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Nanofiltration Rejection of Contaminants of Emerging Concern from Municipal Water Resource Recovery Facility Secondary Effluents for Potable Reuse Applications

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Engineering

by

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ABSTRACT

As reuse of municipal water resource recovery facility (WRRF) effluent becomes vital to augment diminishing fresh drinking water resources, concern exists that conventional barriers may prove deficient and the upcycling of contaminants of emerging concern (CECs) could prove harmful to human health and aquatic species if more effective and robust treatment barriers are not in place.

There are no federal Safe Drinking Water Act (SDWA) regulations in place specifically for direct potable reuse (DPR) of WRRF effluent. Out of necessity, some states are developing their own DPR reuse regulations. Currently, reverse osmosis (RO) is the default full advanced treatment (FAT) barrier for CEC control. However, the potential exists for tight thin-film composite (TFC) nanofiltration (NF) membranes to provide acceptable CEC rejection efficacies for less capital, operations and maintenance (O&M), energy, and waste generated.

Recognizing the inherent complexity of CEC rejection by membranes, this research program was designed to elucidate the vital predictive variables influencing the rejection of 96 CECs found in municipal WRRF effluents. Each of the CECs was cataloged by their intended use and quantitative structure activity relationship (QSAR) properties, and measured in secondary effluent samples from WRRFs in Texas and Oklahoma. These secondary effluent samples were then processed in bench-scale, stirred, dead-end pressure cells with water treatment industry-specified TFC NF and RO membranes.

A multi-level, multi-variable model was developed to predict the probable rejection coefficients of CECs with the studied NF membrane. The model was developed from variables selected for their association with known membrane rejection mechanisms, CEC-specific QSAR properties, and characteristics of the actual solute matrix. R statistics software version 3.1.3 was

utilized for property collinearity analysis, outlier analysis, and regression modeling. The Pearson correlation method was utilized for selection of the most vital predictor variables for modeling. The resulting Quantitative Molecular Properties Model (QMPM) predicted the NF rejection CECs based on size, ionic charge, and hydrophobicity. Furthermore, the QMPM was verified against a CEC rejection dataset published by an independent study for a similar commercially available TFC NF membrane.

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LIST OF ABBREVIATIONS

ACS	American Chemical Society
ADEQ	Arizona Department of Environmental Quality
ADWR	Arizona Department of Water Resources
AFM	Atomic Force Microscopy
ANN	Artificial Neural Network
AOP	Advanced Oxidation Process
AS	Activated Sludge
AWT	Advanced Water Treatment
AWWA	American Water Works Association
ASR	Aquifer Storage and Recovery
BAT	Best Alternative Treatment
BNR	Biological Nutrient Removal
BOD	Biochemical Oxygen Demand
BOR	United States Bureau of Reclamation
CAS	Chemical Abstracts Service
CASN	Chemical Abstracts Service Number
cBOD	Carbonaceous Biochemical Oxygen Demand
CCL	Contaminate Candidate List
CDPH	California Department of Public Health
CEC	Contaminants of Emerging Concern
COK	Central Oklahoma
CWRCB	California Water Resources Control Board

DOS	Dissolved Organic Carbon
DPR	Direct Potable Reuse
DSP	Donan Steric Pore
EDC	Endocrine Disrupting Compound
EEA	Eurofins Eaton Analytical
EfOM	Effluent Organic Matter
EPA	United States Environmental Protection Agency
ESI	Electrospray Ionization
F:M	Food to Microorganism
FAT	Full Advanced Treatment
FDEP	Florida Department of Environmental Protection
FOS	Factor of Safety
GAC	Granulated Activated Carbon
GEPD	Georgia Environmental Protection Division
HB-I	Hydrophobic Ionic
HB-N	Hydrophobic Neutral
HL-I	Hydrophilic Ionic
HL-N	Hydrophilic Neutral
HP	High Pressure
IPR	Indirect Potable Reuse
ISE	Iterative Stepwise Elimination
K_{oa}	Octanol-Air Partition Coefficient
K_{ow}	Octanol-Water Partition Coefficient

LP	Low Pressure
LPRO	Low-Pressure Reverse Osmosis
LS-MS-MS	Liquid Chromatograph Separation and Series Mass Spectrometry
MAST	Membrane Applied Science and Technology
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MDH	Minnesota Department of Health
MF	Microfiltration
MGD	Million Gallons per Day
MLSS	Mixed Liquor Suspended Solids
MOR	Monthly Operating Report
MOS	Membrane Operating System
MPCA	Minnesota Pollution Control Association
MRL	Minimum Reportable Level
MSA	Molecular Surface Area
MW	Molecular Weight
MWCO	Molecular Weight Cutoff
NCOD	National Contaminant Occurrence Database
NF	Nanofiltration
NMED	New Mexico Environmental Department
NOM	Natural Organic Matter
NPDES	National Primary Discharge Elimination System
NPDWR	National Primary Drinking Water Regulations

NSF	National Science Foundation
NTX	North Texas
NWRI	National Water Research Institute
O&M	Operations and Maintenance
ODEQ	Oklahoma Department of Environmental Quality
OPDES	Oklahoma Pollutant Discharge Elimination System
OWRB	Oklahoma Water Resources Board
PFD	Process Flow Diagram
PFA	Perfluorinated
pKa	Acid Dissociation Constant
PPCP	Pharmaceuticals and Personal Care Product
PSA	Polar Surface Area
PSO	Public Service Company of Oklahoma
PTFE	Polytetrafluoroetheylene
PWS	Public Water Supply
QMPM	Quantitative Molecular Properties Model
QSAR	Quantitative Structure Activity Relationship
R	Rejection
RO	Reverse Osmosis
RWC	Recycled Water Contribution
SASA	Solvent Accessible Surface Area
SE	Secondary Effluent
SIU	Significant Industrial Users

SK	Spiegler-Kedem
SOK	Southwest Oklahoma
SOP	Standard Operation Procedure
SRT	Solids Retention Time
S_w	Solubility
SDWA	Safe Drinking Water Act
SWS	Sensitive Water Supply
SWS-R	Sensitive Water Supply-Reuse
SIU	Significant Industrial Users
TCEP	Tris-2-chloroethyl Phosphate
TCEQ	Texas Commission on Environmental Quality
TDS	Total Dissolved Solids
TF	Trickling Filter
TFC	Thin-film Composite
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
TPDES	Texas Pollutant Discharge Elimination System
TSCA	Toxic Substances Control Act
TSS	Total Suspended Solids
TWDB	Texas Water Development Board
UCMR	Unregulated Contaminant Monitoring Rule
UOSA	Upper Occoquan Service Authority
USGS	United States Geological Survey

UV	Ultra-Violet
VDEQ	Virginia Department of Environmental Quality
WEF	Water Environment Federation
WRA	WateReuse Association
WRRF	Water Resource Recovery Facility
WTP	Water Treatment Plant
α	Polarizability
ηg/L	Nanogram per Liter
µg/L	Microgram per Liter

CHAPTER 1 - INTRODUCTION

Record drought, shrinking water supply alternatives, and growing water demand from population centers across the arid West and Coastal Southeast United States (US) have combined to thrust municipal wastewater potable reuse to the forefront as a vital solution to augment public water supplies (Tisdale 2015). Tisdale (2015) reported capital expenditures for potable reuse infrastructure in the US will exceed $11 billion over the next decade. Augmentation of fresh water supplies with reuse water is a significant component of recent state water plan updates for California, Texas, and Oklahoma (CSWRCB 2014; TWDB 2015; ODEQ 2015).

Tchobanoglous et al. (2015) reported 30% of all wastewater collected in California could be used for either direct potable reuse (DPR) or indirect potable reuse (IPR) projects by 2020. The State of California recently updated its Department of Health Title 22 code with the following statement:

> DPR is defined as the planned introduction of reuse water either directly into a public water system or into a raw water supply immediately upstream of a water treatment plant (WTP). If DPR can be demonstrated to be safe and feasible, the State Board's goal of reusing 2 million ac-ft/yr (or 1.8 BGD) by 2025 will be achieved. (CDPH 2011)

As reuse of municipal wastewater becomes vital to augment diminishing fresh drinking water resources, the presence of contaminants of emerging concern (CECs) have become a major concern (EPA 2014). CECs are water soluble contaminants suspected to exist in the water cycle that can have an adverse effect on human health (EPA 2014). CECs in water resource recovery facility (WRRF) effluent include pharmaceuticals and personal care products such as hormones, antibiotics, stimulants, surfactants, preservatives, artificial sweeteners, and caffeine (Spellman 2014). Agricultural pesticide and herbicide CECs, designed to disrupt metabolic processes, have also been found in WRRF effluents.

With implementation of DPR, public water supply (PWS) managers and regulators are faced with new water treatment challenges (NRC 2012). The public is concerned that conventional barriers may prove deficient, and the upcycling of CECs could prove harmful to human health if more effective and robust treatment barriers are not in place (ODEQ 2015). WRRFs were not historically designed for the target removal of CECs (WEF 2012; Lemanik et al. 2007). Although WRRF unit processes can contribute to removal of CECs, validating effective removal has proven a challenge due to the extremely low concentrations (nanograms per liter, ηg/L) and relatively high cost of analysis (Snyder et al. 2003). Degradation and sorption in the bioreactors, precipitation through clarification, steric exclusion through tertiary filtration, and disinfection/oxidation likely decrease the amount of CECs present, though there remains considerable uncertainty regarding the recalcitrant trace residual in WRRF effluent (Watts et al. 2016; Snyder et al. 2005).

A new, robust multi-barrier treatment approach must be taken to successfully implement DPR for augmentation of PWS (Tchobanoglous et al. 2015; McDonald et al. 2015; Gerrity et al. 2013a). Bench-scale studies indicate that RO and NF membrane-based process technologies show potential as an effective barrier for rejection of CECs from lab-synthesized samples (Bellona et al. 2004; Drewes et al. 2006; Kimura et al. 2003; Linden et al. 2012; Ngheim et al. 2004; Dang et al. 2015; Schafer et al. 2003; Snyder et al. 2004; Tchobanoglous et al. 2015; Westerhoff et al. 2005; Yangali-Quintanilla et al. 2011; Yoon et al. 2007). However, more industry-relevant study is needed to validate RO and NF rejection of recalcitrant CECs from WRRF secondary effluents (Mohammad et al. 2015; Salveson et al. 2016; Watts et al. 2016).

IPR with environmental buffer has been practiced for decades in the US, Europe, Australia, and Singapore. As of 2015, there were only three reported full-scale DPR PWS

systems in operation (Tisdale 2015; Gerrity et al. 2013b). Since 1968, the Windhoek, Namibia, DPR system has utilized a multi-barrier treatment approach that does not include RO membranes (Rodriguez et al. 2009). In 2014, Wichita Falls, Texas, implemented a seasonal-use full-scale DPR system that includes RO membranes for control of dissolved solutes (Jones and Sober 2014; Nix and Schreiber 2015). Commissioned in 2013, the Big Spring, Texas, DPR facility provides up to 2.5 million gallons per day (MGD) of highly treated year-round reuse supply to the WTP (Sloan 2013). A process flow diagram of this new DPR facility is presented in Figure 1-1. The DPR treatment process train includes WRRF tertiary treatment, microfiltration (MF) membranes, reverse osmosis (RO) membranes, and an advanced oxidation process (AOP) prior to blending with the conventional WTP raw surface water (SW) supply.

