorobenzene, Bromodichloromethane, Dibromochloromethane, NDMA, Tribromomethane, Trichloromethane |
| DBP precursor | DMA |
| Regulated organic chemical | Tetrachloroethylene |
| Flame retardant | BDP, RDP, TBEP, TCEP, TCPP, TDCP, TEHP, TnBP, TPhP, TPPO |
| Fragrance | 2-Amino-Musk Ketone, 2-Amino-Musk Xylene, 4-Amino-Musk Xylene, Acetyl Cedrene, AHTN, Amberonne,benzyl Acetate, Benzyl Salicylate, Celestolide, Galaxalide, *g*-Methyl Ionine, Hexyl Salicylate, Hexylcinnamaldehyde, HHCB, Isobornyl Acetate, Methyl Dihydrojasmonate, Methyl Salicylate, Musk Ketone, Musk Xylene, OTNE, *p*-*t*-Bucinal, Terpineol, Tonalide, Traseolide, Versalide |
| Fuel additive | MTBE |
| Hormone | 16α-Hydroxyestrone, E1, E1-3G, E1-3S, E1-G, E1-S, E2, E2-17G, E2-17-valerate, E2-3G, E2-3S, E2-Alpha, E2-diS, E2-G, E2-S, E2-S&G, E3, E3-16G, E3-3G, E3-3S, E3-G, E3-S, EE2, Mestrano, Testosterone |
| Household chemical | Caffeine, EDTA, NTA |

*Continued*

**Table 8.1.** ***Continued***

| Compound Class | Compounds Occurring in Secondary/Tertiary-Treated Effluents |
|---|---|
| Iodinated X-ray contrast media | Diatrazoate, Iomeprol, Iopamidol, Iopromide, Iothalamic acid, Ioxithalamic acid |
| Mycoestrogen | Alpha-Zearalanol, Beta-Zearalanol, Zearalenone |
| Others | Phenol, Polydimethylsiloxane |
| Pesticide | 2,4-D, Atrazine, Bayrepel, DEET, Dimethenamide, Irgarol, MCPA, Mecoprop, Metolachlor, Simazine, Tebutam, Terbutryne, Terbutylazine, Triclopyr |
| PhAC | *o*-Hydroxyhippuric acid, Acetaminophen, Acetylsalicylic acid, Atenolol, Betaxolol, Bezafibrate Bisoprolol, Carazolol, Carbamazepine, Celiprolol, Clenbuterol, Clofibrate, Clofibric acid, Cyclophosphamide, Dextropropoxyphene, Diazepam, Diclofenac, Dimethylaminophenazone, Etofibrate, Fenofibrate, Fenofibric acid, Fenoprofen, Fenoterol, Gemfibrizol, Gentisic acid, Ibuprofen, Ifosfamide, Indometacine, Indomethacin, Ketoprofen, Ketorolac, Mefanamic acid, Metoprolol, Nadolol, Naproxen, Paracetamol, Pentoxyfylline, Phenazone, Piroxicam, Primidone, Propanolol, Propyphenazone, Salbutamol, Salicylic acid, Sotalol, Tamoxifen, Terbutalin, Timolol, Trimethoprim |
| Phytoestrogens | 4'6,7-Trihydroxyisoflavone, Biochanin-A, Coumestrol, Daidzein, Daidzin, Formononetin, Genistein, Genistin, Glycitein |
| Plasticizer | BPA, DEHP, Dibutylphthalate |
| Steroid | Coprostanol |
| Sunscreen agent | 4-MBC, BP-3, EHMC, OC |
| Surfactant | Alcohol ether Sulfate, Alcohol Ethoxylates-C12, Alcohol Ethoxylates-C13, Alcohol Ethoxylates-C14, Alcohol Ethoxylates-C15, Alcohol Ethoxylates-C16, Alcohol Ethoxylates-C18, Alcohol Sulfate, Alkyl Ethoxylate alcohol-C12, Alkyl Ethoxylate Alcohol-C13, Alkyl Ethoxylate Alcohol-C14, Alkyl Ethoxylate Alcohol-C15, Nonylphenol, Octylphenol, Secondary Alkane Sulfonate |
| Veterinary PhAC | Meclofenamic acid, Tolfenamic acid |

**Table 8.2. Summary of Wastewater-Derived Contaminants Occurring in Secondary/Tertiary Effluents in Europe and North America**

| Continent of Origin | Compound | Compound Category | Median Concn (ng/L) | Occur-rence Avg. Concn (ng/L) | Occur-rence Min. Concn (ng/L) | Occur-rence Max. Concn (ng/L) | Sample StDev | No. of STPs | Occur-rence (No. of Samples) | No. of NDs | Analytical Method | Reported MDL (ng/L) | Reported LOQ (ng/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Europe | Triclosan | Antibacterial | 127.6 | 336.25 | 4 | 1117 | | 25 | 25 | 0 | GC/MS | 10 | 100 |
| N.A. | | | 1010 | 1165 | 240 | 2400 | | 4 | 4 | 0 | GC/MS | 10 | 100 |
| Europe | Clarithromycin | Antibiotic | 254.83 | 244.00 | 110 | 460 | | 6 | 36 | 0 | LC/MS/MS | | 50 |
| N.A. | | | 87 | 87 | 0 | 536 | | 8 | 8 | 2 | LC/MS/MS | 1 | 50 |
| Europe | Erythromycin | Antibiotic | 918.33 | 297.33 | 50 | 1842 | 240 | 9 | 73 | 25 | LC/MS/MS | 10 | 50 |
| N.A. | | | 80 | 80 | 75 | 85 | 5 | 1 | 1 | 0 | LC/MS/MS | 10 | 50 |
| Europe | Norfloxacin | Antibiotic | 67.50 | 67.50 | 36 | 120 | | 12 | 20 | 0 | LC/MS/MS | 5 | 30.00 |
| N.A. | | Antibiotic | 50 | 50 | 0 | 112 | | 8 | 8 | 4 | LC/MS/MS | 5 | 30.00 |
| Europe | Roxithromycin | Antibiotic | 237.00 | 218.00 | 10 | 1000 | 40 | 9 | 73 | 25 | LC/MS/MS | | 50 |
| N.A. | | Antibiotic | 8.00 | 8 | | 18 | 0 | 9 | 9 | 2 | LC/MS/MS | 1 | 30 |
| Europe | Sulfamethoxa-zole | Antibiotic | 321.75 | 406.67 | 130 | 2000 | 50 | 17 | 94 | 41 | LC/MS/MS | 6.7 | 20 |
| N.A. | | Antibiotic | 279.00 | 279.00 | 130 | 871 | | 10 | 10 | 0 | LC/MS/MS | 1 | 20 |
| Europe | Acetyl cedrene | Fragrance | 230.00 | 500.00 | 70 | 1430 | | 5 | 5 | 0 | GC/MS | | 7 |
| N.A. | | Fragrance | 176.00 | 339.00 | 12 | 1359 | | 12 | 12 | 0 | GC/MS | | 7 |
| Europe | AHTN | Fragrance | 1300.00 | 1440.00 | 620 | 2670 | | 5 | 5 | 0 | GC/MS | | 3 |
| N.A. | | Fragrance | 1130.00 | 966.00 | 24 | 1710 | | 12 | 12 | 0 | GC/MS | | 3 |
| Europe | Benzyl acetate | Fragrance | 100.00 | 118.00 | 60 | 260 | | 5 | 5 | 0 | GC/MS | | 3 |
| N.A. | | Fragrance | 86.00 | 84.00 | 2 | 252 | | 12 | 12 | 0 | GC/MS | | 3 |
| Europe | Benzyl salicylate | Fragrance | 590.00 | 670.00 | 40 | 1960 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 88.00 | 209.00 | 5 | 1025 | | 12 | 12 | 0 | GC/MS | | 2 |

**Table 8.2. Summary of Wastewater-Derived Contaminants Occurring in Secondary/Tertiary Effluents in Europe and North America**

| Continent of Origin | Compound | Compound Category | Median Concn (ng/L) | Occur-rence Avg. Concn (ng/L) | Occur-rence Min. Concn (ng/L) | Occur-rence Max. Concn (ng/L) | Sample StDev | No. of STPs | Occur-rence (No. of Samples) | No. of NDs | Analytical Method | Reported MDL (ng/L) | Reported LOQ (ng/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Europe | *g*-Methyl ionine | Fragrance | 250.00 | 324.00 | 30 | 730 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 34.00 | 60.00 | 7 | 214 | | 12 | 12 | 0 | GC/MS | | 2 |
| Europe | Hexyl salicylate | Fragrance | 250.00 | 324.00 | 10 | 910 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 34.00 | 60.00 | 1 | 243 | | 12 | 12 | 0 | GC/MS | | 2 |
| Europe | Hexylcinnam-aldehyde | Fragrance | 170.00 | 268.00 | 20 | 910 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 14.00 | 22.00 | 10 | 77 | | 12 | 12 | 0 | GC/MS | | 2 |
| Europe | HHCB | Fragrance | 1150.00 | 2310.00 | 980 | 4620 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 1500.00 | 1345.00 | 32 | 2210 | | 12 | 12 | 0 | GC/MS | | 2 |
| Europe | Isobornyl acetate | Fragrance | 70.00 | 124.00 | 10 | 290 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 24.00 | 40.00 | 7 | 112 | | 12 | 12 | 0 | GC/MS | | 2 |
| Europe | Methyl dihydro-jasmonate | Fragrance | 1160.00 | 903.00 | 26 | 1920 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 85.00 | 152.00 | 3 | 456 | | 12 | 12 | 0 | GC/MS | | 2 |
| Europe | Methyl salicylate | Fragrance | 90.00 | 146.00 | 40 | 310 | | 5 | 5 | 0 | GC/MS | | 2 |
| N.A. | | Fragrance | 42.00 | 175.00 | 13 | 693 | | 12 | 12 | 0 | GC/MS | | 2 |
| Europe | Musk ketone | Fragrance | 100.00 | 180.00 | 0 | 770 | | 14 | 14 | 6 | GC/MS | | 0.7 |
| N.A. | | Fragrance | 27.00 | 31.00 | 0 | 67 | | 12 | 12 | 2 | GC/MS | | 0.7 |
| Europe | Musk xylene | Fragrance | 5.00 | 23.00 | 0 | 170 | | 14 | 14 | 8 | GC/MS | 9 | 1 |
| N.A. | | Fragrance | 10.00 | 25.00 | 0 | 112 | | 12 | 12 | 1 | GC/MS | | 1 |
| Europe | OTNE | Fragrance | 1700.00 | 1906.00 | 490 | 3190 | | 5 | 5 | 0 | GC/MS | | 4 |
| N.A. | | Fragrance | 110.00 | 173.00 | 25 | 615 | | 12 | 12 | 0 | GC/MS | | 4 |

**Table 8.2. Summary of Wastewater-Derived Contaminants Occurring in Secondary/Tertiary Effluents in Europe and North America**

| Continent of Origin | Compound | Compound Category | Median Concn (ng/L) | Occur-rence Avg. Concn (ng/L) | Occur-rence Min. Concn (ng/L) | Occur-rence Max. Concn (ng/L) | Sample StDev | No. of STPs | Occur-rence (No. of Samples) | No. of NDs | Analytical Method | Reported MDL (ng/L) | Reported LOQ (ng/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Europe | *p*-*t*-Bucinal | Fragrance | 80.00 | 92.00 | 40 | 180 | | 5 | 5 | 0 | GC/MS | | 1 |
| N.A. | | Fragrance | 41.00 | 76.00 | 13 | 258 | | 12 | 12 | 0 | GC/MS | | 1 |
| Europe | Terpineol | Fragrance | 110.00 | 3124.00 | 80 | 15100 | | 5 | 5 | 0 | GC/MS | | 5 |
| N.A. | | Fragrance | 42.00 | 192.00 | 11 | 1079 | | 12 | 12 | 0 | GC/MS | | 5 |
| Europe | E1 | Hormone | 11.59 | 19.62 | 0.00 | 220.00 | | 50.00 | 94.00 | 9.00 | LC/MS/MS | 0.50 | 1.00 |
| N.A. | | Hormone | 7.05 | 15.95 | 0.00 | 96.00 | | 37.00 | 44.00 | 4.00 | LC/MS/MS | 0.50 | 1.00 |
| Europe | E2 | Hormone | 4.10 | 8.59 | 0 | 88 | | 66 | 110 | 18 | GC/MS | 0.8 | 1 |
| N.A. | | Hormone | 2.70 | 2.70 | 0 | 30 | | 50 | 72 | 15 | HPLC/ELISA | 0.4 | 1 |
| Europe | E3 | Hormone | 1.25 | 17.50 | 0 | 275 | | 14 | 35 | 6 | GC/MS | 0.5 | 1 |
| N.A. | | Hormone | 7.51 | 7.51 | 0 | 4.9 | | 11 | 11 | 8 | HPLC/ELISA | 0.6 | 1 |
| Europe | EE2 | Hormone | 1.50 | 1.04 | 0 | 15 | | 39 | 73 | 42 | GC/MS/MS | 0.5 | 1 |
| N.A. | | Hormone | 0.58 | 0.77 | 0 | 4.1 | | 17 | 20 | 9 | GC/MS/MS | 0.5 | 1 |
| Europe | EDTA | Household | 38000 | 54000 | 14600 | 163700 | | 3 | 21 | 0 | GC/NPD | 0.00 | 1000 |
| N.A. | | Household | 11800 | 11800 | 8000 | 16000 | | 0.00 | 2 | 0.00 | GC/EI/MS | 0.00 | 1000 |
| Europe | NTA | Household | 21000 | 46800 | 15300 | 195000 | | 1 | 11 | 0 | GC/NPD | 0.00 | 200 |
| N.A. | | Household | 400.00 | 400.00 | 300 | 500 | | 0.00 | 2 | 0.00 | GC/EI/MS | 0.00 | 200 |
| Europe | Carbamazepine | PhAC | 1270.00 | 1298.67 | 100 | 6300 | | 22 | 23 | 3 | GC/MS | 50 | 50 |
| N.A. | | PhAC | 439.00 | 133.00 | 0 | 2300 | | 5 | 6 | 3 | GC/MS | 1 | 50 |
| Europe | Clofibric acid | PhAC | 280.00 | 81.50 | 0 | 1600 | | 22 | 23 | 16 | GC/MS | 10 | 50 |
| N.A. | | PhAC | 6.00 | 6.00 | 0 | 30 | | 8 | 8 | 6 | GC/MS | 10 | 50 |
| Europe | Diclofenac | PhAC | 675.63 | 509.00 | 100 | 3464 | | 118 | 219 | 15 | GC/MS | 10 | 20 |
| N.A. | | PhAC | 15.00 | 32.50 | 0 | 80 | | 8 | 8 | 2 | GC/MS | 10 | 20 |

**Table 8.2. Summary of Wastewater-Derived Contaminants Occurring in Secondary/Tertiary Effluents in Europe and North America**

| Continent of Origin | Compound | Compound Category | Median Concn (ng/L) | Occur-rence Avg. Concn (ng/L) | Occur-rence Min. Concn (ng/L) | Occur-rence Max. Concn (ng/L) | Sample StDev | No. of STPs | Occur-rence (No. of Samples) | No. of NDs | Analytical Method | Reported MDL (ng/L) | Reported LOQ (ng/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Europe | Gemfibrozil | PhAC | 573.33 | 629.00 | 0 | 1500 | | 61 | 61 | 10 | GC/MS | 50 | 50 |
| N.A. | | PhAC | 60.00 | 380.00 | 0 | 1300 | | 25 | 25 | 18 | GC/MS | 50 | 50 |
| Europe | Ibuprofen | PhAC | 983.25 | 1146.10 | 0 | 85000 | | 79 | 179 | 30 | GC/MS | 50 | 50 |
| N.A. | | PhAC | 216.67 | 1858.00 | 0 | 24600 | | 25 | 25 | 6 | GC/MS | 50 | 50 |
| Europe | Ketoprofen | PhAC | 359.00 | 304.50 | 0 | 871 | | 55 | 82 | 12 | GC/MS | 20 | 20 |
| N.A. | | PhAC | 35.00 | 27.00 | 0 | 45 | | 25 | 25 | 22 | GC/MS | 20 | 20 |
| Europe | Naproxen | PhAC | 707.75 | 293.63 | 0 | 3500 | | 26 | 54 | 5 | GC/MS | 20 | 20 |
| N.A. | | PhAC | 66.00 | 767.00 | 0 | 33900 | | 25 | 25 | 22 | GC/MS | 20 | 20 |
| Europe | Salicylic acid | PhAC | 2000.00 | 5190.00 | 0 | 13000 | | 38 | 39 | 27 | GC/MS | 50 | 50 |
| N.A. | | PhAC | 841.00 | 841.00 | 0 | 4800 | | 17 | 17 | 11 | GC/MS | 50 | 50 |
| Europe | BPA | Plasticizer | 54.00 | 119.58 | 0 | 1530 | | 45 | 34 | 18 | GC/MS | 15 | 15 |
| N.A. | | Plasticizer | 14.00 | 20.00 | 6 | 50 | | 8 | 7 | 0 | GC/MS | 15 | 15 |
| Europe | Nonylphenol | Surfactant | 1124.50 | 1000.00 | 0 | 2700 | | 45 | 34 | 18 | GC/MS | 100 | 100 |
| N.A. | | Surfactant | 1170.50 | 10675.33 | 171 | 4926 | | 3 | 16 | 1 | GC/MS | 100 | 100 |
| Europe | Octylphenol | Surfactant | 17.60 | 17.60 | 0 | 19.2 | | 2 | 20 | 15 | GC/MS | 20 | 20 |
| N.A. | | Surfactant | 68.00 | 486.00 | 0 | 673 | | 13 | 17 | 2 | GC/MS | 20 | 20 |

**Table 8.3. Internal Occurrence Survey for CSM[a]**

| Compound | LOQ | Median (ng/L) | Range (ng/L) | No. of Samples | No. of Locations (Detected) | Source of Information (i.e. Study, Report, Project) | DR |
|---|---|---|---|---|---|---|---|
| Bisphenol A | n.a. | 246 | n.d.–295 | 16 | 4 (1) | Drewes et al., 2008; D, B | — |
| Caffeine | 40 | 936 | <40–947 | 10 | 3 (1) | Drewes et al., 2008; D, B | 23 |
| Clofibric acid | 4 | n.d. | — | 14 | 4 (0) | Drewes et al., 2008; D, B | — |
| Dichlorprop | 1 | 52 | <1–52 | 14 | 4 (1) | Drewes et al., 2008; D, B | 52 |
| Diclofenac | 1 | 58 | <1–82 | 14 | 4 (4) | Drewes et al., 2008; D, B | 58 |
| Fenofibrate | n.a. | n.d. | — | 14 | 4 (0) | Drewes et al., 2008; D, B | — |
| Gemfibrozil | 4 | 1066 | <4–2546 | 14 | 4 (4) | Drewes et al., 2008; D, B | 266 |
| Ibuprofen | 4 | 367 | <4–1337 | 14 | 4 (3) | Drewes et al., 2008; D, B | 92 |
| Ketoprofen | 4 | 103 | <4–141 | 14 | 4 (2) | Drewes et al., 2008; D, B | 26 |
| Mecoprop | 2 | 58 | <2–81 | 14 | 4 (2) | Drewes et al., 2008; D, B | 29 |
| Naproxen | 1 | 344 | <1-889 | 14 | 4 (4) | Drewes et al., 2008; D, B | 344 |
| Phenacetine | 1 | n.d. | — | 14 | 4 (0) | Drewes et al., 2008; D, B | — |
| TCEP | 30 | 701 | 421–935 | 14 | 4 (4) | Drewes et al., 2008; D, B | 23 |
| TCPP | 30 | 1724 | 938–3593 | 14 | 4 (4) | Drewes et al., 2008; D, B | 57 |
| TDCPP | n.a. | 595 | n.d. –810 | 14 | 4 (4) | Drewes et al., 2008; D, B | — |

[a]B, from field study in Brighton, CO; not published yet;
D, from field study in Denver, CO; not published yet; n.d., not determined.

**Table 8.4. Internal Occurrence Survey for UC**

| Compound | Detection Limit | Median (ng/L) | Range (ng/L) | No. of Samples | No. of Locations | Detects (%) | Reference | DR |
|---|---|---|---|---|---|---|---|---|
| Ciprofloxacin | 50 | 351 | <30–860 | 12 | 5 | 50 | Sedlak et al. (2005) | 7.0 |
| Diclofenac | 10 | 55 | <10–78 | 12 | 6 | 88 | Sedlak et al. (2005) | 5.5 |
| Enrofloxacin | 50 | 145 | <30–150 | 12 | 5 | 25 | Sedlak et al. (2005) | 2.9 |
| Gemfibrozil | 10 | 1279 | 92–5500 | 12 | 6 | 100 | Sedlak et al. (2005) | 128 |
| Ibuprofen | 10 | 50 | <10–320 | 12 | 6 | 50 | Sedlak et al. (2005) | 5 |
| Indometacine | 10 | 31 | <10–36 | 12 | 6 | 50 | Sedlak et al. (2005) | 3.1 |
| Ketoprofen | 10 | 28 | <10–55 | 12 | 6 | 25 | Sedlak et al. (2005) | 2.8 |
| Metoprolol | 10 | 60 | <10–160 | 16 | 8 | 100 | Sedlak et al. (2005) | 6.0 |
| Naproxen | 10 | 730 | 100–3200 | 12 | 6 | 100 | Sedlak et al. (2005) | 73 |
| Norfloxacin | 50 | 135 | <30–190 | 12 | 6 | 22 | Sedlak et al. (2005) | 2.7 |
| Ofloxacin | 50 | 256 | <30–600 | 11 | 5 | 86 | Sedlak et al. (2005) | 5.1 |
| Propranolol | 10 | 30 | <10–64 | 16 | 8 | 75 | Sedlak et al. (2005) | 3.0 |
| Sulfamethazine | 50 | 500 | <30–500 | 7 | 4 | 20 | Sedlak et al. (2005) | 10 |
| Sulfamethoxazole | 50 | 1197 | <30–2000 | 10 | 4 | 83 | Sedlak et al. (2005) | 24 |
| Trimethoprim | 50 | 832 | <30–1900 | 12 | 6 | 88 | Sedlak et al. (2005) | 17 |