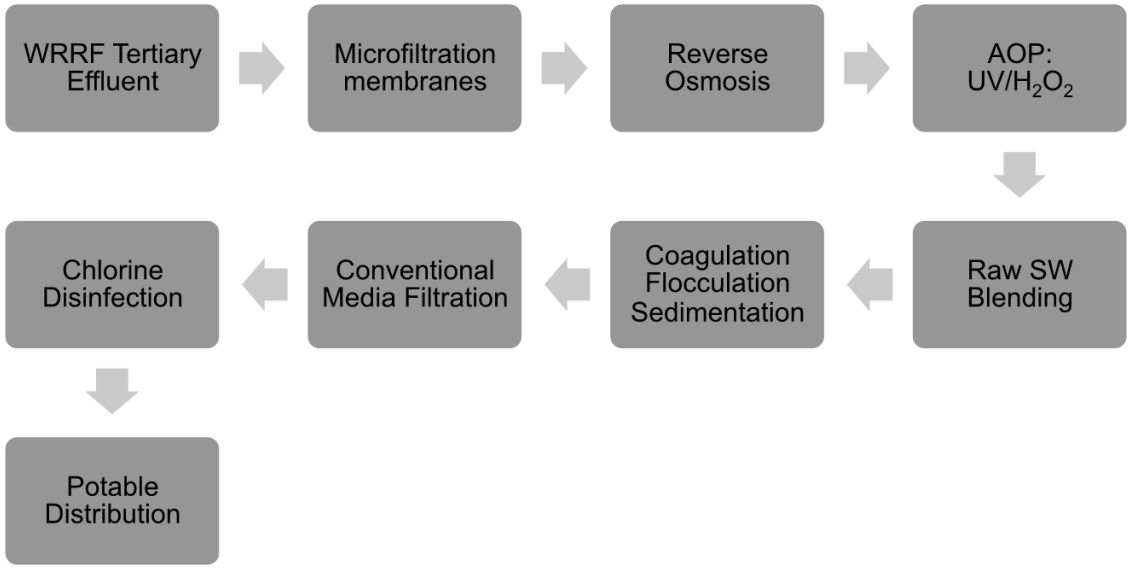


Figure 1-1: Big Spring, Texas, Direct Potable Reuse Facility (commissioned in 2013)

With the lack of experience for CEC control in PWS, the default approach to implementing the best available technology (BAT) can be overly conservative and costly (ODEQ

2015). RO in the two existing US DPR treatment facilities has trended as the default BAT for CEC control (Sloan 2013; Nix and Schreiber 2015). RO represents a major capital and operations and maintenance (O&M) cost not typical of conventional water treatment technologies (Watts et al. 2016; ODEQ 2015; Jones et al. 2014). Further, an RO system produces a brine reject waste that can result in additional treatment and disposal challenges (Watts et al. 2016; ODEQ 2015; Jones et al. 2014; Wickramasinghe and Jones 2013). The default RO approach to CEC control may be questioned if we consider commercially available thin film composite (TFC) NF membranes (Watts et al. 2016; Jones and Sober 2014). Potentially, these TFC NF membranes can provide similar CEC rejection efficacies as RO for less capital, O&M, power, and waste generated (Watts et al. 2016; Jones and Sober 2014; Jones et al. 2014).

Currently, no federal or state regulations exist specifically for DPR (Tchobanoglous et al. 2015). Although the US Environmental Protection Agency (EPA) recently published the first edition of "Guidelines for Water Reuse," no federal Safe Drinking Water Act (SDWA) regulations are in place for DPR drinking water systems (US EPA 2012). Out of necessity, some states are developing their own DPR regulations (TWDB 2015; ODEQ 2015; CSWRCB 2014a). State regulators and PWS managers have turned to water industry advisory boards and committees to provide the knowledge and tools to identify the BAT and where to apply them in the water use cycle (Tchobanoglous et al. 2015; TWDB 2015; ODEQ 2015; CSWRCB 2014a).

This research is needed to validate the NF and RO rejection of recalcitrant CECs occurring in typical WRRF secondary effluents. Furthermore, a primary objective is to conceive and develop a sound practical decision science tool (i.e., model), derived from the quantitative structure-activity relationship (QSAR) properties of CECs and membrane rejection mechanisms,

for regulators and PWS managers to utilize when selecting the BAT to implement for DPR applications.

CHAPTER 2 - LITERATURE REVIEW

2.1 Potable Reuse

PWS in the US have historically originated from fresh (i.e., low dissolved solids) groundwater and surface water, but population growth, arid climate, and extended drought are stressing these supplies in some regions (Tchobanoglous et al. 2015). The US Southwest has experienced spells of prolonged, severe drought throughout its history (Cayan et al. 2010). Recent climate studies indicate significant risk for a 35-year or longer mega drought by 2100 in this region (Cook et al. 2015).

New strategies are needed to help meet water demands and develop more sustainable water supplies. One such strategy is planned potable reuse, in which treated municipal wastewater is utilized to augment PWS (CSWRCB 2014; TWDB 2015; ODEQ 2015; McDonald et al. 2015). At present, planned potable reuse in the US involves either IPR where treated wastewater is introduced into an environmental buffer (e.g., groundwater aquifer, surface water reservoir, lake, or river) before blended water is introduced into a PWS, or DPR where highly treated wastewater is introduced without environmental buffer into a PWS (Tchobanoglous et al. 2015). In recent years, WRRF reuse in Texas (e.g., Big Spring and Wichita Falls) has expanded from non-potable reuse and IPR to DPR applications (Sloan 2013; Nix and Schreiber 2015).

2.1.1 Applications

Planned IPR with an environmental buffer between wastewater reclamation and drinking water treatment is not a new approach to PWS (McDonald et al. 2015). Planned full-scale IPR has been implemented successfully in the US, Europe, Australia, and Singapore (Rodriguez et al. 2009). Rodriguez (2009) reported that in the US, California has the most planned IPR systems with over 40 years of successful operation. Other US states with operating full-scale IPR systems

include Arizona, Colorado, Texas, Nevada, Florida, Virginia, and Georgia (Rodriguez et al. 2009; Gerrity et al. 2013b).

Several European countries, including Belgium, England, and Switzerland, utilize a planned IPR approach to provide PWS (Rodriguez et al. 2009; Gerrity et al. 2013b; Ryan 2016). Israel leads the world with reuse of more than 78 percent of its total municipal wastewater (i.e., 287 of 366 MGD); however, to date, Israel's reuse has been for non-potable applications as required to meet agricultural and industrial water supply demands (Tirosh and Eting 2016). In response to severe drought, Queensland, Australia, implemented three advanced treatment systems (over 600 MGD in combined capacity) in 2008 with the intent to reclaim wastewater to augment the public water supply portfolio. Due to public opposition, these systems have been relegated to date for non-potable and emergency use IPR applications only (Rodriguez et al. 2009; Gerrity et al. 2013b; Ryan 2016). Since 2000, Singapore has successfully implemented four operating full-scale IPR systems with a combined capacity of over 50 MGD (Rodriguez et al. 2009; Gerrity et al. 2013b). As such, the planned IPR approach to potable reuse is widely practiced in the US and internationally.

The DPR approach to potable reuse, where advanced barrier treatment technology is utilized to replace the environmental buffer and shorten the reuse cycle time, is not widely practiced. Although several systems are reported to be in planning or permitting, there are only three full-scale (two year-round and one seasonal) DPR systems in operation world-wide for public drinking water supply (Gerrity et al. 2013b; Tisdale 2015). In operation since 1968, with several upgrades since original commissioning, Windhoek, Namibia (Africa), maintains a DPR system that provides up to 35 percent of the total potable water supply portfolio (Gerrity et al. 2013b). The Windhoek treatment process train, as diagramed in Figure 2-1, includes multiple

barriers designed for a variety of contaminants. Reverse osmosis membranes are not utilized treatment barriers for the Windhoek DPR system.

The Big Spring, Texas, DPR system, commissioned in 2013, provides year-round reuse supply of up to 2.5 MGD (Gerrity et al. 2013b; Sloan 2013). As shown in Figure 2-1, the Big Spring DPR process train includes series membrane treatment with RO and an advanced oxidation process (AOP) prior to conventional drinking water treatment. In response to severe drought in 2014, Wichita Falls, Texas, commissioned a seasonal use full-scale DPR system with up to 5 MGD capacity to augment the potable water supply (Jones and Sober 2014; Nix and Schreiber 2015). Similar to Big Spring, the Wichita Falls treatment train, diagramed in Figure 2-1, also includes series membrane process units with RO barriers prior to conventional water treatment. Another US DPR project is for the resort community of Cloudcroft, New Mexico. Stalled in implementation and not yet in operation, the Cloudcroft treatment train with a planned capacity of 100,000 gallons per day (gpd) is designed with RO membranes and AOP barriers (Gerrity et al. 2013b; Edwards 2014; NMED 2014). RO membranes are trending as a barrier treatment technology for US-based DPR systems.

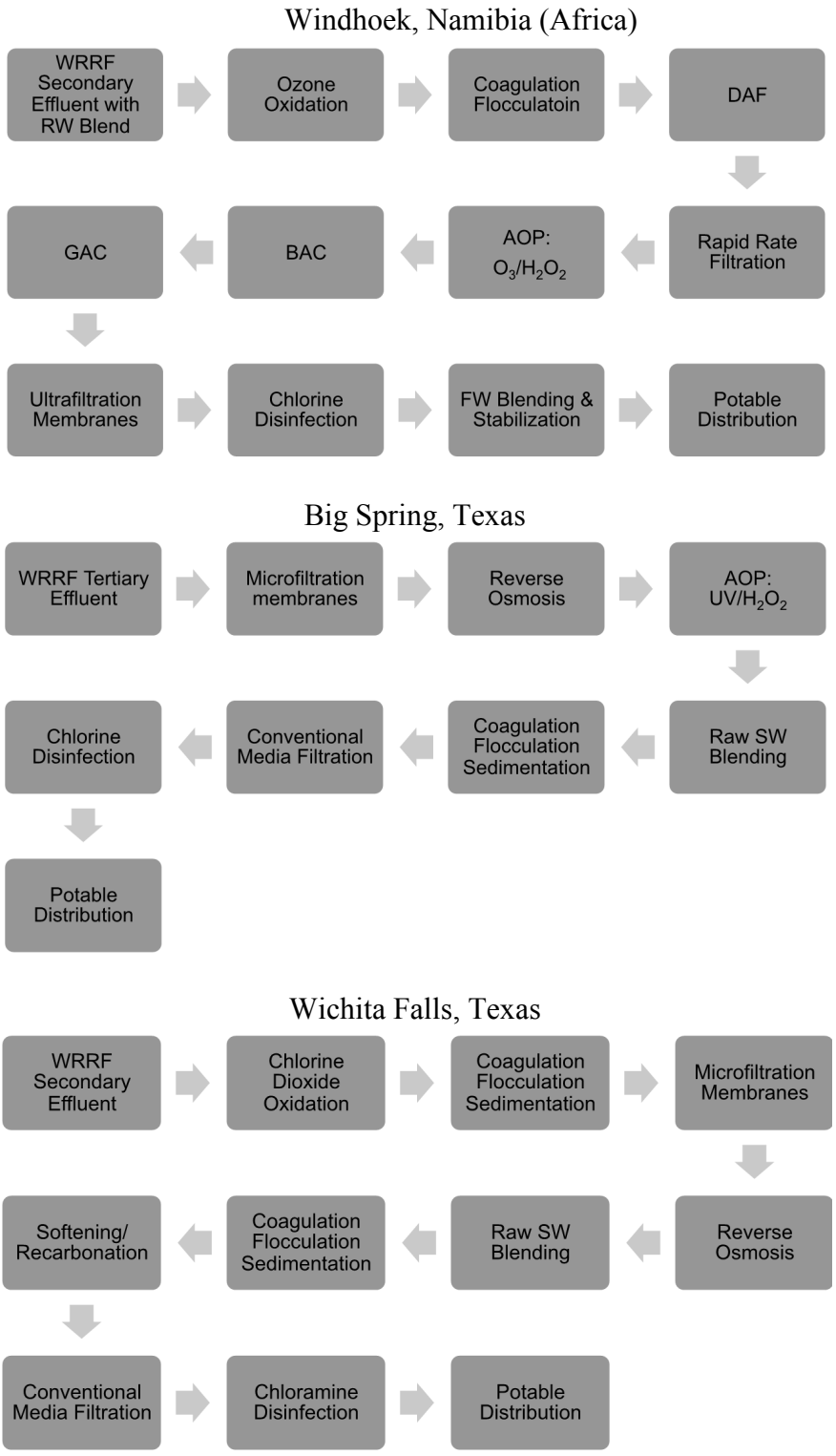


Figure 2-1: Full-Scale Operating Direct Potable Reuse Treatment Trains Ref. Gerrity (2013b), Sloan (2013), Jones (2014), Nix (2015)

2.1.2 Concern with DPR

To help offset the public "yuk" and "toilet-to-tap" factor associated with potable reuse of municipal wastewater, the water industry has responded accordingly with recent action by the Water Environment Federation (WEF). Founded in 1928, WEF is a leading organization of engineers and water industry stakeholders in the field of municipal wastewater and water reuse (WEF 2012). The term "water resource recovery facility" (WRRF), rather than "wastewater treatment plant" (WWTP), was adopted by the WEF Board of Trustees in July 2012 (WEF 2012). "WEF changing WWTP to WRRF is the kind of thing we need to sustain ourselves. It focuses on the concept of a renewable resource rather than waste. Words are powerful; they motivate people," said Julian Sandino, a vice president and water practice leader with the international consulting firm CH2M Hill (WEF 2012).