**Table 8.5. Internal Occurrence Survey for SNWA**

| Compounds | Limit of Quantification | Median (ng/L) | Range (ng/L) | No. of Samples (detected) | Source of Information (i.e. Study, Report, Project) | DR |
|---|---|---|---|---|---|---|
| Acetaminophen | 1.0 | 9.6 | <1–51 | 14 (11) | Las Vegas Wash, NV | 10 |
| Acriflavine | 1.0 | <1 | <1 | 4 (0) | WERF 03-CTS-21UR | - |
| Androstenedione | 1.0 | 1.9 | <1–2.6 | 14 (6) | Las Vegas Wash, NV | 2 |
| Atrazine | 1.0 | 1.3 | <1–1.6 | 14 (4) | Las Vegas Wash, NV | 1 |
| BHA | 1.0 | 198 | 170–226 | 4 (2) | WERF 03-CTS-21UR | 198 |
| Caffeine | 1.0 | 90 | <1–315 | 14 (12) | Las Vegas Wash, NV | 90 |
| DEET | 1.0 | 163 | 32–383 | 14 (14) | Las Vegas Wash, NV | 163 |
| Diazepam | 1.0 | 1.4 | <1–2.3 | 14 (10) | Las Vegas Wash, NV | 1 |
| Diclofenac | 1.0 | 3.9 | <1–7.2 | 14 (13) | Las Vegas Wash, NV | 4 |
| Dilantin | 1.0 | 79 | <1–151 | 14 (14) | Las Vegas Wash, NV | 79 |
| 17β-ethynylestradiol | 1.0 | < 1 | <1 | 14 (0) | Las Vegas Wash, NV | - |
| 17β-estradiol | 1.0 | 1.2 | <1–1.2 | 14 (1) | Las Vegas Wash, NV | 1 |
| Fluoxetine | 1.0 | 4.6 | <1–12 | 14 (10) | Las Vegas Wash, NV | 5 |
| Gemfibrozil | 1.0 | 62 | <1–271 | 14 (12) | Las Vegas Wash, NV | 62 |
| Hydrocodone | 1.0 | 62 | 7.1–104 | 14 (14) | Las Vegas Wash, NV | 62 |
| Hydrocortisone | 1.0 | 33 | <1 | 4 (1) | WERF 03-CTS-21UR | 33 |
| Ibuprofen | 1.0 | 18 | 5.6–12 | 14 (14) | Las Vegas Wash, NV | 18 |
| 3-Indolebutyric acid | 1.0 | 173 | 82–363 | 4 (4) | WERF 03-CTS-21UR | 173 |
| Iopromide | 1.0 | 116 | 4.6–253 | 14 (14) | Las Vegas Wash, NV | 116 |
| Isobutylparaben | 0.25 | 4.9 | 2.6–7.8 | 4 (4) | WERF 03-CTS-21UR | 20 |
| Meprobamate | 1.0 | 304 | 61–440 | 14 (14) | Las Vegas Wash, NV | 304 |
| Naproxen | 1.0 | 16 | <1–99 | 14 (13) | Las Vegas Wash, NV | 16 |
| *o*-Phenylphenol | 10.0 | 196 | <10–270 | 4 (2) | WERF 03-CTS-21UR | 20 |
| Oxybenzone | 1.0 | 35 | <1–35 | 14 (1) | Las Vegas Wash, NV | 35 |
| Pentoxifylline | 1.0 | 2.2 | <1–3.3 | 14 (6) | Las Vegas Wash, NV | 2 |
| Progesterone | 1.0 | < 1 | <1 | 14 (0) | Las Vegas Wash, NV | - |
| Propylparaben | 0.25 | 6.2 | <0.25–7.3 | 4 (3) | WERF 03-CTS-21UR | 25 |
| Simazine | 1.0 | 19 | <1–19 | 4 (1) | WERF 03-CTS-21UR | 19 |
| TCEP | 1.0 | 187 | 91–354 | 14 (14) | Las Vegas Wash, NV | 187 |
| Testosterone | 1.0 | 1.3 | <1–1.5 | 14 (3) | Las Vegas Wash, NV | 1 |
| Triclocarban | 0.1 | 81 | 21–121 | 4 (4) | WERF 03-CTS-21UR | 805 |
| Trimethoprim | 1.0 | 28 | 2.4–96 | 14 (14) | Las Vegas Wash, NV | 28 |

**Table 8.6. 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]<br>0.46[1] | 0.34[3] | 9.38 (acid)[1]<br>9.46 (acid)[4] | Uncharged | LM: Fast (1.0)<br>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)<br>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)<br>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)<br>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]<br>1.96[1] | 1.93[3] | n.a. | Uncharged | LM: Fast (0.98)<br>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)<br>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]<br>11.05 (acid)[6] | Uncharged | LM: Fast (1.0)<br>NLM: Fast (0.99) | HHC plasticizer |
| Bucinal (*p*-*t*-bucinal) | $C_{14}H_{20}O$ | 80-54-6 | 204.3 | 4.07[3]<br>4.36[2] | 4.07[3] | n.a. | Uncharged | LM: Fast (0.75)<br>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)<br>NLM: Fast (0.87) | PCP antioxidant |
| Caffeine | $C_8H_{10}N_4O_2$ | 58-08-2 | 194.1926 | −0.07[1]<br>−0.79[4] | −0.79[4] | 1.5 (base)[4] | Uncharged | LM: Fast (0.65)<br>NLM: Fast (0.56) | stimulant |

**Table 8.6. 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 |
|---|---|---|---|---|---|---|---|---|---|
| Carbamazepine | $C_{15}H_{12}N_2O$ | 298-46-4 | 236.3 | 2.67[3]<br>2.45[1] | 2.67[3] | 0.37 (base)[4]<br>−3.55 (base)[4] | Uncharged | LM: Fast (0.63)<br>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)<br>NLM: Slow (0.01) | DBP |
| Ciprofloxacin | $C_{17}H_{18}FN_3O_3$ | 85721-33-1 | 331.3 | 1.31[3]<br>0.28[1] | −1.2[3] | 2.74 (most acidic)[3]<br>8.76 (most basic)[3] | Charged (− and +) | LM: Slow (-0.4)<br>NLM: Slow (0) | PhAC antibiotic |
| DEET | $C_{12}H_{17}NO$ | 134-62-3 | 191.3 | 1.96[3]<br>2.18[1] | 1.96[3] | n.a. | Uncharged | LM: Fast (0.92)<br>NLM: Fast (0.97) | PCP insecticide |
| Dichlorprop | $C_9H_8Cl_2O_3$ | 120-36-5 | 235.1 | 3.43[1]<br>2.94[3] | −1.1[5] | 3.1 (acid)[1] | Charged (−) | LM: Slow (0.48)<br>NLM: Slow (0.19) | HHC pesticide |
| Diclofenac | $C_{14}H_{11}Cl_2NO_2$ | 15307-86-5 | 296.2 | 3.28[3]<br>3.97[4] | 1.28[3] | 4.15 (acid)[1]<br>4.0 (acid)[4]<br>−2.18 (base)[4] | Charged (−) | LM: Slow (0.13)<br>NLM: Slow (0.003) | PhAC analgesic |
| Dilantin | $C_{15}H_{12}N_2O_2$ | 57-41-0 | 252.3 | 2.47[1]<br>2.28[4] | 2.27[4] | 8.33(acid)[1]<br>9.13 (acid)[4]<br>19.83 (acid)[4] | Uncharged | LM: Fast (0.7)<br>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]<br>11.2 (most basic)[3] | Charged (− and +) | LM: Slow (0.49)<br>NLM: Slow (0.05) | PCP complexing metal agent |

**Table 8.6. 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 |
|---|---|---|---|---|---|---|---|---|---|
| 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]<br>8.1 (most basic)[3]<br>7.6 (most basic)[6] | Charged (+) | LM: Slow (-1.4)<br>NLM: Slow (0) | PhAC antibiotic |
| Estriol (E3) | $C_{18}H_{24}O_3$ | 50-27-1 | 288.4 | 2.94[3]<br>2.45[1] | 2.94[3] | 10.4 (most acidic)[3] | Uncharged | LM: Fast (0.96)<br>NLM: Fast (0.81) | Steroidal hormone |
| Estrone (E1) | $C_{18}H_{22}O_2$ | 53-16-7 | 270.4 | 3.69[3]<br>3.13[1] | 3.69[3] | 10.34 (acid)[3]<br>10.37 (acid) | Uncharged | LM: Fast (0.67)<br>NLM: Slow (0.28) | Steroidal hormone |
| Fluoxetine | $C_{17}H_{18}F_3NO$ | 54910-89-3 | 309.3 | 4.35[3]<br>4.05[1] | 1.57[3] | 10.05 (base)[3] | Charged (+) | LM: Slow (0.49)<br>NLM: Slow (0.13) | PhAC antidepressant |
| Galaxolide (HHCB) | $C_{18}H_{26}O$ | 1222-05-5 | 258.4 | 5.95[3] | 5.95[3] | n.a. | Uncharged | LM: Slow (-.04)<br>NLM: Slow (0) | PCP fragrance |
| Gemfibrozil | $C_{15}H_{22}O_3$ | 25812-30-0 | 250.3 | 4.39[3]<br>4.77[2] | 1.78[3] | 4.75 (acid)[3] | Charged (−) | LM: Fast (0.76)<br>NLM: Fast (0.86) | PhAC lipid regulator |
| Hexyl salicylate | $C_{13}H_{18}O_3$ | 6259-76-3 | 222.3 | 5.06[2]<br>4.89[3] | 4.86[3] | 8.17 (acid) | Uncharged | LM: Fast (1.0)<br>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)<br>NLM: Fast (1.0) | PCP fragrance |
| Hydrocodone | $C_{18}H_{21}NO_3$ | 125-29-1 | 299.4 | 2.0[3]<br>2.16[2] | 0.51[3] | 8.48 (base) | Charged (+) | LM: Fast (0.54)<br>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)<br>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]<br>2.3[1] | 0.18[3] | 4.7 (acid)[2]<br>4.83 (acid)[3]<br>0.4 (base)[3] | Charged (−) | LM: Fast (0.78)<br>NLM: Fast (0.79) | PCP plant growth regulator |

**Table 8.6. 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 |
|---|---|---|---|---|---|---|---|---|---|
| Iopromide | $C_{18}H_{24}I_3N_3O_8$ | 73334-07-3 | 791.1 | −3.24[3]<br>−2.05[1] | -3.24[3] | 10.6 (most acidic)[3] | Uncharged | LM: Slow (-0.98)<br>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)<br>NLM: Fast (0.70) | PCP fragrance |
| Isobutylparaben | $C_{11}H_{14}O_3$ | 4247-02-3 | 194.2 | 3.28[3]<br>3.4[2] | 3.25[3] | 8.17 (acid)[3] | Uncharged | LM: Fast (0.95)<br>NLM: Fast (0.99) | PCP antimicrobial cosmetics |
| Ketoprofen | $C_{16}H_{14}O_3$ | 22071-15-4 | 254.3 | 3.12[1]<br>2.81[3] | 0.04[5] | 4.45 (acid)[1]<br>4.23 (acid)[3] | Charged (−) | LM: Fast (0.88)<br>NLM: Fast (0.89) | PhAC analgesic |
| Mecoprop | $C_{10}H_{11}ClO_3$ | 93-65-2 | 214.6 | 3.13[1]<br>2.835[3] | −1.08[5] | 3.1 (acid)[1] | Charged (−) | LM: Fast (0.72)<br>NLM: Fast (0.80) | HHC pesticide |
| Meprobamate | $C_9H_{18}N_2O_4$ | 57-53-4 | 218.3 | 0.7[3]<br>0.7[1] | 0.7[3] | 10.9 (most basic)[4] | Charged (+) | LM: Fast (0.62)<br>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)<br>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)<br>NLM: Slow (0.11) | PCP fragrance |
| Methyl salicylate | $C_8H_8O_3$ | 119-36-8 | 152.1 | 2.23[3]<br>2.55[1] | 2.23[3] | 9.76 (acid)[3]<br>9.87 (acid)[1] | Uncharged | LM: Fast (0.97)<br>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]<br>9.17 (base)[3] | Charged (+) | LM: Fast (0.77)<br>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)<br>NLM: Slow (0) | PCP fragrance |
| Musk xylene | $C_{12}H_{15}N_3O_6$ | 81-15-2 | 297.3 | 3.83[3]<br>4.45[2] | 3.83[3] | n.a. | Uncharged | LM: Slow (-0.38)<br>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)<br>NLM: Fast (0.96) | PhAC analgesic |

**Table 8.6. 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 |
|---|---|---|---|---|---|---|---|---|---|
| NDMA | $C_2H_6N_2O$ | 62-75-9 | 74.1 | −0.64[3]<br>−0.57[1] | −0.64[3] | 3.56 (base)[3] | Uncharged | LM: Slow (0.19)<br>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)<br>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]<br>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)<br>NLM: Slow (0.05) | PCP fragrance |
| Phenylphenol (*o*-phenylphenol) | $C_{12}H_{10}O$ | 90-43-7 | 170.2 | 2.94[3]<br>3.09[1] | 2.94[3] | 9.99 (acid)[3]<br>9.97 (base)[1] | Uncharged | LM: Fast (0.91)<br>NLM: Fast (0.96) | PCP antimicrobial |
| Primidone | $C_{12}H_{14}N_2O_2$ | 125-33-7 | 218.3 | −0.844[3]<br>0.91[1] | −0.81[3] | 12.3 (most acidic)[3]<br>11.13 (acid)[4]<br>12.25 (acid)[4] | Uncharged | LM: Fast (1.0)<br>NLM: Fast (0.99) | PhAC antiepileptic |
| Propranolol | $C_{16}H_{19}NO_2$ | 525-66-6 | 259.3 | 3.1[3]<br>3.48[1] | 0.99[3] | 13.84 (acid)[3]<br>9.14 (base)[3]<br>9.42 (base)[1] | Charged (+) | LM: Fast (1.07)<br>NLM: Fast (0.98) | PhAC beta blocker |
| Propylparaben | $C_{10}H_{12}O_3$ | 94-13-3 | 180.2 | 2.93[3]<br>3.04[1] | 2.93[3] | 8.23 (acid)[3]<br>8.5 (acid)[4] | Uncharged | LM: Fast (0.95)<br>NLM: Fast (0.99) | PCP antimicrobial cosmetics |

**Table 8.6. 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 |
|---|---|---|---|---|---|---|---|---|---|
| Salicylic acid | $C_7H_6O_3$ | 69-72-7 | 138.1 | 2.26[3]<br>1.19[1] | −1.68[3] | 3.01 (most acidic)[3]<br>2.97 (most acidic)[1] | Charged (−) | LM: Fast (0.97)<br>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)<br>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]<br>0.89[1] | −0.33[3] | 6.16 (acid)[4]<br>1.97 (base)[4]<br>0.24 (base)[4] | Charged (−) | LM: Slow (0.45)<br>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]<br>1.44[1] | 0.48[3] | n.a. | Uncharged | LM: Fast (0.59)<br>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]<br>2.59[1] | 1.52[3] | n.a. | Uncharged | LM: Fast (0.57)<br>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]<br>3.65[1] | 1.79[3] | n.a. | Uncharged | LM: Fast (0.19)<br>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)<br>NLM: Slow (0.29) | PCP fragrance |
| Tonalide (AHTN) | $C_{18}H_{26}O$ | 21145-77-7<br>1506-02-1 | 258.4 | 6.37[3] | 6.37[3] | n.a. | Uncharged | LM: Slow (0.32)<br>NLM: Slow (0.02) | PCP fragrance |
| Triclocarban | $C_{13}H_9Cl_3N_2O$ | 101-20-2 | 315.6 | 5.74[3]<br>4.90[2] | 5.74[3] | 10.6 (acid)[4]<br>17.1 (acid)[4] | Uncharged | LM: Slow (0.05)<br>NLM: Slow (0) | PCP antimicrobial |

**Table 8.6. 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 |
|---|---|---|---|---|---|---|---|---|---|
| Triclosan | $C_{12}H_7Cl_3O_2$ | 3380-34-5 | 289.5 | 5.8[3]<br>4.76[1] | 5.75[3] | 7.8 (acid)[3] | Uncharged | LM: Slow (0.31)<br>NLM: Slow (0.02) | PCP antimicrobial |
| Trimethoprim | $C_{14}H_{18}N_4O_3$ | 738-70-5 | 290.3 | 0.79[3]<br>0.91[1] | 0.28[3] | 7.34 (most basic)[3] 7.12 (most basic)[1]<br>7.16 (base)[4]<br>−0.9 (base)[4] | Uncharged & Charged (+) | LM: Fast (0.59)<br>NLM: Fast (0.92) | PhAC antibiotic |

[a] 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 ChemiID 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 8.7. Absolute Indicator Compound Concentrations Observed at SAT Operation No. 1 (Facility 7)[a]**

| | | First Sampling Campaign | | | Second Sampling Campaign | | |
|---|---|---|---|---|---|---|---|
| Analyte | Lab | Recharge Basin (ng/L) | Monitoring Well 5 day (ng/L) | Monitoring Well 2 Weeks (ng/L) | Recharge Basin (ng/L) | Monitoring Well day (ng/L) | Monitoring Well 2 Weeks (ng/L) |
| Atenolol | CSM | na | na | na | 1530 | 61 | <0.25 |
| Atorvastatin | SNWA | na | na | na | 102 | 0.76 | <0.25 |
| Caffeine | CSM | 3831 | <40 | <40 | <40 | <40 | <40 |
| Carbamazepine | CSM | nq | nq | 439 | 1540 | nq | 1146 |
| Carbamazepine | SNWA | na | na | na | 387 | 438 | 495 |
| Diclofenac | CSM | <1 | <1 | <1 | 31 | <1 | <1 |
| Diclofenac | UCB | <8 | <8 | <8 | 37 | <8 | <8 |
| Diclofenac | SNWA | na | na | na | 153 | 25 | 1.5 |
| Dilantin | SNWA | na | na | na | 222 | 368 | 59 |
| EDTA (Total) | UCB | 202 | 185 | <18 | <18 | <18 | <18 |
| Estradiol (17β-) | UCB | na | na | na | 0.8 | <0.3 | <0.3 |
| Estrone | UCB | na | na | na | 13 | 0.2 | <0.2 |
| Fluoxetine | SNWA | na | na | na | 73 | 0.97 | <0.50 |
| Gemfibrozil | CSM | 1914 | 1861 | <2 | 1054 | nq | <2 |
| Gemfibrozil | UCB | 330 | 180 | <8 | 1103 | 108 | <8 |
| Gemfibrozil | SNWA | na | na | na | 3250 | 1300 | 0.29 |
| Ibuprofen | CSM | 477 | 542 | <4 | 115 | nq | <4 |
| Ibuprofen | UCB | 151 | 109 | <8 | 182 | 66 | <8 |
| Meprobamate | SNWA | na | na | na | 576 | 682 | 43 |
| Naproxen | CSM | 1338 | 951 | <1 | 129 | nq | <1 |
| Naproxen | UCB | 128 | 60 | <8 | 65 | <8 | <8 |
| Naproxen | SNWA | na | na | na | 290 | 117 | <0.50 |
| NDMA | UCB | na | na | na | 38 | 16 | <12.5 |
| Norfluoxetine | SNWA | na | na | na | 16 | <0.50 | <0.50 |
| o-Hydroxy atorvastatin | SNWA | na | na | na | 58 | <0.50 | <0.50 |
| p-Hydroxy atorvastatin | SNWA | na | na | na | 92 | <0.50 | <0.50 |
| Primidone | CSM | nq | 152 | 77 | 220 | nq | 116 |
| Salicylic acid | CSM | 1461 | 208 | 6 | 937 | nq | < 2 |
| Simvastatin hydroxy acid | SNWA | na | na | na | 22 | <0.25 | <0.25 |
| Sulfamethoxazole | SNWA | na | na | na | 721 | 1520 | 30 |
| TCEP | CSM | 241 | 334 | 116 | 551 | nq | 139 |
| TCPP | CSM | 417 | 536 | 153 | 814 | nq | 223 |
| TDCPP | CSM | 353 | 418 | 218 | 683 | nq | 292 |
| Triclosan | SNWA | na | na | na | 143 | 15 | <1.0 |
| Trimethoprim | SNWA | na | na | na | 451 | 70 | <0.25 |

[a]Conditions: travel time in subsurface, 5 days and 14 days; predominant redox conditions, oxic.
nq - not quantifiable (detected)
na - not analyzed

**Table 8.8. Absolute Indicator Compound Concentrations Observed at SAT Operation No. 2 (Facility 1)**[a]

| Analyte | Lab | Recharge Basin (ng/L) | Monitoring Well 2 Weeks (ng/L) |
|---|---|---|---|
| Acetaminophen | SNWA | 20 | 1.1 |
| Caffeine | SNWA | 255 | <10 |
| Carbamazepine | SNWA | 148 | 167 |
| Carbamazepine | CSM | 634 | 150 |
| DEET | SNWA | 72 | 4.6 |
| Diclofenac | SNWA | 29 | <1.0 |
| Dilantin | SNWA | 114 | 29 |
| EDTA (Total) | UCB | 215 | <18 |
| Erythromycin-$H_2O$ | SNWA | 218 | <1.0 |
| Estradiol (17β-) | SNWA | <1.0 | <1.0 |
| Estradiol (17β-) | UCB | <0.3 | <0.3 |
| Estrone | SNWA | 15 | <1.0 |
| Fluoxetine | SNWA | <10 | <1.0 |
| Gemfibrozil | SNWA | 378 | <1.0 |
| Gemfibrozil | UCB | 46 | <8 |
| Gemfibrozil | CSM | 189 | <2 |
| Hydrocodone | SNWA | 45 | <1.0 |
| Ibuprofen | SNWA | 115 | <1.0 |
| Iopromide | SNWA | 2140 | 4.8 |
| Meprobamate | SNWA | 252 | 1.2 |
| Metoprolol | UCB | 21 | <8 |
| Naproxen | SNWA | 56 | <1 |
| Naproxen | CSM | 30 | <1 |
| Primidone | CSM | 276 | 58 |
| Salicylic acid | CSM | 525 | 10 |
| Sulfamethoxazole | SNWA | 427 | 107 |
| TCEP | SNWA | 232 | <10 |
| TCEP | CSM | 224 | 31 |
| TCPP | CSM | 423 | 80 |
| TDCPP | CSM | 246 | 55 |
| Triclosan | SNWA | <10 | <1.0 |
| Trimethoprim | SNWA | 70 | <1.0 |

[a]Conditions: travel time in subsurface, 14 days; predominant redox conditions, anoxic.