While the focus of engineered treatment systems for potable reuse projects begins with minimizing the risk associated with wastewater pathogens, non-regulated trace organic contaminants, referred to as CECs, have become important considerations for treatment system design (Dickenson and Drewes 2008; Gerrity et al. 2013a; EPA 2014; Tchobanoglous et al. 2015). CECs can be defined as unregulated chemical solutes potentially found in effluent discharges and surface waters at trace levels, nanograms per liter (ηg/L), that may or may not have an impact on human health (EPA 2015a; US BOR 2009). The majority of the well-studied CECs have been classified as biodegradable to some degree (Rattier et al. 2014). Therefore, the first critical treatment barrier for CEC mitigation is a biological wastewater treatment process. Water quality monitoring from wastewater-receiving streams, however, indicates that a single treatment barrier for CECs is not adequate to prevent downstream contamination (Gerrity et al. 2013b; Kolpin et al. 2002). As both public and regulatory concern grows over CECs in the water

cycle, the use of advanced treatment barrier systems following biological treatment is increasingly common at WRRFs to remove the recalcitrant CECs (Al-Rifai et al. 2011; Gomez et al. 2012; Sloan 2013).

2.2 CEC Occurrence

To understand the occurrence of CECs in municipal wastewater, it is helpful to first consider their origin and intended use.

2.2.1 Origin and Intended Use

There are approximately 13,500 chemical manufacturing facilities in the US owned by more than 9,000 companies (Spellman 2014). Over 84,000 chemicals, as inventoried by the EPA under the Toxic Substances Control Act (TSCA), are in use today with approximately 700 new chemicals added each year (EPA 2014). Water-soluble organic chemicals, or CECs, enter the water cycle through rainfall runoff or disposal to municipal wastewater collections systems (Tchobanoglous et al. 2015). These CECs can be generally characterized by the following intended use classifications (Anderson et al. 2010; CDPH 2011; NRC 2012; Luo et al. 2014; MDH 2015):

1. Endocrine Disrupting Compounds (EDCs)
2. Pharmaceuticals
3. Stimulants
4. Preservatives
5. Artificial sweeteners
6. Pesticides
7. Flame retardants

Each of these CEC classifications is further characterized in Table 2-1.

Table 2-1: CEC Intended Use Characterization

CEC	Classification	Sub-classification
4-nonylphenol	EDC	Surfactant
4-tert-Octylphenol	EDC	Surfactant
Andorostenedione	EDC	Steroid hormone
Bisphenol-A (BPA)	EDC	Plasticizer
Estradiol	EDC	Estrogen hormone
Estrone	EDC	Estrogen hormone
Ethinyl Estradiol - 17α	EDC	Contraceptive
Norethisterone	EDC	Steroid hormone
Progesterone	EDC	Steroid hormone
Testosterone	EDC	Male hormone
Acetaminophen	Pharmaceutical	Analgesic
Albuterol	Pharmaceutical	Anti-asthmatic
Amoxicillin	Pharmaceutical	Antibiotic
Atenolol	Pharmaceutical	Cardio
Azithromycin	Pharmaceutical	Antibiotic
Bendroflumethiazide	Pharmaceutical	Anti-hypertension
Bezafibrate	Pharmaceutical	Cardio
Butalbital	Pharmaceutical	Analgesic
Carbadox	Pharmaceutical	Antibiotic
Carbamazepine	Pharmaceutical	Anti-seizure
Carisoprodol	Pharmaceutical	Muscle relaxer
Chloramphenicol	Pharmaceutical	Antibiotic
Cimetidine	Pharmaceutical	Cardio
Dehydronifedipine	Pharmaceutical	Cardio
Diazepam	Pharmaceutical	Anti-anxiety
Diclofenac	Pharmaceutical	Anti-inflammatory
Dilantin	Pharmaceutical	Anti-seizure
Erythromycin	Pharmaceutical	Antibiotic
Flumeqine	Pharmaceutical	Antibiotic
Fluoxetine	Pharmaceutical	Antidepressant
Gemfibrozil	Pharmaceutical	Cardio
Ibuprofen	Pharmaceutical	Analgesic
Iohexal	Pharmaceutical	X-ray contrast
Iopromide	Pharmaceutical	X-ray contrast
Ketoprofen	Pharmaceutical	Anti-inflammatory
Ketorolac	Pharmaceutical	Anti-inflammatory
Lidocaine	Pharmaceutical	Analgesic
Lincomycin	Pharmaceutical	Antibiotic
Lopressor	Pharmaceutical	Cardio
Meclofenamic Acid	Pharmaceutical	Anti-inflammatory
Meprobamate	Pharmaceutical	Anti-anxiety
Naproxen	Pharmaceutical	Analgesic
Nifedipine	Pharmaceutical	Cardio
Oxolinic acid	Pharmaceutical	Antibiotic
Pentoxifylline	Pharmaceutical	Blood thinner
Phenazone	Pharmaceutical	Analgesic
Primidone	Pharmaceutical	Anti-seizure
Sulfachloropyridazine	Pharmaceutical	Antibiotic
Sulfadiazine	Pharmaceutical	Antibiotic
Sulfadimethoxine	Pharmaceutical	Antibiotic
Sulfamerazine	Pharmaceutical	Antibiotic
Sulfamethazine	Pharmaceutical	Antibiotic
Sulfamethizole	Pharmaceutical	Antibiotic
Sulfamethoxazole	Pharmaceutical	Antibiotic
Sulfathiazole	Pharmaceutical	Antibiotic
Theophylline	Pharmaceutical	Anti-asthmatic
Warfarin	Pharmaceutical	Cardio
1,7-Dimethylxanthine	Stimulant	Caffeine degradate
Caffeine	Stimulant	-
Cotinine	Stimulant	Nicotine degradate
Theobromine	Stimulant	Caffeine degradate
Butylparaben	Preservative	Anti-microbial
Ethylparaben	Preservative	Antifungal
Isobutylparaben	Preservative	Antibacterial/fungal
Methylparaben	Preservative	Antibacterial/fungal
Propylparaben	Preservative	Antibacterial/fungal
Triclosan	Preservatives	Antibacterial
Trimethoprim	Preservatives	Antibacterial
Acesulfame-K	Sweetener	Sugar substitute
Sucralose	Sweetener	Sugar substitute
2,4-D	Pesticide	Herbicide
Atrazine	Pesticide	Herbicide
Bromacil	Pesticide	Herbicide
Chloridazon	Pesticide	Herbicide
Chlorotoluron	Pesticide	Herbicide
Clofibric Acid	Pesticide	Herbicide
Cyanazine	Pesticide	Herbicide
DACT	Pesticide	Atrazine degradate
DEA	Pesticide	Atrazine degradate
DEET	Pesticide	Mosquito repellant
DIA	Pesticide	Atrazine degradate
Diuron	Pesticide	Herbicide
Isoproturon	Pesticide	Herbicide
Linuron	Pesticide	Herbicide
Metazachlor	Pesticide	Herbicide
Propazine	Pesticide	Herbicide
Quinoline	Pesticide	Herbicide feedstock
Simazine	Pesticide	Herbicide
TCEP	Flame Retardant	Fabric coating
TCPP	Flame Retardant	Fabric coating
TDCPP	Flame Retardant	Fabric coating

Sources: Anderson et al. 2010; CDPH 2011; NRC 2012; Eaton et al. 2012; Luo et al. 2014; MDH 2015

2.2.2 Occurrence in WRRF Effluents

Municipal WRRF primary and secondary effluents have been found to contain trace levels of CECs (Purdom et al. 1994; Folmar et al. 1996; Harries et al. 1997; Rodgers-Gray et al. 2000; Drewes et al. 2006; Behera et al. 2011; Luo et al. 2014). Primary effluent (PE) indicates water treated by physical processes (e.g., primary clarification) associated with WRRF primary treatment, while SE indicates water treated by biological processes (e.g., activated sludge) associated with WRRF secondary treatment (Tchobanoglous et al. 2014). Table 2-2 shows the detectable concentrations of CECs and the variability in biodegradability observed between PE and SE treated municipal wastewater effluents.

Table 2-2: CEC Occurrence in Wastewater Effluent

CEC	Range in Primary Effluents (ηg/L)	Range in Secondary Effluents (ηg/L)
17α-Ethynyl Estradiol	ND – 13	ND - 7.5
17β-Estradiol	ND – 150	ND - 43
4-t-Octylphenol	100 - 13,000	ND - 1,300
Bisphenol A	40 -100	ND - 17,300
Estriol	ND – 802	ND - 18
Estrone	7.3 -132	ND - 108
Nonylphenol	1,300 - 343,000	ND - 9,100
Testosterone	24 -180	ND
Acetaminophen	3,540 – 10,234	ND - 27
Atenolol	5,113 – 11,239	261 – 5,911
Carbamazepine	43 – 127	40 - 74
Diclofenac	59 -243	13 - 49
Gemfibrozil	101 – 318	26-Sep
Ibuprofen	1,599 – 2,853	15 - 75
Ketoprofen	81 – 286	ND - 37
Lincomycin	3,095 – 19,401	1,437 – 21,278
Naproxen	1,360 – 5,033	37 - 166
Sulfamethazine	ND – 343	ND - 408
Sulfamethoxazole	79 – 216	20 - 162
Caffeine	1,608 – 3,217	ND - 60
Triclosan	247 – 785	79 - 149
Trimethoprim	101 – 277	13 - 154
Atrazine	20 – 28,000	4 - 730
Clofibric acid	ND – 65	ND - 6
DEET	2,560 – 3,190	610 – 1,580
Diuron	30 – 1,960	2 – 2,530
TCEP	60 – 500	60 – 2,400
TCPP	180 – 4,000	100 – 21,000

ND = Below analytical detection limit
Source: Drewes et al. 2006; Behera et al. 2011; Luo et al. 2014

Table 2-2 shows SE may contain recalcitrant (i.e., non-biodegraded fraction) concentrations of natural and synthetic endocrine disruptors, pharmaceuticals, personal care products, and pesticides in the nanogram per liter (ηg/L) range with some surfactant phenols, pharmaceuticals, and flame retardants in the microgram per liter (µg/L) range (Drewes et al. 2006; Behera et al. 2011; Luo et al. 2014). Table 2-2 also reveals that the biological processes associated with secondary treatment are effective for at least partial removal of most CECs.