**Table 8.9. Absolute Indicator Compound Concentrations Observed at SAT Operation No. 3 (Facility 1)[a]**

| Analyte | Lab | Recharge Basin (ng/L) | Monitoring Well 1 month (ng/L) | Monitoring Well 3 months (ng/L) |
|---|---|---|---|---|
| Caffeine | CSM | <40 | <40 | <40 |
| Carbamazepine | CSM | 116 | 81 | 67 |
| Diclofenac | CSM | <1 | <1 | <1 |
| Diclofenac | UCB | <8 | <8 | <8 |
| Estradiol (17β-) | UCB | 0.6 | <0.3 | na |
| Estrone | UCB | 0.7 | <0.2 | na |
| Gemfibrozil | CSM | 47 | <2 | <2 |
| Ibuprofen | CSM | <4 | <4 | <4 |
| Ibuprofen | UCB | <8 | <8 | <8 |
| Mecoprop | CSM | 40 | <2 | <2 |
| Naproxen | CSM | 26 | <1 | <1 |
| NDMA | UCB | 298 | <12.5 | <12.5 |
| Primidone | CSM | 62 | 55 | 33 |
| TCEP | CSM | 311 | 124 | nq |
| TCPP | CSM | 442 | 293 | 158 |
| TDCPP | CSM | 333 | 107 | 63 |

[a]Conditions: travel time in subsurface, 1 and 3 months; predominant redox conditions, anoxic.
nq - not quantifiable (detected)
na - not analyzed

**Table 8.10. Absolute Indicator Compound Concentrations Observed at a Full-Scale MBR Operation (Facility 10)[a]**

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| Analyte | Lab | MBR Influent (ng/L) | After MBR (ng/L) | MBR Influent (ng/L) | After MBR (ng/L) |
| Atenolol | SNWA | 2490 | 944 | 3090 | 779 |
| Atorvastatin | SNWA | 174 | 65 | 198 | 32 |
| Bisphenol A | SNWA | 514 | 33 | 747 | <5.0 |
| Caffeine | CSM | nq | <40 | 129,753 | <40 |
| Carbamazepine | SNWA | 444 | 409 | 538 | 410 |
| Diclofenac | SNWA | 63 | 62 | 83 | 58 |
| Dilantin | SNWA | 156 | 240 | 252 | 243 |
| EDTA (Total) | UCB | 318 | 125 | 513 | 155 |
| Enalapril | SNWA | 31 | 0.82 | 19 | 0.70 |
| Estradiol (17β-) | UCB | nq | 0.4 | nq | <0.3 |
| Estrone | UCB | nq | 2.2 | nq | 1.9 |
| Fluoxetine | SNWA | 52 | 38 | 63 | 42 |
| Gemfibrozil | CSM | 2459 | 571 | 708 | 65 |
| Gemfibrozil | UCB | 671 | 56 | 1076 | <8 |
| Gemfibrozil | SNWA | 3810 | 839 | 4180 | 247 |
| Ibuprofen | CSM | 43,533 | 743 | 16,811 | 133 |
| Ibuprofen | UCB | 16,196 | 115 | 17,820 | 80 |
| Mecoprop | CSM | 393 | 63 | 340 | 87 |
| Meprobamate | SNWA | 317 | 310 | 345 | 352 |
| Naproxen | CSM | 13,873 | 266 | 9798 | 112 |
| Naproxen | UCB | 2846 | 12 | 5616 | 15 |
| Naproxen | SNWA | 22,700 | 337 | 26,600 | 308 |
| NDMA | UCB | 138 | 17 | 158 | 50 |
| Norfluoxetine | SNWA | 37 | 3.2 | 29 | 2.5 |
| o-Hydroxy atorvastatin | SNWA | 185 | 61 | 226 | 30 |
| Phenacetine | CSM | nq | nd | 4052 | <1 |
| p-Hydroxy atorvastatin | SNWA | 305 | 119 | 344 | 44 |
| Salicylic acid | CSM | 150,932 | 503 | 61,714 | 172 |
| Simvastatin | SNWA | 12 | <0.25 | <2.5 | <0.25 |
| Simvastatin hydroxy acid | SNWA | 26 | 6.2 | 16 | 1.3 |
| Sulfamethoxazole | SNWA | 2410 | 1580 | 4060 | 1090 |
| TCEP | CSM | 1324 | 711 | 684 | 428 |
| TCPP | CSM | 1717 | 1339 | 1050 | 842 |
| TDCPP | CSM | nq | 777 | nq | 503 |
| Triclosan | SNWA | 1690 | 78 | 2520 | 48 |
| Trimethoprim | SNWA | 909 | 520 | 1190 | 387 |

[a]Conditions: nitrification/denitrification; SRT, 10–15 days; MLSS, 7500 mg/L.
nq - not quantifiable (detected)

**Table 8.11. Absolute Indicator Compound Concentrations Observed at a Pilot-Scale MBR Operation (Facility 1)[a]**

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| Analyte | Lab | MBR Influent (ng/L) | After MBR (ng/L) | MBR Influent (ng/L) | After MBR (ng/L) |
| Acetaminophen | SNWA | 19,800 | <1.0 | na | na |
| Benzophenone | SNWA | 3110 | 60 | na | na |
| Butylated hydroxyanisole | SNWA | 128 | 2.7 | na | na |
| Butylated hydroxyanisole | SNWA | 92 | <25.0 | na | na |
| Bisphenol A | SNWA | 241 | 225 | na | na |
| Caffeine | CSM | 6431 | <40 | 14,453 | <40 |
| Caffeine | SNWA | 71,600 | <10 | na | na |
| Carbamazepine | CSM | nq | 307 | nq | 348.7 |
| Carbamazepine | SNWA | 124 | 196 | na | na |
| DEET | SNWA | 371 | 130 | na | na |
| DEET | SNWA | 74 | 44 | na | na |
| DEET | SNWA | 316 | 90 | na | na |
| Diclofenac | CSM | <1 | <1 | nq | 38 |
| Dilantin | SNWA | 40 | 103 | na | na |
| EDTA (Total) | UCB | 107 | 125 | 186 | 172 |
| Erythromycin-$H_2O$ | SNWA | 440 | <1.0 | na | na |
| Estradiol (17β-) | UCB | nq | <0.3 | nq | nq |
| Estrone | UCB | nq | <0.2 | nq | 1.8 |
| Gemfibrozil | CSM | 2863 | 20 | 1787 | 284 |
| Gemfibrozil | UCB | na | na | 1226 | 26 |
| Ibuprofen | CSM | 8409 | <4 | 7616 | 10.7 |
| Ibuprofen | UCB | na | na | 2578 | <8 |
| Indolebutyric acid | SNWA | 2200 | 53 | na | na |
| Isobutylparaben | SNWA | 333 | 0.29 | na | na |
| Menthol | SNWA | 11,760 | <50.0 | na | na |
| Meprobamate | SNWA | 188 | 294 | na | na |
| Naproxen | CSM | 8784 | n.q. | 4923 | 67 |
| Phenylphenol (o-) | SNWA | 1160 | 17 | na | na |
| Phenylphenol (o-) | SNWA | 1200 | 34 | na | na |
| Oxybenzone | SNWA | 311 | <1.0 | na | na |
| Phenoxyethanol | SNWA | 15,160 | 173 | na | na |
| Primidone | CSM | nq | 140 | nq | 97.2 |
| Propylparaben | SNWA | 1480 | 0.88 | na | na |
| Salicylic acid | CSM | 115 | n.q. | 37,467 | 65 |
| Sulfamethoxazole | SNWA | 421 | 820 | na | na |
| TCEP | CSM | 574 | 168 | nq | 382 |
| TCPP | CSM | 1989 | 490 | nq | 907 |
| TDCPP | CSM | nq | 261 | nq | 521 |
| Triclosan | SNWA | 480 | 47 | na | na |
| Trimethoprim | SNWA | 335 | <1.0 | na | na |
| Vanillin | SNWA | 5150 | 410 | na | na |

[a]Conditions: nitrification/denitrification; SRT, 12 days; MLSS, 8500 mg/L.
nq - not quantifiable (detected)
na - not analyzed

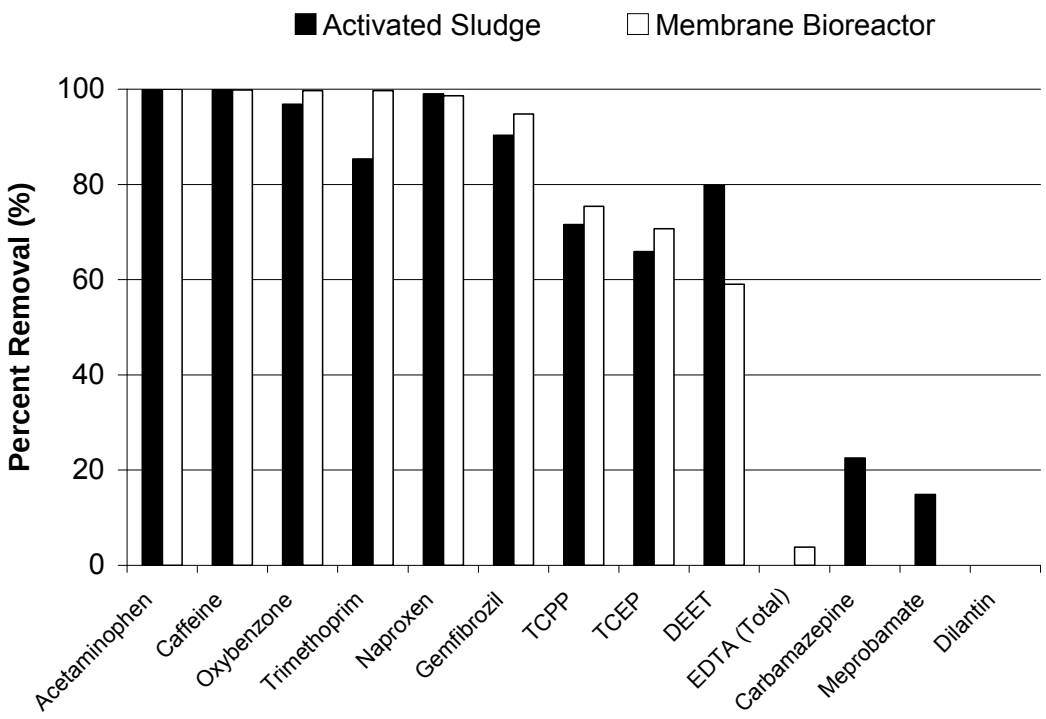



**Figure 8.1. Removal of Indicator Compounds during Activated Sludge vs. MBR Treatment at Facility 1.**

**Table 8.12. Absolute Indicator Compound Concentrations Observed during Ozonation (Facility 5)**[a]

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| Analyte | Lab | Before Ozone (ng/L) | After Ozone (ng/L) | Before Ozone (ng/L) | After Ozone (ng/L) |
| Atenolol | SNWA | na | na | 14 | 1.2 |
| Atorvastatin | SNWA | na | na | <0.25 | <0.25 |
| Atrazine | SNWA | na | na | 7.8 | 4.8 |
| Bisphenol A | SNWA | na | na | 14 | 5.5 |
| Caffeine | CSM | <40 | <40 | <40 | <40 |
| Carbamazepine | SNWA | na | na | 48 | <0.50 |
| Diclofenac | CSM | <1 | <1 | <1 | <1 |
| Diclofenac | SNWA | na | na | 1.0 | <0.25 |
| Dilantin | SNWA | na | na | 78 | 20 |
| EDTA (Total) | UCB | 265 | 213 | 180 | 140 |
| Estradiol (17β-) | UCB | <0.3 | <0.3 | <0.3 | <0.3 |
| Estrone | UCB | <0.2 | <0.2 | <0.2 | <0.2 |
| Fluoxetine | SNWA | na | na | <0.50 | <0.50 |
| Gemfibrozil | SNWA | na | na | 3.5 | <0.25 |
| Hydroxy atorvastatin (o-) | SNWA | na | na | <0.50 | <0.50 |
| Hydroxy atorvastatin (p-) | SNWA | na | na | <0.50 | <0.50 |
| Ibuprofen | CSM | <4 | <4 | <4 | <4 |
| Ibuprofen | UCB | <8 | <8 | <8 | <8 |
| mecoprop | CSM | <2 | <2 | 17 | <2 |
| Meprobamate | SNWA | na | na | 227 | 97 |
| Naproxen | CSM | <1 | <1 | <1 | <1 |
| Naproxen | SNWA | na | na | <0.50 | <0.50 |
| NDMA | UCB | na | na | <12.5 | <12.5 |
| Norfluoxetine | SNWA | na | na | <0.50 | <0.50 |
| Primidone | CSM | <1 | <1 | na | na |
| salicylic acid | CSM | 32 | 52 | nq | nq |
| Simvastatin hydroxy acid | SNWA | na | na | <0.25 | <0.25 |
| Sulfamethoxazole | SNWA | na | na | 251 | 3.2 |
| TCEP | CSM | 363 | 389 | 298 | 338 |
| TCPP | CSM | 604 | 684 | 447 | 466 |
| TDCPP | CSM | nq | nq | 138 | 141 |
| Triclosan | SNWA | na | na | 1.0 | <1.0 |
| Trimethoprim | SNWA | na | na | 4.4 | <0.25 |

[a]Conditions: Ozone dose of ~1 mg/L and contact time < 1 minute
nq - not quantifiable (detected)
na - not analyzed

**Table 8.13. Absolute Indicator Compound Concentrations Observed during Laboratory-Scale Ozonation and Advanced Oxdiation Analyte**

| | Lab | Before Ozone (ng/l) | Ozone 2.1 mg/L 6 min contact time (ng/l) | Ozone 3.6 mg/L 18 min contact time (ng/l) | Ozone 7.0 mg/L 2 min contact time (ng/l) | Ozone 7.0 mg/L 6 min contact time (ng/l) | Ozone 7.1 mg/L 18 min contact time (ng/l) | Before AOP (ng/l) | AOP - Ozone 2.1 mg/L $H_2O_2$ 1 mg/L 10 min contact time (ng/l) | AOP - Ozone 3.6 mg/L $H_2O_2$ 2 mg/L 10 min contact time (ng/l) | AOP - Ozone 7.1 mg/L $H_2O_2$ 3.5 mg/L 2 min contact time (ng/l) | AOP - Ozone 7.1 mg/L $H_2O_2$ 3.5 mg/L 6 min contact time (ng/l) | AOP - Ozone 7.1 mg/L $H_2O_2$ 3.5 mg/L 10 min contact time (ng/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Benzophenone | SNWA | 48 | na | <25.0 | na | na | <25.0 | 157 | na | 72 | na | na | <25.0 |
| BHA | SNWA | 19 | na | <1.0 | na | na | <1.0 | 67 | na | <1.0 | na | na | <1.0 |
| Bisphenol A | SNWA | 2370 | na | 1400 | na | na | 508 | 1014 | na | 644 | na | na | 113 |
| Caffeine | SNWA | 21 | 14 | <10 | <10 | <10 | <10 | 31 | 30 | 11 | <10 | <10 | <10 |
| Carbamazepine | SNWA | 139 | <1.0 | <1.0 | <1.0 | <1.0 | <1.1 | 139 | 2.7 | <1.0 | <1.0 | <1.0 | <1.0 |
| DEET | SNWA | 133 | 77 | 43 | 22 | 8.7 | 5.1 | 123 | 104 | 54 | 2.4 | 1.9 | 1.8 |
| DEET | SNWA | 92 | na | 27 | na | na | 3.2 | 89 | na | 30 | na | na | 1.0 |
| DEET | SNWA | 111 | na | 55 | na | na | 32 | 125 | na | 66 | na | na | <25.0 |
| Dibutyl Phthalate | SNWA | 291 | na | 196 | na | na | 134 | 188 | na | 125 | na | na | 87 |
| Diclofenac | SNWA | 73 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 71 | 1.7 | <1.0 | <1.0 | <1.0 | <1.0 |
| Dilantin | SNWA | 143 | 81 | 40 | 18 | 2.9 | 2.0 | 110 | 91 | 42 | <1.0 | <1.0 | <1.0 |
| Erythromycin-H2O | SNWA | 162 | 2.6 | <1.0 | <1.0 | <1.0 | <1.1 | 149 | 31 | <1.0 | <1.0 | <1.0 | <1.0 |
| Estriol | SNWA | 5.7 | 7.7 | 11.15 | 10.0 | 10 | <5.0 | <5.0 | 18 | 7.4 | <5.0 | <5.0 | <5.0 |
| Estrone | SNWA | 4.3 | 6.6 | <1.0 | 9.1 | 4.3 | <1.0 | 19.7 | 11 | 13 | <1.0 | <1.0 | <1.0 |
| Fluoxetine | SNWA | 14 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 11 | 2.2 | <1.0 | <1.0 | <1.0 | <1.0 |
| Gemfibrozil | SNWA | 16 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 567 | 148 | <1.0 | <1.0 | <1.0 | <1.0 |
| Hydrocodone | SNWA | 199 | 1.8 | <1.0 | <1.0 | <1.0 | <1.0 | 161 | 20 | <1.0 | <1.0 | <1.0 | <1.0 |
| Ibuprofen | SNWA | 5.6 | 12 | <1.0 | 1.4 | <1.0 | <1.0 | 15.0 | 27 | 18 | <1.0 | <1.0 | <1.0 |
| Indolebutyric acid | SNWA | 123 | na | 66 | na | na | 23 | 197 | na | 79 | na | na | 19 |
| Iopromide | SNWA | 139 | 119 | 87 | 73 | 58 | 26 | 45.0 | 54 | 35 | 56 | 34 | 44 |
| Meprobamate | SNWA | 796 | 552 | 469 | 281 | 196 | 138 | 737 | 584 | 441 | 74 | 63 | 64 |
| Naproxen | SNWA | 25 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 70.7 | 3.1 | <1.0 | <1.0 | <1.0 | <1.0 |
| Sulfamethoxazole | SNWA | 669 | 50 | 3.2 | 1.2 | <1.0 | <1.0 | 695 | 116 | 24 | <1.0 | <1.0 | <1.0 |
| TCEP | SNWA | 235 | 192 | 272 | 218 | 287 | 232 | 187 | 168 | 179 | 155 | 157 | 170 |
| Triclocarban | SNWA | 75.5 | na | 3.3 | na | na | 0.8 | 113 | na | 19 | na | na | 1.8 |
| Triclosan | SNWA | 35 | 1.7 | 1.6 | <1.0 | <1.0 | <1.0 | 57.7 | 1.7 | 1.6 | <1.0 | <1.0 | <1.0 |
| Triclosan | SNWA | 41 | na | 1.6 | na | na | <1.0 | 90.5 | na | 1.6 | na | na | 1.9 |
| Trimethoprim | SNWA | 191 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 229 | 11 | <1.0 | <1.0 | <1.0 | <1.0 |
| Vanillin | SNWA | 223 | na | 183 | na | na | 165 | 225 | na | 200 | na | na | 119 |

na - not analyzed

**Table 8.14. Absolute Indicator Compound Concentrations Observed during Chloramination (Facility 6)[a]**

| Analyte | Lab | Before CLM (ng/L) | After CLM (ng/L) |
|---|---|---|---|
| Benzophenone | SNWA | 63 | 72 |
| Butylated Hydroxyanisole | SNWA | 57 | <25.0 |
| Butylated Hydroxyanisole | SNWA | 50 | 3.3 |
| Bisphenol A | SNWA | 1210 | 860 |
| Caffeine | CSM | <40 | <40 |
| Carbamazepine | CSM | <20 | <20 |
| DEET | SNWA | 246 | 256 |
| DEET | SNWA | 205 | 202 |
| Diclofenac | CSM | 14 | nq |
| EDTA (Total) | UCB | 237 | 234 |
| Estradiol (17β-) | UCB | <0.3 | <0.3 |
| Estrone | UCB | <0.4 | <0.4 |
| Gemfibrozil | CSM | 386 | 423 |
| Gemfibrozil | UCB | 14 | 26 |
| Ibuprofen | CSM | <4 | <4 |
| Ibuprofen | UCB | <8 | <8 |
| Indolebutyric acid | SNWA | 271 | 257 |
| Isobutylparaben | SNWA | 0.50 | 0.31 |
| Naproxen | CSM | 221 | 142 |
| NDMA | UCB | na | na |
| Primidone | CSM | <1 | <1 |
| Propylparaben | SNWA | 0.78 | 0.26 |
| Salicylic acid | CSM | 38 | 33 |
| TCEP | CSM | 350 | 355 |
| TCPP | CSM | 656 | 688 |
| TDCPP | CSM | <30 | <30 |
| Triclocarban | SNWA | 127 | 127 |
| Triclosan | SNWA | 93 | 18 |
| Vanillin | SNWA | 853 | 293 |