The occurrence of CECs in municipal wastewater effluents is not new (Tchobanoglous et al. 2015). It is reasonable to assume that as long as pharmaceuticals, personal care products, and pesticides have been in use, these products and their metabolites have contributed to the effluent trace contaminant load. However, our ability to analyze and detect trace amounts of these CECs in water is new and evolving (Eaton and Haghani 2012; Vanderford et al. 2012; Tchobanoglous et al. 2015).

The City of Norman, Oklahoma (Norman), in conjunction with Eurofins Eaton Analytical of Monrovia, California, conducted an IPR Study to consider potential WTP impacts from the augmentation of Lake Thunderbird surface water supply with SE from the Norman WRRF (Crowley and Mattingly 2009). To prepare for the study, Norman conducted an analytical survey for a study set of 96 (Norman 96) CECs in SE discharged from the WRRF.

The Norman 96 was selected based on review of occurrence data from gray literature surveys conducted by WateReuse Association (WRA), National Water Research Institute (NWRI), EPA, US Geological Survey (USGS), and the US Bureau of Reclamation (BOR). The data reflected a compilation of CECs suspected to occur in WRRF effluents that could be analyzed by an established standard method with acceptable precision and accuracy. The "Framework for Direct Potable Reuse" released in 2015 by the WRA, NWRI, WEF, and

American Water Works Association (AWWA), recommends 13 (see Appendix A) of the Norman 96 CECs to be considered as control indicators when planning DPR projects (Tchobanoglous et al. 2015). As such, the Norman 96 appears to be a relatively comprehensive CEC study set.

Table 2-3 shows that CEC concentrations in the Norman WRRF SE range from non-detection to well above minimum reportable level (MRL). The higher concentration CECs include pharmaceuticals for control of infection, blood pressure, cholesterol, pain, seizures, and anxiety. Some of the estrogen-based hormones (e.g., estrone) were detected, but the testosterone-based hormones were non-detectable. Perhaps most revealing were the relatively high concentrations of artificial sweeteners (e.g., acesulfame-K, sucralose). It is apparent such compounds do not biodegrade (or biosorb) in the WRRF bioreactor. These data suggest artificial sweeteners may be an ideal control indicator with which to monitor breakthrough integrity for future membrane-based DPR treatment process trains. Unlike the artificial sweeteners, caffeine is evidently biodegradable as concentrations were only slightly detectable. Also, pesticides were found in the SE at recalcitrant trace residual (Crowley and Mattingly 2009).

Table 2-3: Norman 96 Survey in WRRF Secondary Effluent

Compound	Effluent (ηg/L)	MRL (ηg/L)	Compound	Effluent (ηg/L)	MRL (ηg/L)
4-nonylphenol - semi quantitative	ND	100	Primidone	170	5
4-tert-Octylphenol	78	50	Sulfachloropyridazine	ND	5
Andorostenedione	ND	5	Sulfadiazine	ND	5
Bisphenol-A (BPA)	ND	10	Sulfadimethoxine	ND	5
Estradiol	ND	5	Sulfamerazine	ND	5
Estrone	130	5	Sulfamethazine	12	5
Ethinyl Estradiol - 17 alpha	ND	5	Sulfamethizole	ND	5
Norethisterone	ND	5	Sulfamethoxazole	1,300	5
Progesterone	ND	5	Sulfathiazole	33	5
Testosterone	ND	5	Theophylline	ND	20
Acetaminophen	ND	5	Warfarin	ND	5
Albuterol	ND	5	1,7-Dimethylxanthine	42	10
Amoxicillin (semi-quantitative)	4,600	20	Caffeine	60	5
Atenolol	300	5	Cotinine	42	10
Azithromycin	ND	20	Theobromine	ND	10
Bendroflumethiazide	ND	5	Butylparaben	ND	5
Bezafibrate	ND	5	Ethylparaben	ND	20
Butalbital	54	5	Isobutylparaben	ND	5
Carbadox	ND	5	Methylparaben	ND	20
Carbamazepine	400	5	Propylparaben	24	5
Carisoprodol	130	5	Triclosan	43	10
Chloramphenicol	ND	10	Trimethoprim	1,000	5
Cimetidine	ND	5	Acesulfame-K	4,100	20
Dehydronifedipine	82	5	Sucralose	49,000	100
Diazepam	ND	5	2,4-D	ND	5
Diclofenac	93	5	Atrazine	16	5
Dilantin	130	20	Bromacil	ND	5
Erythromycin	220	10	Chloridazon	ND	5
Flumeqine	ND	10	Chlorotoluron	ND	5
Fluoxetine	90	10	Clofibric Acid	ND	5
Gemfibrozil	550	5	Cyanazine	ND	5
Ibuprofen	ND	10	DACT	ND	5
Iohexal	ND	10	DEA	11	5
Iopromide	270	5	DEET	ND	10
Ketoprofen	150	5	DIA	100	5
Ketorolac	ND	5	Diuron	ND	5
Lidocaine	370	5	Isoproturon	ND	100
Lincomycin	15	10	Linuron	ND	5
Lopressor	1,200	20	Metazachlor	ND	5
Meclofenamic Acid	ND	5	Propazine	ND	5
Meprobamate	460	5	Quinoline	ND	5
Naproxen	ND	10	Simazine	220	5
Nifedipine	34	20	TCEP	830	10
Oxolinic acid	ND	10	TCPP	510	100
Pentoxifylline	ND	5	TDCPP	530	100
Phenazone	5.6	5			

ηg/L = nanograms per liter.
ND = Non-detetectable. MRL = Minimum reportable level, EPA Method MS/MS/LS-ESI.
Source: Crowley and Mattingly 2009

2.3 Human Health Criterion

CECs and their associated degradates represent a challenge for regulators to establish human health based criterion due to the limited scientific knowledge regarding acute and chronic health effects (Tchobanoglous 2015). There is limited public record of CEC human health effects from ingestion of reuse water supply reported by epidemiology and toxicology studies.

2.3.1 Epidemiology

Epidemiological studies assess the measurable difference in disease incidence between human populations exposed to a given set of conditions as compared to populations experiencing less exposure (Tchobanoglous 2015). One limitation to epidemiology studies for establishing human health criterion for the control of trace CECs in public water supply is the difficulty in assessing or differentiating the incremental risks from background exposure to other environmental sources such as food and pharmaceuticals that can be influenced by genetics and socio-economics (Tchobanoglous 2015). An epidemiological study of the Windhoek DPR system concluded that differences in diarrheal disease prevalence was associated with socio-economic factors, not the source of water supply (Rodriguez et al. 2009). An epidemiological study of the Montebello, California, IPR project concluded no evidence existed that the reuse water had an adverse effect on liver cancer incidence, mortality, or infectious disease outcome (Rodriguez et al. 2009). Another epidemiology study of the same California IPR project concluded no significant association between reuse water and adverse birth outcomes, including 19 categories of birth defects, over a 10-year period (Rodriguez et al. 2009).

2.3.2 Toxicology

Animal or cellular toxicology dose-response testing is another approach to human health risk assessments for I/DPR projects. A drawback to this approach is the dose levels tend to be

orders of magnitude greater than human ingestion levels from drinking water. As such, the observed dose-response relationship must be extrapolated to low dose potentially giving rise to overly conservative public health criterion (Tchobanoglous 2015). Chronic toxicology testing with rats and mice was conducted for DPR demonstration projects in Denver, Tampa, and Singapore. All three animal toxicology studies concluded no adverse reproductive, developmental, or carcinogenic outcomes from lifetime consumption of reuse water over two generations (Lauer 1993; Rodriguez et al. 2009). Cellular mutagenic studies, utilizing the Ames test with bacteria *Salmonella typhimurium*, were conducted for a variety of source waters in San Diego, Tampa, Potomac, Orange County, and Montebello (Nellor et al. 1995). In general, mutagenic activity was observed (in declining order) for wet weather surface water, dry weather surface water, recycled water, and ground water. High false positive mutagenic activity was reported for finished drinking waters due to disinfecting residuals (Nellor et al. 1995).

2.3.3 Suggested CEC Criterion

In recognition of the lack of human health based criterion related to reuse water supply, the National Water Research Institute (NWRI) convened an independent advisory panel (IAP) to develop a list of recommended CECs, based on collective knowledge, to be considered as performance monitoring protocol for DPR systems (NWRI 2013). The IAP suggested risk-based human health criterion for the control of 13 CECs in DPR applications is provided in Table 2-4.

Table 2-4: NWRI Risk-Based Human Health Criterion

CEC	Criterion (ηg/L)	Rationale
Ethinyl estradiol 17-β-estradiol	MRL: 5 MRL: 5	Should evaluate its presence in source water
Estrone	320	Surrogate for steroids
Cotinine Primidone Dilantin	1,000 10,000 2,000	Surrogate for low MW ionic CECs
Meprobamate Atenolol	200,000 4,000	Occurs frequently at ηg/L level
Carbamazepine	10,000	Unique structure
Sucralose	150,000,000	Surrogate for hydrophilic neutral CECs
TCEP	5,000	CEC of interest
DEET	200,000	Common CEC in highly treated effluents
Triclosan	50,000	CEC of interest

Source: NWRI (2013)

2.4 CEC Regulatory Framework for DPR

Despite the rapidly increasing interest in potable reuse, no jurisdictions have established CEC regulations for DPR projects (Tchobanoglous et al. 2015). The EPA has discussed the status of potable reuse in its "2012 Guidelines for Water Reuse," but has not prepared minimum standards or other documents establishing a baseline for the design of DPR facilities and projects (EPA 2012). In fact, EPA states in the 2012 Guidelines: "Water reclamation and reuse standards in the US are the responsibility of state and local agencies – there are no federal regulations for reuse."

Unplanned reuse of treated wastewater effluent as a PWS is common practice in many of the nation's PWS systems, with some drinking WTPs using water with a large fraction originating as wastewater effluent from upstream communities, especially under low-flow

effluent dominated conditions (NRC 2012). The following sections summarize the potable reuse regulatory status of the EPA and all US primacy states with active CEC control initiatives related to potable reuse or prominent DPR projects.

2.4.1 Federal Framework

The US SDWA, as amended in 1996, requires EPA to publish a list every five years of currently unregulated contaminants that may pose risks for drinking water (80 CFR 6076, EPA 2015b). EPA uses the Unregulated Contaminant Monitoring Rule (UCMR) program to collect data for contaminants suspected to be present in PWS as required to generate a Contaminant Candidate List (CCL). The 1996 SDWA Amendments provide the following for UCMR database generation:

- Monitoring by large systems and a representative sample of public water systems serving less than or equal to 10,000 people
- Storing analytical results in a National Contaminant Occurrence Database (NCOD)

The EPA CCL is a list of contaminants that are currently not subject to any proposed or promulgated national primary drinking water regulations (NPDWR), but are known or anticipated to occur in PWS and may require subsequent regulation under the EPA SDWA (EPA 2012). Since first announced in 1998, four CCLs have been published by the EPA in the Federal Register. CCL1 listed 60 contaminants. No regulatory action was determined for nine and 51 were carried forward. CCL2 listed the 51 carried forward contaminants. No regulatory action was determined for 11, two were promulgated, and 38 were carried forward (EPA 2015b). CCL3 listed 116 (104 chemicals and 12 microbial). A summary of the NCOD occurrence data for the UCMR3 is provided in Appendix A (EPA 2015b). No regulatory action was determined for four, two were promulgated, and 100 were carried forward from CCL3 (EPA 2015b,c).

With publication of Draft CCL4 in 2015, the total list of carried forward and new includes 100 chemical and 12 microbial contaminants (EPA 2015c). The CCL4 list of chemical contaminants is provided in Appendix A (EPA 2015c). The SDWA identifies three criteria to determine whether a CCL contaminant may require regulation:

1. The contaminant may have an adverse effect on human health.
2. The contaminant is known to occur or there is substantial likelihood that the contaminant will occur in PWS with a frequency and at levels of public health concern.
3. In the sole judgement of the Administrator, regulation of such contaminant presents a meaningful opportunity for health risk reduction for persons served by PWS.