[a]Conditions: 1-h contact time; 2.6-mg/L residual concentration.
nq - not quantifiable (detected)
na - not analyzed

**Table 8.15. Absolute Indicator Compound Concentrations Observed during Chloramination (Facility 7)**[a]

| | | First Sampling Campaign | | | Second Sampling Campaign | |
|---|---|---|---|---|---|---|
| Analyte | Lab | Before CLM (ng/L) | After CLM River Discharge (ng/L) | After CLM Recharge Basin (ng/L) | Before CLM (ng/L) | After CLM Recharge Basin (ng/L) |
| Bisphenol A | CSM | nq | nq | nq | na | na |
| Caffeine | CSM | 3202 | 3887 | 3831 | <40 | <40 |
| Carbamazepine | CSM | nq | nq | nq | na | na |
| Diclofenac | CSM | <1 | <1 | <1 | 35 | 31 |
| Diclofenac | UCB | <8 | <8 | <8 | nq | 37 |
| Diclofenac | SNWA | na | na | na | na | 153 |
| EDTA (Total) | UCB | 395 | 191 | 202 | 199 | < 18 |
| Estradiol (17β-) | UCB | na | na | na | 0.4 | 0.8 |
| Estrone | UCB | na | na | na | 1.8 | 13 |
| Gemfibrozil | CSM | 2012 | 2196 | 1914 | 1393 | 1054 |
| Gemfibrozil | UCB | 243 | 120 | 330 | nq | 1103 |
| Gemfibrozil | SNWA | na | na | na | na | 3250 |
| Ibuprofen | CSM | 419 | 567 | 477 | 102 | 115 |
| Ibuprofen | UCB | 98 | 82 | 151 | 66 | 182 |
| Naproxen | CSM | 1368 | 1495 | 1338 | 173 | 129 |
| Naproxen | UCB | 64 | 27 | 128 | nq | 65 |
| Naproxen | SNWA | na | na | na | na | 290 |
| NDMA | UCB | na | na | na | 53 | 38 |
| Primidone | CSM | nq | nq | nq | na | na |
| Salicylic acid | CSM | 1208 | 1794 | 1461 | 532 | 937 |
| TCEP | CSM | 232 | 246 | 241 | 526 | 551 |
| TCPP | CSM | 418 | 430 | 417 | 668 | 814 |
| TDCPP | CSM | 341 | 361 | 353 | 581 | 683 |

[a]Conditions: 0.75-h contact time; 3.5- to 4.5-mg/L residual concentration.
nq - not quantifiable (detected)
na - not analyzed

**Table 8.16. Absolute Indicator Compound Concentrations Observed during Chloramination (Facility 9)**[a]

| Analyte | Lab | Before CLM (ng/L) | After CLM (ng/L) |
|---|---|---|---|
| Bisphenol A | CSM | nq | nq |
| Caffeine | CSM | 4369 | 5557 |
| Carbamazepine | CSM | nq | nq |
| Diclofenac | CSM | 87 | 74 |
| EDTA (Total) | UCB | 203 | 171 |
| Estradiol (17β-) | UCB | nq | nq |
| Estrone | UCB | 2.8 | 0.8 |
| Gemfibrozil | CSM | 5062 | 4231 |
| Ibuprofen | CSM | 667 | 667 |
| Naproxen | CSM | 948 | 781 |
| NDMA | UCB | na | na |
| Primidone | CSM | 570 | 546 |
| Salicylic acid | CSM | 500 | 1032 |
| TCEP | CSM | 496 | 584 |
| TCPP | CSM | 852 | 939 |
| TDCPP | CSM | 560 | 671 |

[a]Conditions: 1-h cotact time; 2.5-mg/L residual concentration.
nq - not quantifiable (detected)
na - not analyzed

**Table 8.17. Absolute Concentrations of Indicator Compounds during Bench-Scale Chlorination**[a]

| Analyte | Lab | Before Chlorine (ng/L) | After Chlorine 1.8 mg/L (ng/L) | After Chlorine 3 mg/L (ng/L) |
|---|---|---|---|---|
| Acetaminophen | SNWA | 76 | <1.0 | <1.0 |
| Atrazine | SNWA | 267 | 239 | 187 |
| Caffeine | SNWA | 261 | 217 | 171 |
| Carbamazepine | SNWA | 258 | 215 | 163 |
| DEET | SNWA | 265 | 247 | 200 |
| Diazepam | SNWA | 257 | 221 | 167 |
| Dilantin | SNWA | 241 | 213 | 161 |
| Fluoxetine | SNWA | 190 | 102 | 63 |
| Hydrocodone | SNWA | 305 | <1.0 | <1.0 |
| Meprobamate | SNWA | 258 | 228 | 170 |
| Oxybenzone | SNWA | 157 | <1.0 | <1.0 |
| Pentoxifylline | SNWA | 255 | 205 | 155 |
| Sulfamethoxazole | SNWA | 185 | <1.0 | <1.0 |
| TCEP | SNWA | 252 | 236 | 179 |
| Trimethoprim | SNWA | 265 | <1.0 | <1.0 |

[a]Conditions: 0.8 mg-Cl/mg-C; 24-h contact time; pH = 7.

**Table 8.18. Absolute Indicator Compound Concentrations Observed during UV Disinfection (Facility 2)[a]**

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| Analyte | Lab | Before UV (ng/L) | After UV (ng/L) | Before UV (ng/L) | After UV (ng/L) |
| Butylated Hydroxyanisole | SNWA | 24 | 26 | na | na |
| Butylated Hydroxyanisole | SNWA | 46 | 39 | na | na |
| Bisphenol A | SNWA | 2290 | 2550 | na | na |
| Caffeine | CSM | <40 | <40 | <40 | <40 |
| Caffeine | SNWA | 33 | 29 | na | na |
| Carbamazepine | SNWA | 220 | 150 | na | na |
| DEET | SNWA | 122 | 83 | na | na |
| DEET | SNWA | 62 | 51 | na | na |
| DEET | SNWA | 109 | 115 | na | na |
| Diclofenac | CSM | 43.9 | 23.4 | 69 | <1 |
| Dilantin | SNWA | 163 | 115 | na | na |
| EDTA (Total) | UCB | na | na | 225 | 151 |
| Erythromycin-$H_2O$ | SNWA | 231 | 175 | na | na |
| Estradiol (17β-) | UCB | na | na | <0.3 | <0.3 |
| Estrone | UCB | na | na | <0.2 | <0.2 |
| Fluoxetine | SNWA | 19 | 10 | na | na |
| Gemfibrozil | CSM | 57 | 51 | <2 | <2 |
| Hydrocodone | SNWA | 216 | 164 | na | na |
| Ibuprofen | CSM | <4 | <4 | <4 | <4 |
| Ibuprofen | UCB | <8 | <8 | <8 | <8 |
| Indolebutyric acid | SNWA | 280 | 285 | na | na |
| Meprobamate | SNWA | 989 | 766 | na | na |
| Naproxen | CSM | 80 | 71 | 64 | 58 |
| Salicylic acid | CSM | 39 | 90 | 232 | 217 |
| Sulfamethoxazole | SNWA | 1200 | 671 | na | na |
| TCEP | CSM | 215 | 202 | 886 | 766 |
| TCEP | SNWA | 180 | 107 | na | na |
| TCPP | CSM | 388 | 347 | 1393 | 1093 |
| TDCPP | CSM | 337 | 294 | 539 | 502 |
| Triclocarban | SNWA | 115 | 111 | na | na |
| Triclosan | SNWA | 36 | 43 | na | na |
| Trimethoprim | SNWA | 273 | 219 | na | na |
| Vanillin | SNWA | 464 | 465 | na | na |

[a]Conditions: low-pressure UV; 41 mJ/cm$^2$.
na - not analyzed

**Table 8.19. Absolute Indicator Compound Concentrations Observed during UV Disinfection (Facility 10)[a]**

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| Analyte | Lab | Before UV (ng/L) | UV Effluent (ng/L) | Before UV (ng/L) | UV Effluent (ng/L) |
| Caffeine | CSM | <40 | <40 | <40 | <40 |
| Dichlorprop | CSM | 90 | 93 | <1 | <1 |
| EDTA (Total) | UCB | 125 | 110 | 155 | 160 |
| Estradiol (17β-) | UCB | 0.4 | 0.4 | <0.3 | <0.3 |
| Estrone | UCB | 2.2 | 2.5 | 1.9 | 1.5 |
| Gemfibrozil | CSM | 571 | 548 | 65 | 68 |
| Gemfibrozil | UCB | 56 | 68 | na | na |
| Gemfibrozil | SNWA | 839 | na | 247 | na |
| Ibuprofen | CSM | 743 | 717 | 133 | 126 |
| Ibuprofen | UCB | 115 | 108 | 80 | 48 |
| Mecoprop | CSM | 63 | 63 | 87 | 85 |
| Naproxen | CSM | 266 | 257 | 112 | 103 |
| Naproxen | UCB | 12 | 11 | 15 | <8 |
| Naproxen | SNWA | 337 | na | 308 | na |
| NDMA | UCB | 17 | 18 | 50 | 58 |
| Salicylic acid | CSM | 503 | 572 | 172 | 178 |
| TCEP | CSM | 711 | 731 | 428 | 410 |
| TCPP | CSM | 1339 | 1251 | 842 | 786 |
| TDCPP | CSM | 777 | 737 | 503 | 493 |

[a]Conditions: low-pressure UV; 41 mJ/cm$^2$.
na - not analyzed

**Table 8.20. Absolute Indicator Compound Concentrations Observed during Full-Scale GAC Treatment (Facility 5)**[a]

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| Analyte | Lab | Before GAC (ng/L) | After GAC (ng/L) | Before GAC (ng/L) | After GAC (ng/L) |
| Atenolol | SNWA | na | na | 719 | 14 |
| Atorvastatin | SNWA | na | na | <0.25 | <0.25 |
| Atrazine | SNWA | na | na | 4.1 | 7.8 |
| Caffeine | CSM | <40 | <40 | <40 | <40 |
| Carbamazepine | SNWA | na | na | 232 | 48 |
| Diclofenac | CSM | 45 | <1 | nq | <1 |
| Diclofenac | SNWA | na | na | 85 | 1.0 |
| Dilantin | SNWA | na | na | 153 | 78 |
| EDTA (Total) | UCB | 294 | 265 | 218 | 180 |
| Estradiol (17β-) | UCB | 0.3 | <0.3 | 0.6 | <0.3 |
| Estrone | UCB | <0.2 | <0.2 | 1.3 | <0.2 |
| Fluoxetine | SNWA | na | na | 23 | <0.50 |
| Gemfibrozil | SNWA | na | na | 18 | 3.5 |
| Hydroxy atorvastatin (o-) | SNWA | na | na | <0.50 | <0.50 |
| Hydroxy atorvastatin (p-) | SNWA | na | na | <0.50 | <0.50 |
| Ibuprofen | CSM | <4 | <4 | <4 | <4 |
| Ibuprofen | UCB | <8 | <8 | <8 | <8 |
| Mecoprop | CSM | 125 | <2 | 51 | 17 |
| Meprobamate | SNWA | na | na | 318 | 227 |
| Naproxen | CSM | 31 | <1 | 20 | <1 |
| Naproxen | SNWA | na | na | 19 | <0.50 |
| NDMA | UCB | na | na | 27.5 | <12.5 |
| Norfluoxetine | SNWA | na | na | 1.4 | <0.50 |
| Primidone | CSM | <1 | <1 | na | na |
| Salicylic acid | CSM | 156 | 32 | 47 | nq |
| Simvastatin hydroxy acid | SNWA | na | na | 0.26 | <0.25 |
| Sulfamethoxazole | SNWA | na | na | 510 | 251 |
| TCEP | CSM | 424 | 363 | 542 | 298 |
| TCPP | CSM | 833 | 604 | 783 | 447 |
| TDCPP | CSM | 491 | nq | 425 | 138 |
| Triclosan | SNWA | na | na | 61 | 1.0 |
| Trimethoprim | SNWA | na | na | 144 | 4.4 |