If the EPA determines that these three statutory criteria are met and makes a final determination to regulate a contaminant, the agency has 24 months to publish a proposed Maximum Contaminant Level Goal (MCLG) and NPDWR (EPA 2012). Following comment period, the agency has 18 months to publish and promulgate a final MCL and NPDWR.

Since the first CCL, the EPA has promulgated NPDWR MCLs for three herbicide CECs as indicated in Table 2-5.

Table 2-5: CEC MCLs - NPDWR[a]

CEC	Intended Use	NPDWR MCL
Atrazine	herbicide	3,000 ηg/L
2, 4-Dichlorophenoxyacetic	herbicide	70,000 ηg/L
Simazine	herbicide	4,000 ηg/L

[a]Adapted from EPA 2012, 2015b,c

2.4.2 State Framework

Activity related to the control of CECs for I/DPR by the states has been on an as-needed basis. The following discussion focuses on activity by the states known to be developing CEC-specific regulatory control or that have DPR projects in implementation phase or operational.

2.4.2.1 California

Out of necessity, California has been a leader in the research and planning of IPR and DPR options. The Orange County Water District and Los Angeles County Sanitation Districts have led the effort for IPR over the last several decades to supplement groundwater supplies (CSWRCB 2014a,b). This practice has been utilized for decades for saltwater intrusion barriers, but is now being adapted for groundwater supply augmentation (Crook 2010). The City of San Diego is nearing the end of a multi-year process to demonstrate the feasibility of IPR to augment surface water supplies through a large-scale pilot treatment facility (CSWRCB 2014b). They have also implemented a long-term, high-profile public education program to gain acceptance of the proposed augmentation of surface water by IPR (CSWRCB 2014b). Due to the increase in interest of reuse of municipal WRRF effluents, the State of California is developing regulations to govern IPR and DPR systems and the control of CECs (CAEPA 2006; CDPH 2011).

2.4.2.1.1 Groundwater IPR

The California Department of Public Health (CDPH) published groundwater recharge regulations under Title 22 in 2011 and has since updated these draft regulations several times, most recently on May 30, 2014 (CDPH 2011, CSWRCB 2014a). On June 30, 2014 the California legislature directed that these rules be adopted on an emergency basis. The regulations represent a working understanding of requirements for the use of reuse water to recharge potable groundwater supplies. These regulations also represent a starting point in the development of

regulations for surface water augmentation IPR and likely development of DPR regulations. Key provisions of the groundwater IPR regulations include:

1. Minimum retention times within the aquifer
2. Limits on reuse water contribution (RWC), with initial limit of 20% and provisions for increasing contribution in step-wise fashion subject to maximum of 75% with continued successful operation
3. Reuse water must be treated with full advanced treatment (FAT), defined to include RO (with 99% salt rejection) and an AOP process
4. Monitoring protocol for identified indicator CECs
5. Aquifer retention time shall not be less than 2 months prior to withdrawal

2.4.2.1.2 Surface Water IPR

The legislature has directed the CDPH and the California State Water Resources Control Board (CSWRCB) to adopt regulations for surface water augmentation with IPR by December 31, 2016. No draft regulations are currently available, but an advisory group has been named, and they in turn have made recommendations for selection of an expert panel to advise the CDPH in developing criteria (CSWRCB 2014a).

2.4.2.1.3 Direct Potable Reuse

The legislature has also directed the CDPH and CSWRCB to investigate and report to on the feasibility of developing regulatory criteria for DPR (CSWRCB 2014a). A public review draft report is due September 1, 2016. The final DPR report is scheduled for December 31, 2016 (CSWRCB 2014a).

CDPH formed a CEC Expert Advisory Group in 2012 that is working with the CSWRCB to develop a list of CECs for monitoring and bioassay testing. As reported at the May 2014

CWRCB Meeting, 15 CECs as shown in Table 2-6 were adopted for monitoring of WRRF effluents (CSWRCB 2014b).

Table 2-6: California CEC Monitoring List for DPR

Bisphenol-A	17-beta estradiol
Bis (2-ethylhexyl) phthalate (BEHP)	Galaxolide (HHCB)
Butylbenzyl phthalate (BBP)	Ibuprofen
Bifenthrin	PBDE -47 and -99
Chlorpyrifos	Permethrin
Diclofenac	PFOS
Estrone	p-Nonylphenol
Estradiol	Trisclosan

Source: CSWRCB 2014b

2.4.2.2 Texas

Texas has PWS systems practicing both IPR and DPR, but has no regulations specifically designed for these projects (TWDB 2015). The Texas Commission on Environmental Quality (TCEQ) and Texas Water Development Board (TWDB) have exercised control of IPR through discharge permitting conditions and water rights provisions. These include groundwater injection (El Paso), river transport and withdrawal followed by artificial wetland treatment (North Texas Municipal Water District and Tarrant Regional Water District), and water accounting programs within several reservoirs (Trinity River Authority) subject to significant effluent discharges. According to the 2012 Texas State Water Plan, water reuse will provide approximately 1.53 million acre-feet per year of water supply statewide by the year 2060 and will meet approximately 18% of the projected water needs. However, TWDB reports there is significantly more potential for development of water reuse as a water management strategy than is currently include in the state water plan. Much of this potential is likely to be realized as more reuse

projects are implemented and progress is made in communicating the advantages, benefits and safety of potable reuse to the public (TWDB 2015).

Three DPR projects (without environmental buffer) have been authorized, with at least one additional project (El Paso) in development and review. One of these projects (Colorado River Municipal Water District, in Big Spring) has been in operation since April 2013, while a second (City of Wichita Falls) began production in early July of 2014. The third DPR project, in Brownwood, has been authorized for construction (Sloan 2013; Jones and Sober 2014; Nix and Schreiber 2015).

Over the course of reviewing and approving the three DPR projects, TCEQ has developed some internal consensus-based standards it applies for such projects. The overarching goal is to consistently and conservatively meet the requirements of the SWDA (McDonald et al. 2015). Key features required for DPR projects to date include:

1. Approximate "doubling" of SWTR pathogen inactivation is required: 8-log for viruses (9-log if chloramine disinfection is utilized), 6-log for *Giardia* and 5.5-log for *Cryptosporidium* using multiple barriers. This inactivation includes subsequent surface water treatment if applicable, but does not recognize any credit from upstream WRRF treatment processes. Higher requirements could be imposed if the source water is at risk of elevated pathogen levels compared to sources tested for recent DPR proposals.
2. Critical treatment processes require continuous online monitoring with provisions for automatic shutdown if treatment goals for acute health protection are jeopardized. A storage buffer could be required if satisfactory real-time monitoring cannot be achieved.

3. Continuous monitoring of flows and calculation of blend ratio is required to maintain reuse water fraction within established limit for system.
4. Advanced pilot testing is required to demonstrate extended satisfactory performance.
5. Industrial pretreatment program is subject to review to identify potential public health vulnerabilities.

Approved blending ratios have varied and no standard limit is established. It is anticipated that up to 50% of blended finished water could be approved from a reuse water source without special measures beyond those applied to other DPR projects (TWDB 2015).

Out of necessity, the TWDB recently took the lead to bring together several industry and academic experts to form advisory committees, similar to California, and develop the "2015 Direct Potable Reuse Resource Document" to provide public water systems with information on the practice, risks, benefits, and potential guidelines for potable reuse (McDonald et al. 2015). The TWDB identified 51 CECs for monitoring where public water systems are planning DPR augmentation with WRRF secondary or tertiary effluents. As provided in Table 2-7, this list of 51 was derived from the 90th percentile measured occurrence from the EPA NCOD for CCL3 (McDonald et al. 2015).

Table 2-7: Texas CEC List for DPR Systems

CEC	Usage	CEC	Usage
17α-estradiol	hormone	Meprobamate	tranquilizer
17β-estradiol	hormone	Metoprolol	cardio med
4-Nonylphenol	surfactant	Naproxen	pain med
4-Octylphenol	surfactant	o-Hydroxy atorvastatin	cardio med
Bisphenol A	plasticizer	Primidone	anti-seizure
cis-Testosterone	hormone	Propanolol	cardio med
Diethylstilbestrol	hormone	Prozac	antidepressant
Estrone	hormone	Salicylic acid	pain med
Ethinyl Estradiol	hormone	Sulfamthoxazole	antibiotic
Progesterone	hormone	Warfarin	cardio med
Testosterone	hormone	Zocor	cardio med
Acetaminophen	pain med	Caffeine	stimulant
Atenolol	cardio med	Triclocarban	preservative
Azithromycin	antibiotic	Triclosan	preservative
Carbamazepine	anti-seizure	Trimethoprim	preservative
Ciprofloxacin	antibiotic	Sucralose	sweetener
Diclofenac	pain med	Clofibric acid	pesticide
Dilantin	anti-seizure	DEET	pesticide
Erythromycin	antibiotic	Methylisothio-cyanate	pesticide
Flurosemide	diuretic	TCDPP	flame retardant
Gemfibrozil	cardio med	TCEP	flame retardant
Ibuprofen	pain med	TCPP	flame retardant
Iopromide	radiology agent	Musk ketone	fragrance
Ketoprofen	pain med	NDMA	DBP
Lipitor	cardio med	PFOA	non-stick coating
17α-estradiol	hormone		

Source: TWBD 2015

2.4.2.3 Oklahoma

According to a July 2015 report to the state legislature, the Oklahoma Department of Environmental Quality (ODEQ) has commissioned a water quality standards and technology work group comprised of a cross-section of industry stakeholders (ODEQ 2015). The work group is charged with:

1. Providing information regarding historical and ongoing research related to potable reuse

2. Drafting regulations and guidelines for IPR and DPR
3. Identifying challenges and questions that need to be addressed related to implementation of potable reuse in Oklahoma
4. Developing recommendations for a process and revised timeline for establishing indirect and direct potable reuse regulations in Oklahoma

ODEQ identified "Category 1" with three sub-categories to address reuse involving potable applications. Category specific recommendations from the July 2015 report for each reuse category are described in the following paragraphs (ODEQ 2015).

2.4.2.3.1 Category 1a - DPR

If necessary, until specific DPR guidance is developed, DPR projects should be considered on a case-by-case basis under the variance process, similar to what has been done in other states (e.g., Texas). Initiation of guidelines development was deferred until 2016 to allow the work group to take advantage of resources being utilized for IPR initiatives (ODEQ 2015).

2.4.2.3.2 Category 1b – IPR (Surface Water)

The stakeholder group defined surface water IPR as the use of reclaimed water for potable purposes by intentionally discharging municipal wastewater to a surface water supply source such as a lake or river. The mixed reuse and natural surface water then receives additional treatment before entering the drinking water distribution system. Definition of what, if any, additional water quality or treatment requirements are needed remains in progress. However, the general approach that is currently being pursued includes the definition of a "default" best alternative treatment (BAT) advanced treatment scheme that, if implemented, would receive approval without the need for site specific modeling studies. The default BAT advanced treatment scheme currently under consideration includes:

1. Source control
2. Pretreatment for reverse osmosis
3. Reverse osmosis
4. Ultraviolet disinfection with advanced oxidation process (AOP)

Treatment schemes (e.g., NF) other than the default BAT scheme would require the applicant to demonstrate (e.g., pilot treat) compliance with surface water quality standards and requirements still to be determined (ODEQ 2015).

2.4.2.3.3 Category 1c – IPR (Groundwater)

Development of Category 1c reuse guidance documents are planned following the development of guidance for Category 1a and Category 1b (ODEQ).

2.4.2.4 New Mexico

The New Mexico Environment Department (NMED) has approved construction of a DPR project in Cloudcroft, a remote resort town in the southeastern part of the state, but does not have published regulations for potable reuse (EPA 2012). The Cloudcroft project has been subject to lengthy delays and is understood to not yet be operational (NMED 2014). NMED governs non-potable uses with the "Guidance Document on Above Ground Use of Reclaimed Domestic Wastewater" and indicates their highest classification, Class 1A, reuse wastewater may be used for any purpose except direct consumption, food handling and processing, and spray irrigation of food crops (NMED 2007). The document also specifies other uses of reuse

wastewater not included will be evaluated on a case-by-case basis by NMED to determine the appropriate water quality classification for the given use (NMED 2007).

2.4.2.5 Arizona

Arizona currently does not have regulations specific to IPR or DPR, but in 2013, they established the Steering Committee on Arizona Potable Reuse (SCAPR 2013) with the following goals to advance potable reuse in the state:

1. Identify impediments
2. Define a common terminology
3. Gather best practices, state of the industry information, and case studies
4. Track California and Texas efforts
5. Create Advisory Panels
6. Conduct a scoping process to provide recommendations to the Arizona Department of Environmental Quality (ADEQ) and the Arizona Department of Water Resources (ADWR)
7. Develop a road map to I/DPR in Arizona

2.4.3 CEC Regulatory Summary

The EPA provides potable reuse regulation directly for CEC control through the setting of NPDWR standard. To date, MCLs have been established for only three pesticide CECs. EPA provides potable reuse regulation indirectly for CEC control through the CCL program and "2012 Guidelines for Water Reuse." Table 2-8 summarizes the CEC control regulatory status for the states reviewed with ongoing DPR activity.

Table 2-8: State Regulatory Summary for CEC Control

State	Indirect Potable Reuse (IPR)		Direct Potable Reuse (DPR)
	Groundwater Augmentation	Surface Water Augmentation	
California	Regulated: CEC monitoring	In development: planned for 2016	In development: planned for 2016
Texas	Case-by-case: 1 system in operation	No CEC control other than WRRF TPDES	Case-by-case: CEC monitoring 2 systems in operation; 1 system in implementation
Oklahoma	In development: planned for 2017	In development: planned for 2016	In development: planned for 2016
New Mexico	Case-by-case	Case-by-case	Case-by-case: 1 system in implementation
Arizona	Case-by-case: 1 system in operation	In development	Under consideration

Sources: EPA, CDPH, CEPA, CSWRCB, TCEQ, TWDB, ODEQ, OWRB, NMED, ADEQ, SCAPR

Out of critical necessity to meet water demand, several cases are indicated in Table 2-8 where DPR systems are in operation or implementation prior to the establishment of regulations for CEC control. For regulation to catch up with necessity, states are now under advisement from stakeholder committees consisting of academia, engineers, industry consultants, and PWS managers to provide the vital knowledge required for the control of CECs in I/DPR applications. Direction is required for what CECs to monitor, what CEC treatment levels to achieve, and what treatment technologies (i.e. BAT, FAT) are best suited for the control of CECs (SCAPR 2013; NWRI 2013; CSWRCB 2014a,b; TWDB 2015; ODEQ 2015; Tchobanoglous et al. 2015; McDonald et al. 2015).

2.5 Best Available Technology for CEC Control

BAT is a term introduced by the EPA when the SWDA was passed in 1974 to assist PWS managers with selecting and implementing the best water treatment process technology or technologies to comply with the new act (EPA 2015a,c; Jones 1990). Although PWS managers have since adopted a multi-barrier approach to meet the increasingly stringent water quality criteria of the SDWA and subsequent amendments, they face new treatment challenges (e.g., CECs) with implementation of DPR programs (Tchobanoglous et al. 2015). BAT in addition to conventional treatment barriers will be required to meet these new treatment challenges (TWDB 2015; ODEQ 2015).

2.5.1 Regulatory BAT

Although the federal government has opted thus far not to develop DPR regulations, the EPA has identified membrane filtration as a BAT for I/DPR in the "Guidelines for Water Reuse" (EPA 2012). RO is identified in this document as an effective treatment barrier for CEC control.

California, Washington, and Florida require RO membrane treatment for IPR systems prior to direct injection of reclaimed water into an aquifer utilized for potable supply (CDPH 2011; WSL 2007; FDEP 2014). For PWS considering DPR, Texas has identified six multi-barrier treatment schemes, five with membranes (TWDB 2015). In Oklahoma, RO membrane treatment has been identified as BAT in the default advanced barrier approach for PWS considering IPR (ODEQ 2015).

2.5.2 Industry BAT

Gerrity et al. (2013b) reported the findings of a world-wide survey of multi-barrier process trains for the whole gamut of planned and unplanned potable reuse applications. Both IPR and DPR application examples are cited. This survey identified only one international and

two US-based DPR systems world-wide that are in operation (Gerrity et al. 2013). Integrated membrane systems using MF followed by RO membranes are the adopted industry standard for IPR applications via direct injection into an aquifer (Drewes et al. 2006; Asano et al. 2007; NRC 2012). In the absence of established DPR-specific regulations, both operational DPR PWS in Texas (Big Spring and Wichita Falls) have adopted an advanced barrier approach including an integrated membrane system with RO membranes followed by an advanced oxidation process (AOP) in complement with conventional barriers (TWDB 2015). In the "Framework for Direct Potable Reuse" recently published by AWWA, WEF, NWRI, and Water Reuse Research Foundation, RO membranes and AOP are recommended final barriers in an integrated treatment scheme to achieve advanced water treatment (AWT) for DPR application. In general, where RO membranes are used, finished water is of higher quality than conventionally treated waters with respect to total organic carbon (TOC), total dissolved solids (TDS), and trace CEC; however, regulators, public health professionals, and practitioners have not reached consensus as to the appropriate framework and governing BAT parameters for potable reuse (Tchobanoglous et al. 2015).

2.5.3 Membrane Classification

Membranes are man-made proprietary separation materials that provide a physical barrier in which structural parameters such as pore size, molecular weight cutoff (MWCO), surface charge (zeta potential), and hydrophobicity (contact angle) are designed for the rejection of target constituents or contaminants such as CECs and their QSAR properties (Wickramasinghe and Jones 2013; Abolmaali et al. 2015). Figure 2-2 illustrates the membrane filtration spectrum by process separation classification, pore size, MW, and relative size of common materials.

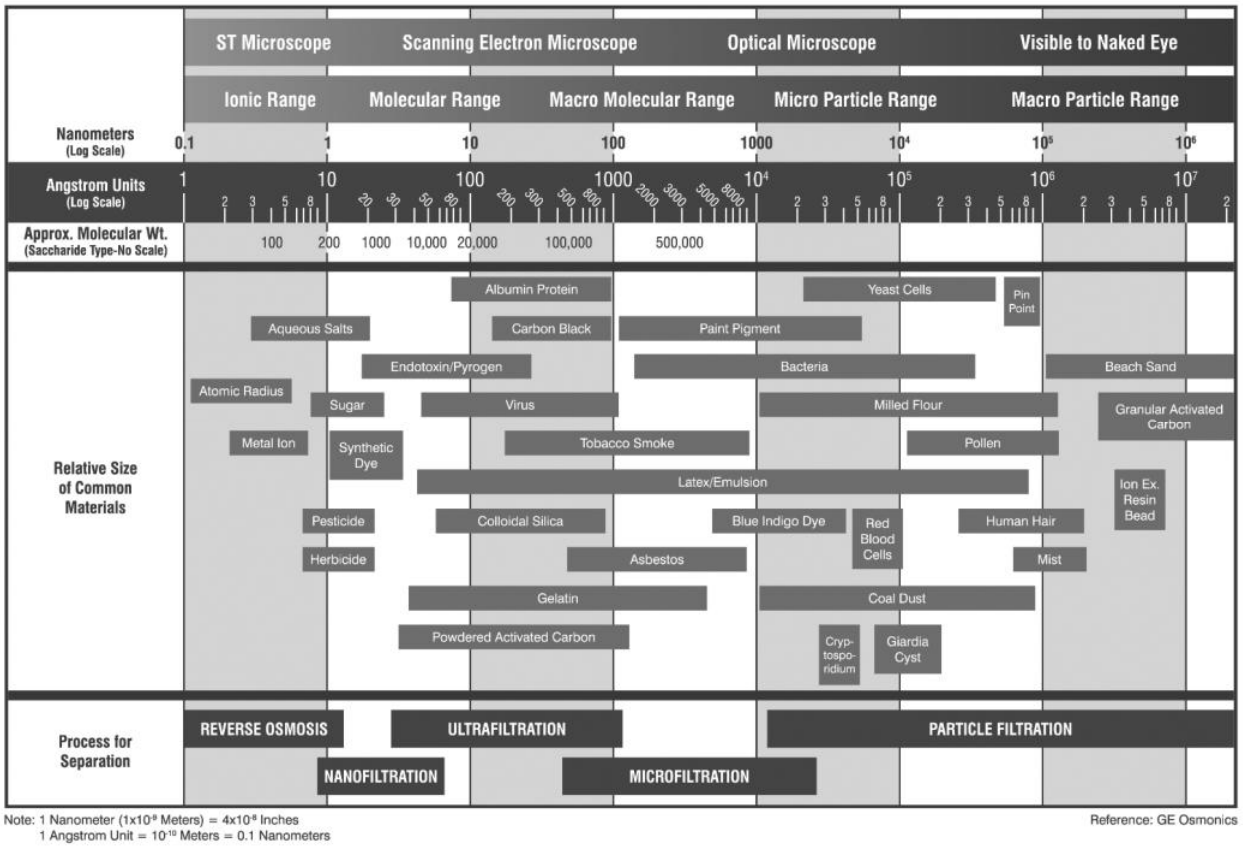


Figure 2-2: Membrane Filtration Spectrum

Membranes are classified according to their respective pore size, MWCO, and transmembrane pressure (TMP). The pore size for a membrane quantifies the general size of individual opening or void. MWCO is an approximate size of molecule that will be excluded from passing through the membrane. TMP is the driving force required to force the solution through the membrane. A general classification of membranes according to these parameters is presented in Table 2-9 (Jonsson 1985; Bellona et al. 2004; Asano et al. 2007; Wickramasinghe and Jones 2013; EPA 2014; Abolmaali et al. 2015).

Table 2-9: Membrane Classifications for Water Treatment

Membrane Classification	Typical TMP Range (psi)	MWCO (Da)	Pore Size Range (μm)	Typical Target Contaminants
Microfiltration (MF)	15 - 60	ND	0.1 - 1.0	TSS, bacteria, Giardia, Crypto
Ultrafiltration (UF)	30 - 100	$\geq 10^3$	0.01 - 0.1	virus
Nanofiltration (NF)	50 - 150	≥ 200	ND	CEC: EDC, pesticides, PPCP
Reverse Osmosis (RO)	100 – 1,000	< 200	ND	TDS, salts

Source: Jonsson 1985; Bellona 2004; Asano 2007; EPA 2014; Wickramasinghe 2013; Abolmaali 2015
ND = nondefinable

As shown in Table 2-9, membrane treatment processes are distinguished by the size of contaminants removed. Microfiltration (MF) and ultrafiltration (UF) remove suspended solids via steric exclusion based on the size of the membrane pores relative to the particulate matter. NF and RO membranes, which do not have definable pores, remove dissolved solids (i.e. solutes) and are thereby industry classified by MWCO (EPA 2014).

TMP can be energy intensive. The osmotic pressure alone for desalination of ocean water, with 30,000 mg/L total dissolved solids (TDS), is over 300 psi. Osmotic pressure combined with TMP, an RO desalination system pressure can approach 1,000 psi (Wickramasinghe and Jones 2013; Abolmaali et.al 2015).