[a]Conditions: tertiary-treated wastewater; TOC = 3–7 mg/L; material used: Norit GAC 820, EBCT = 15 min.
nq - not quantifiable (detected)
na - not analyzed

**Table 8.21. Absolute Indicator Compound Concentrations Observed during RO Treatment (Facility 4)**[a]

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| **Analyte** | **Lab** | **Before RO (ng/L)** | **After RO (ng/L)** | **Before RO (ng/L)** | **After RO (ng/L)** |
| Atenolol | SNWA | 1440 | 11 | na | na |
| Atorvastatin | SNWA | 59 | <0.25 | na | na |
| Atorvastatin (o-Hydroxy) | SNWA | 63 | <0.50 | na | na |
| Atorvastatin (p-Hydroxy) | SNWA | 96 | <0.50 | na | na |
| Atrazine | SNWA | 3.6 | <0.25 | na | na |
| Bisphenol A | SNWA | 247 | <5.0 | na | na |
| Carbamazepine | SNWA | 342 | 0.80 | na | na |
| Diclofenac | CSM | na | na | 73 | <1 |
| Diclofenac | SNWA | 77 | <0.25 | na | na |
| Dilantin | SNWA | 164 | <1.0 | na | na |
| EDTA (Total ) | UCB | 460 | < 18 | 79 | <18 |
| Estradiol (17β-) | UCB | na | na | <0.3 | <0.3 |
| Estrone | UCB | na | na | 18 | <0.2 |
| Fluoxetine | SNWA | 19 | <0.50 | na | na |
| Gemfibrozil | CSM | na | na | 1082 | <2 |
| Gemfibrozil | UCB | na | na | 100 | <8 |
| Gemfibrozil | SNWA | 2660 | 4.5 | na | na |
| Ibuprofen | CSM | na | na | 197 | <4 |
| Ibuprofen | UCB | na | na | 68 | <8 |
| Meprobamate | SNWA | 323 | 0.62 | na | na |
| Naproxen | CSM | na | na | 344 | <1 |
| Naproxen | UCB | na | na | 12 | <8 |
| Naproxen | SNWA | 78 | <0.50 | na | na |
| NDMA | UCB | na | na | 54 | 27 |
| Norfluoxetine | SNWA | 9.0 | <0.50 | na | na |
| Salicylic acid | CSM | na | na | 975 | nq |
| Simvastatin hydroxy acid | SNWA | 4.8 | <0.25 | na | na |
| Sulfamethoxazole | SNWA | 939 | 2.0 | na | na |
| TCEP | CSM | na | na | 686 | <30 |
| TCPP | CSM | na | na | 1073 | <30 |
| TDCPP | CSM | na | na | 549 | <40 |
| Triclosan | SNWA | 372 | 24 | na | na |
| Trimethoprim | SNWA | 468 | 2.1 | na | na |

[a]Conditions: ESPA 2; pH = 6.5; permeate flux, ~12 gfd (~20 LMH).
nq - not quantifiable (detected)
na - not analyzed

**Table 8.22. Absolute Indicator Compound Concentrations Observed during RO Treatment (Facility 8)[a]**

| Analyte | Lab | Before RO (ng/L) | After RO (ng/L) |
|---|---|---|---|
| Caffeine | CSM | <40 | <40 |
| EDTA (Total) | UCB | 71 | < 18 |
| Estradiol (17β-) | UCB | <0.3 | <0.3 |
| Estrone | UCB | <0.2 | <0.2 |
| Gemfibrozil | CSM | 63 | <2 |
| Ibuprofen | CSM | <4 | <4 |
| Metoprolol | UCB | 239 | <8 |
| Naproxen | CSM | 56 | <1 |
| Propranolol | UCB | 72 | <8 |
| Salicylic acid | CSM | 108 | <2 |
| TCEP | CSM | 1105 | <30 |
| TCEP | SNWA | 258 | na |
| TCPP | CSM | 928 | <30 |
| TDCPP | CSM | 401 | <40 |

[a]Conditions: TFC-HR; pH = 6.5; permeate flux, ~12 gfd (~20 LMH).
na - not analyzed

**Table 8.23. Absolute Indicator Compound Concentrations Observed during Pilot-Scale NF Treatment (Facility 8)[a]**

| | | First Sampling Campaign | | Second Sampling Campaign | |
|---|---|---|---|---|---|
| Analyte | Lab | Before NF (ng/L) | After NF (ng/L) | Before NF (Spiked) (ng/L) | After NF (ng/L) |
| Acetaminophen | SNWA | <10 | <1.0 | 257 | 270 |
| Atrazine | SNWA | <10 | <1.0 | 752 | 52 |
| Bisphenol A | CSM | <20 | <20 | 93 | 36 |
| Caffeine | CSM | <40 | <40 | 1396 | 249 |
| Caffeine | SNWA | <100 | <10 | 583 | 71 |
| Carbamazepine | CSM | nq | <20 | 640 | 50 |
| Carbamazepine | SNWA | 241 | 9.5 | 728 | 28 |
| Clofibric acid | CSM | <2 | <2 | 727 | 3 |
| DEET | SNWA | 487 | 30 | 1190 | 72 |
| Dichlorprop | CSM | <1 | <1 | 561 | 13 |
| Diclofenac | CSM | <1 | <1 | 421 | 7 |
| Dilantin | SNWA | 87 | 4.2 | 85 | 3.6 |
| EDTA (EDTA) | UCB | na | 215 | 183 | 218 |
| Erythromycin-H2O | SNWA | 83 | <1.0 | 96 | <1.0 |
| Estradiol (17β-) | UCB | <0.3 | <0.3 | 120 | 3.3 |
| Estrone | UCB | <0.2 | <0.2 | 2 | <0.2 |
| Gemfibrozil | CSM | 63 | <2 | 628 | 10 |
| Hydrocodone | SNWA | 12 | <1.0 | 23 | <1.0 |
| Ibuprofen | CSM | <4 | <4 | 2306 | <4 |
| Ketoprofen | CSM | <2 | <2 | 514 | 12 |
| Mecoprop | CSM | <2 | <2 | 607 | 8 |
| Meprobamate | SNWA | 722 | 30 | 693 | 26 |
| Metoprolol | UCB | 239 | <8 | 278 | <8 |
| Naproxen | CSM | 56 | 6 | 512 | 17 |
| Phenacetine | CSM | <1 | <1 | 333 | 239 |
| Primidone | CSM | <1 | <1 | 780 | <1 |
| Propranolol | UCB | 72 | <8 | 31 | <8 |
| Salicylic acid | CSM | 108 | <2 | 276 | <2 |
| Sulfamethoxazole | SNWA | 321 | 20 | 928 | 53 |
| TCEP | CSM | 1105 | 32 | 1845 | 156 |
| TCEP | SNWA | 258 | 26 | 1060 | 105 |
| TCPP | CSM | 928 | <30 | 2610 | <30 |
| TDCPP | CSM | 401 | <40 | 1754 | <40 |
| Testosterone | UCB | <0.3 | <0.3 | 230 | 2.5 |
| Trimethoprim | SNWA | 46 | 2.4 | 73 | 3.9 |

[a]Conditions: NF-4040 (Dow/Fimtec); pH = 6.5; permeate flux ~12 gfd (~20 LMH).
nq - not quantifiable (detected)
na - not analyzed

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# GLOSSARY

| | |
|---|---|
| AdsAna | Adsorption analysis |
| AD | Acidic drugs |
| 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 |
| APCI | Atmospheric pressure chemical ionization |
| BAC | Biological activated carbon |
| BDOC | Biodegradable dissolved organic carbon |
| BHA | Butylated hydroxyanisole |
| BOD | Biochemical oxygen demand |
| BPA | Bisphenol A |
| 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 |
| 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 |
| EDSTAC | Endocrine Disruptor Screening and Testing Advisory Committee |
| 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 |
| H | Hormones |
| HAAs | Haloacetic acids |
| HHCB | 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta[g][2]benzopyran |
| HPLC | High-performance liquid chromatography |
| IMS | Integrated membrane system |
| IR | Infrared |
| LC/MS | High-performance liquid chromatography with mass spectroscopy |
| LC/MS-MS | High-performance 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 | MBR |
| MDL | Method detection limit |
| MF | Microfiltration |
| MTBSTFA | *N*-(*t*-Butyldimethylsilyl)-*N*-methyl-trifluoroacetamide |
| MW | Molecular weight |
| N.A. | North America |
| NDMA | *N*-Nitrosodimethylamine |
| NF | Nanofiltration |
| NMR | Nuclear magnetic resonance |
| NOM | Natural organic matter |
| NTA | Nitrilotriacetic acid |
| OCSD | Orange County Sanitation District |
| 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 |
| RBF | Riverbank filtration |
| RL | Reporting level |
| RO | Reverse osmosis |
| RSD | Relative standard deviation |
| SAC | Stakeholder Advisory Committee |
| SAP | Science Advisory Panel |
| SAT | Soil-aquifer treatment |
| SCADA | Supervisory control and data acquisition |
| SEC | Size exclusion chromatography |
| SFLUOR | Specific fluorescence |
| SM | Standard methods |
| SMPs | Soluble microbial products |
| SNWA | Southern Nevada Water Authority |
| SPE | Solid-phase extraction |
| SUVA | Specific UV absorbance |
| TCEP | Tris(2-chloroethyl)phosphate |
| TCIPP | 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 |
| UC | University of California–Berkeley |
| UF | Ultrafiltration |
| URI | UV ratio index |
| USGS | United States Geological Survey |
| UV | UV light |
| UVA | UV light absorbance |
| WERF | Water Environment Research Foundation |
| WRF | WateReuse Foundation |
| WTP | Water treatment plant |

# *Advancing the Science of Water Reuse and Desalination*



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