MWCO is a high pressure (e.g., NF and RO) membrane-specific parameter that is often applied for selection of the appropriate membrane for solute separation. The industry accepted practice for membrane MWCO identification is the minimum solute MW that is retained or rejected by 90% or greater. Often, the MWCO for salt-rejecting membranes, such as NF, are determined with freshly-prepared membrane coupons in idealized, pH buffered, salt solutions

(typically $CaCl_2$, NaCl, Na_2SO_4 and $MgSO_4$) (Lin et al. 2007). A comparison of MWCO and atomic force microscopy for assessing the mean pore diameter of membranes found excellent agreement for low-MWCO membranes, like NF (Bowen and Doneva 2000). However, it has also been shown that solvent-membrane interactions affect the MWCO determination for NF membranes of equivalent pore size but varying membrane composition (Zwijnenberg et al. 2012). Therefore, while the manufacturer-supplied MWCO is useful in the initial screening of membranes, a complete analysis of the system (i.e., solvent, solute for separation, membrane properties) is necessary for optimized separation applications.

Membrane surface charge is quantified by zeta potential. Manufacturers design modern TFC NF and RO membranes with a negative surface charge to resist fouling. Because many CECs in reuse water are also charged, the negative membrane surface charge enhances the rejection of ionic CECs. A membrane surface with a high affinity for water is called hydrophilic, while those with a low affinity are called hydrophobic. The contact angle provides a measure of hydrophobicity of a membrane surface. For hydrophobic membranes, the contact angle will have a value greater than 90º, whereas the hydrophilic membranes will have a contact angle value less than 90º (Yangali-Quintanilla et al. 2011; Wickramasinghe and Jones 2013; Abolmaali et al. 2015).

Membrane materials generally utilized for water treatment include cellulose acetates, synthetic polymers (polyamides and polytetrafluoroethylene), and ceramics (Seader et al. 2011; Abolmaali et al. 2015). Commercially available membranes in use today for DPR applications are polymeric hollow-core fibers for low pressure removal of suspended solids and TFC for high pressure rejection of dissolved solids (Drewes et al. 2001; Asano et al. 2007; Al-Rifari et al. 2011; EPA 2014; Jones and Sober 2014; McDonald et al. 2015; Abolmaali et al. 2015).

Manufacturers of newer proprietary TFC membranes can add chemical functionality such as sulfonic or carboxylic acid groups in order to improve target CEC rejection while allowing for thinner membranes and a decrease in system pressure requirements (Bellona et al. 2004; Asano et al. 2007).

Series membrane system configurations utilizing low-pressure (LP) membranes in series with high-pressure (HP) membranes are the water industry standard for the treatment of reuse source waters such as WRRF effluent, brackish water, and seawater (Drewes et al. 2001; Asano 2007; Wickramasinghe and Jones 2013; Sloan 2013; Nix and Schreiber 2015). LP membranes serve as the best pretreatment to remove constituents attributable to HP fouling. The LP membranes are typically designed in a submerged vacuum (described previously) or pressure modular configuration, whereas operating pressures required for HP membranes dictate spiral-wound pressure module configurations (Asano et al. 2007).

2.6 NF Advantages over RO

There has been abundant work to verify the best membrane separation system to achieve the treatment objective for the least required energy and least waste generated (Bellona et al. 2008; Bellona et al. 2012; Jones and Kruger 2013; Jones et al. 2014; Abolmaali et al. 2015; ODEQ 2015; Watts et al. 2016). RO represents a major capital and O&M expense not seen with conventional PWS treatment technologies. For PWS source water applications of TDS < 2,000 mg/L, required TMP for RO is typically 100 psi or more than NF. This translates into more energy requirements and higher pressure classifications for process pumps, pipes, and valves. An RO system also produces a brine reject waste that can represent new treatment and disposal challenges to a PWS.

Previous side-by-side pilot testing of NF and RO membranes at a WRRF in California (Bellona et al., 2008) observed nearly identical water recovery rates (>80%), TOC rejection rates (>98%), ammonia rejection rates (>93%), and rejection of UV absorbing organics (>90%). Using a DOW Filmtec NF-90 membrane filtration system, pilot performance indicated a significant cost-savings (due to higher operating permeate fluxes) for full-scale water recycling with NF as opposed to conventional RO membrane filtration. A critical economic comparison of the two processes for full-scale potable reuse implementation estimated between $55,000 and $188,000 annual cost savings when operating NF membranes (instead of RO) at permeate fluxes between 17 and 25.5 LMH (Bellona et al. 2012).

Three commercially available NF and RO membranes by Dow Filmtec, Toray, and GE Osmonics were pilot tested by Jones et al. (2014) in parallel for implementation of a new 4 MGD series membrane WTP in Alabama. Both NF and RO were verified to meet treatment performance objectives. Based on pilot testing results, it was determined total capital cost could be reduced by $2.2 million and annual energy cost reduced by $55,000 with implementation of NF rather than RO. An ancillary reject waste treatment process was required with the RO option. The reject waste processing was not required with the NF option as reject was determined acceptable for discharge to the WRRF (Jones et al. 2014).

An additional economic consideration for selection of ion-rejecting membrane is the cost of concentrate treatment and disposal. Where RO rejects both mono- and multivalent ions, NF rejects only the multivalent ions. An ongoing alternative water supply study for an Oklahoma community estimated that RO concentrate disposal from a planned new DPR facility would require $14 million for the construction of up to 2 MGD of RO reject conveyance and disposal via deep-well injection (Watts et al. 2016). Due to the high initial capital costs of RO concentrate

management, this project is currently evaluating NF as an alternative to RO that would produce a less saline concentrate that could be safely discharged to the WRRF or a receiving stream (Watts et al. 2016).

The default RO FAT approach to CEC control for DPR may be questioned if we consider new commercially available tight (i.e., MWCO ≤ 200 Da) TFC NF membranes. Tight TFC NF membranes may provide acceptable CEC rejection efficacies for less capital, O&M, power, and waste generated (Bellona et al. 2008; Bellona et al. 2012; Jones and Kruger 2013; Jones et al. 2014; Abolmaali et al. 2015; ODEQ 2015; Watts et al. 2016).

2.7 Reported CEC Removal

The following section reviews previous literature on reported CEC removal by WRRF biological and membrane treatment barriers.

2.7.1 Degradation and Sorption by WRRF

A conventional WRRF, required to meet National Primary Discharge Elimination System (NPDES) secondary standards, is the first barrier treatment in a reuse system and typically includes a liquid treatment process train consisting of physical, biological, and chemical units (Tchobanoglous et al. 2014; Kolpin et al. 2002). Primary treatment typically includes screening, grit removal, and primary clarification. Secondary treatment typically includes a biological reactor and disinfection process. The biological process can range from a fixed-film reactor for biochemical oxygen demand (BOD) removal to suspended-growth activated sludge for BOD removal and ammonification to a biological nutrient removal (BNR) process that includes anaerobic/anoxic/aerobic swing zones for BOD removal, ammonification, nitrification, de-nitrification, and phosphorus removal. In the event the NPDES permit requires disinfection, chlorination/de-chlorination or ultra-violet (UV) oxidation is typically employed. Additional

biodegradation (or digestion) can be provided in the solids treatment processing via either aerobic or anaerobic digester units followed by dewatering, drying, and/or stabilization prior to land application, landfill, or otherwise terminal application.

Previous work has been performed to provide a comprehensive description of the behavior of CECs in WRRF processes (Luo et al. 2014; Rattier et al. 2014; Gerrity et al. 2013; Dickenson and Drewes 2008; Drewes et al. 2006; Birkett and Lester 2003). Three main removal pathways for CECs were identified:

1. Biodegradation and sorption to the mixed liquor suspended solids (MLSS)
2. Additional biodegradation through extended solids retention time (SRT) in suspended-growth reactors and the solids destruction digesters
3. Oxidation in the disinfection process

CECs with relatively high (>2.0) octanol-water partitioning coefficients (K_{ow}) may sorb to MLSS before significant degradation occurs (Johnson and Sumpter 2001; Holbrook et al. 2002). As such, sorption to biosolids has been found to be a significant CEC removal mechanism. Many studies have examined the removal of CECs by sorption to biosolids by comparing influent, effluent, and solids concentrations of CECs. The highest concentration of CECs were found in the biosolids at concentrations 1,000 times greater than that found in the influent (Holbrook et al. 2002; Clara et al. 2004).

Biodegradation of CECs has also been demonstrated. Study of WRRFs has revealed impressive CEC removal at SRT values greater than 10 days and food to microorganism (F:M) ratios of 0.2 – 0.3 kg BOD_5/kg TSS·day. It was reported that the relatively low F:M ratio requires the microorganisms to be more selective, thereby improving CEC removal performance (Lee et al. 2003; Kreuzinger et al. 2004).

Oxidation for removal of CECs by chlorination (30% to 82%) has been found more effective than UV (<1 to 52%), thereby indicating disinfection processes not subject to transmissivity may be more effective for CEC removal in secondary effluents and UV disinfection more suitable for tertiary effluents (Luo et al. 2014). Table 2-10 shows that a comprehensive evaluation of several secondary treatment WRRFs for the removal of CECs revealed overall efficiencies ranging from 5% to 99% (Drewes et al. 2006; Behera et al. 2011; Luo et al. 2014).

As shown previously in Table 2-2, and below in Table 2-10, others have reported varying degrees of CEC biodegradability between WRRF primary and secondary treatment (Drewes et al. 2006; Behera et al. 2011; Oppenheimer et al. 2011; Luo et al. 2014).

Table 2-10: CEC Removal by WRRF Secondary Treatment

CEC	Hydro Classification[a]	Range in Primary Effluents (ng/L)	Range in Secondary Effluents (ng/L)	Removal Efficiency[b] (%)
17α-Ethynyl Estradiol	HB-N	ND – 13	ND - 7.5	100
17β-Estradiol	HB-N	ND – 150	ND - 43	100
4-t-Octylphenol	HB-N	100 - 13,000	ND - 1,300	48.4
Bisphenol A	HB-N	40 -100	ND - 17,300	81.1
Estriol	HB-N	ND – 802	ND - 18	100
Estrone	HB-N	7.3 -132	ND - 108	87.1
Nonylphenol	HB-N	1,300 - 343,000	ND - 9,100	60.4
Testosterone	HB-N	24 -180	ND	100
Acetaminophen	HL-N	3,540 – 10,234	ND - 27	99.9
Atenolol	HL-N	5,113 – 11,239	261 – 5,911	64.5
Carbamazepine	HB-N	43 – 127	40 - 74	< 10
Diclofenac	HB-I	59 -243	13 - 49	81.4
Gemfibrozil	HB-N	101 – 318	9 - 26	92.3
Ibuprofen	HB-I	1,599 – 2,853	15 - 75	98.2
Ketoprofen	HB-N	81 – 286	ND - 37	94.2
Lincomycin	HL-I	3,095 – 19,401	1,437 – 21,278	< 10
Naproxen	HB-N	1,360 – 5,033	37 - 166	95.7
Sulfamethazine	HL-I	ND – 343	ND - 408	13.1
Sulfamethoxazole	HL-I	79 – 216	20 - 162	51.9
Caffeine	HL-N	1,608 – 3,217	ND - 60	99.2
Triclosan	HB-I	247 – 785	79 - 149	79.6
Trimethoprim	HL-I	101 – 277	13 - 154	69
Sucralose	HL-N	14,000 – 49,000	15,000 – 43,000	< 10
Atrazine	HB-N	20 – 28,000	4 - 730	12.5
Clofibric acid	HB-N	ND – 65	ND - 6	93.6
DEET	HB-N	2,560 – 3,190	610 – 1,580	61.9
Diuron	HB-N	30 – 1,960	2 – 2,530	48.5
TCEP	HB-N	60 – 500	60 – 2,400	< 10
TCPP	HB-N	180 – 4,000	100 – 21,000	< 10

ND = Below analytical detection limit

Sources: Drewes 2006; Behera 2011; Oppenheimer 2011; Luo 2014; ACS 2015, ChemAxon 2015; Yangali-Quintanilla 2010

[a] Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge

[b] Calculated average values

In summary, reported data proves that WRRF secondary treatment is effective for removal of some CECs. Best performance was seen with biological reactors optimized for 10-day or greater SRT and lower than typical F:M ratios. For WRRF secondary treatment process trains optimized for CEC removal, efficiencies greater than 50% should be anticipated for EDCs, stimulants, and most pharmaceuticals. However, the literature indicates less than 50% removal efficiencies can be expected from WRRF secondary treatment for preservatives, flame retardants, pesticides, artificial sweeteners, and some pharmaceutical antibiotics.

2.7.2 Rejection by NF and RO

The following section reviews previous literature on reported CEC rejection for bench, pilot, and full-scale NF and RO membranes. In some cases results represent the total rejection efficacy of an NF/RO membrane in series following an MF/UF membrane.

Appleman et al. (2013) reported the results of a bench-scale study comparing a loose NF membrane (NF270) to three granular activated carbon (GAC) adsorption columns for the removal of eight perfluorinated (PFA) compounds ranging in MW from 214 to 400 g/mole. The testing used lab-synthesized PFA compounds in DI water as well as in a simulated ground water matrix. Virgin membrane as well as membranes fouled with humic acids were employed. The membrane experiments revealed that greater than 93% removal can be obtained for all of the selected PFA compounds including the shortest chain compound. The data revealed that the presence of natural organic matter (NOM) did not have a negative effect on the rejection of PFA compounds (Appleman et al. 2013).

Yangali-Quintanilla (2010) conducted a bench-scale with two Dow Filmtec NF membranes using synthetically contaminated water. The CEC rejection results and corresponding hydrophobicity classification are provided in Table 2-11.

Table 2-11: Bench-Scale CEC Rejection by NF Membranes

CEC	Classification[a]	NF 90[b] (%)	NF 200[c] (%)
17β-estradiol	HB-N	92.7	80.6
Bisphenol-A	HB-N	91.5	50.4
Estrone	HB-N	93	92.2
Nonylphenol	HB-N	91.3	91.7
Acetaminophen	HL-N	75.2	68.5
Carbamazpine	HB-N	91.3	78.8
Ibuprofen	HB-I	96.2	77.3
Metronidazole	HL-N	83.5	53.7
Naproxen	HB-I	96.2	76.8
Phenacetin	HL-N	80	50.4
Phenazone	HL-N	85.9	60.4
Sulfamethoxazole	HL-I	94.5	61.6
Caffeine	HL-N	84.8	62.7
Atrazine	HB-N	95.7	88.6

Source: Yangali-Quintanilla 2010

[a] Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic

[b] NF90: MWCO = 200 Da; [c] NF200: MWCO = 300 Da

Drewes et al. (2006) studied the rejection of synthetic water spiked with CECs in a pilot study using a single-stage Koch 2540 TFC-HR spiral wound element, an RO membrane with full-scale installations in service for I/DPR. The pilot feed water was an effluent organic matter matrix representing both a common makeup of secondary treated effluents (after MF) and a consistent background quality throughout the test run. The synthetic matrix was prepared with secondary effluent from a local WRRF in Colorado. The secondary effluent was microfiltered and then concentrated to a 3:1 ratio using a Dow FilmTec XLE RO membrane. After a feed

blank was taken for background control, the target CECs were spiked from the stock solution to the feedwater in a SST drum and mixed overnight. During the pilot RO operation, the recovery rate was established at 90.2%. To season the element, 20L of feedwater was passed through the element and allowed to stabilize overnight. After 180L of additional feedwater was passed through the membrane vessel, final samples were taken from the permeate and reject. Total rejection was observed for the estrogen-based CECs. The phenol-based CECs were rejected at 99%. Table 2-12 shows that the rejection of CECs from the spiked water matrix during pilot testing.

Table 2-12: Pilot-Scale CEC Rejection by RO

CEC	Spiked EfOM Feedwater (ng/L)	Koch TFC-HR		
		Permeate (ng/L)	Reject (ng/L)	Removal (%)
Nonylphenol	6,958	86.1	8,814	98.8
4-t-Octylphenol	812	11.1	1,053	98.6
Bisphenol A	80,720	689.4	115,042	99.1
17β-Estradiol	21.9	ND	28.9	100
Estrone	43.2	ND	57.5	100
17α-Ethinylestradiol	25	ND	42.5	100

Source: Drewes et al. 2006
ND = non-detectable

Snyder et al. (2004) evaluated the rejection of CECs for tertiary effluent in a full-scale MF/RO integrated membrane operating system (MOS). Facility I, as it is known, is currently in operation with a RO capacity of 12 MGD. The process train for Facility I consists of a typical WRRF secondary effluent followed by MF/RO and includes grit removal, primary clarification, activated sludge biological treatment through a sequence of anoxic and aerobic swing zones, secondary clarification, tertiary dual-media filtration (anthracite/sand), chloramine disinfection, and MF in series with RO. The MF/RO finished water is used for aquifer storage and recovery

(ASR) via direct injection. Full-scale testing occurred over a 48-hr period using RO Train #4 with a process capacity of 1.0 MGD. The RO feedwater was nitrified/denitrified tertiary filtered water that was pH adjusted to 6.3 using sulfuric acid, microfiltered (Siemens Memcor MF), and dosed with an antiscalent (Hypersperse, GE Betz). The process train operated with an overall recovery rate of 85%. The RO MOS design was a three-stage configuration of Koch TFC-H Magnum spiral-wound elements (24-10-5) loaded with a specific flux of 0.07 gfd/psi (Snyder et al. 2004).

Sampling of the full-scale RO MOS demonstrated rejection below the detection limit for the suite of CECs tested. The tested CECs in these evaluations are all considered hydrophobic, with low K_{ow} values in the range of 3.13 to 5.28. Their molecular weights vary from 266-340 Da and therefore represent a size well above the MWCO of the tested Koch RO membrane. Therefore, hydrophobic/hydrophobic interactions between solutes and membrane as well as steric exclusion were determined responsible for the high removal efficiencies observed for this suite of CECs. Based on the CECs rejection results reported in Table 2-13, the research group concluded RO is an effective barrier for CECs in reuse application (Snyder et al. 2004).

Table 2-13: Full-Scale CEC Rejection by MF/RO Series Membranes

CEC	Feedwater (MF Permeate)			RO Permeate			Removal (%)
	C_1 (ng/L)	C_2 (ng/L)	C_3 (ng/L)	P_1 (ng/L)	P_2 (ng/L)	P_3 (ng/L)	
Nonylphenol	208	441	766	ND	33	ND	100
4-t-Octylphenol	13	14	61	ND	ND	ND	100
Testosterone	4.6	3.8	4.7	ND	ND	ND	100
Estrone	4.7	6.6	23.3	ND	ND	ND	100

Source: Snyder et al. 2004
ND = non-detectable

The BOR and 14 Southern California PWS partners evaluated WRRF secondary effluent for suitability for I/DPR application and conducted a demonstration study to verify membrane technology as an effective barrier for CEC control (USBOR 2009; Snyder et al. 2007). Table 2-14 shows the rejection results of 36 CECs for the demonstrated NF and RO membranes.

Table 2-14: CEC Rejection Demonstration by NF and RO Membranes

CEC	NF (%)	RO (%)	CEC	NF (%)	RO (%)
Andorostenedione	50-80	>61	Iopromide	>80	>99
Estradiol	50-80	N/A	Lindane (a-BHC)	50-80	N/A
Estriol	50-80	N/A	Meprobamate	50-80	>99
Estrone	50-80	>95	Naproxen	20-50	>99
Ethinyl Estradiol	50-80	N/A	Pentoxifylline	50-80	>96
Oxybenzone	>80	>93	Sulfamethoxazole	50-80	>99
Progesterone	50-80	N/A	Caffeine	50-80	>99
Testosterone	50-80	N/A	Triclosan	>80	>97
Acetaminophen	25-50	>90	Trimethoprim	50-80	>99
Carbamazepine	50-80	>99	Atrazine	50-80	N/A
Diazepam (Valium)	50-80	N/A	DDT	>80	N/A
Diclofenac	50-80	>97	DEET	50-80	>95
Dilantin	50-80	>99	Metazachlor	50-80	N/A
Erythromycin	>80	>98	TCEP	50-80	>91
Fluoxetine (Prozac)	>80	>96	Benzo(a)pyrene	>80	>90
Gemfibrozil	50-80	>99	Fluorene	>80	N/A
Hydrocodone	50-80	>98	Galaxolide	50-80	>98
Ibuprofen (Advil)	50-80	>99	Musk Ketone	>80	N/A

Source: USBOR 2009; Snyder et al. 2007
N/A: Not Available

The EPA has released the results of an extensive literature review of published studies of the effectiveness of various treatment technologies for CECs (EPA 2014). In response to emerging concerns about the possible impacts of pharmaceuticals, hormones, detergents, and other chemicals on human health and aquatic organisms, the EPA searched over 400 publications that referenced treatment of CECs. About 100 of those sources contained treatment information which was entered into the database. The EPA compiled and summarized the results reported by

researchers in the last five years. The research occurred primarily in the US, Canada, and Europe. Although the EPA database includes results from over 400 publications on the subject, there were fewer than 10 operating RO membrane units, zero full-scale, and only 13 bench-scale NF membrane units from which to report CEC rejection efficacies (EPA 2014). A query of the database specific to full-scale membrane rejection yielded the data for 51 CECs as provided in Table 2-15.

Table 2-15: Full-Scale CEC Rejection by RO Membranes

CEC	(% / #)	CEC	(% / #)
17α-estradiol	23 / 1	Meprobamate	99 / 5
Andorostenedione	81 / 1	Monensin	90 / 1
Bisphenol A	33 / 2	Nalidixic acid	25 / 1
Diethylstilbestrol	65 / 1	Naproxen	73 / 5
Equilin	31 / 1	Norfloxacin	90 / 1
Estradiol	65 / 2	Pentoxifylline	98 / 2
Estrone	77 / 4	Primidone	98 / 1
Ethinyl Estradiol	19 / 1	Roxithromycin	88 / 1
Oxybenzone	75 / 7	Sulfachloropyridazine	12 / 1
Testosterone	75 / 2	Sulfamethazine	19 / 1
Acetaminophen	64 / 4	Sulfamethizole	17 / 1
Carbadox	35 / 1	Sulfamethoxazole	81 / 5
Carbamazepine	84 / 6	Sulphasalazine	89 / 1
Cephalexin	85 / 1	Caffeine	66 / 5
Ciprofloxacin	98 / 1	Triclosan	95 / 4
Diazepam (Valium)	58 / 1	Trimethoprim	95 / 5
Diclofenac	97 / 4	Atraton	5 / 1
Dilantin	99 / 5	DEET	93 / 6
Enfroflaxacin	83 / 1	Metolachlor	14 / 1
Erythromycin	99 / 4	TCPP	98 / 1
Fluoxetine (Prozac)	90 / 4	TDCPP	89 / 1
Gemfibrozil	84 / 5	Tri(chloroethyl) phosphate	97 / 6
Hydrocodone	98 / 4	Alachlor	6 / 1
Ibuprofen (Advil)	91 / 4	Galaxolide	99 / 3
Iopromide	87 / 6	Musk Ketone	85 / 3
Lincomycin	80 / 1		

Source: EPA 2014. http://water.epa.gov/scitech/swguidance/ppcp/results.cfm. Reported rejection rates are reported Average Rejection % / # units.
No NF membrane units reporting

2.8 NF Membrane Rejection Theory

This section reviews previous work relative to membrane rejection theory for the control of CECs in I/DPR applications. Specifically, an understanding of relative CEC QSAR properties and membrane rejection mechanisms is necessary for modeling purposes.

2.8.1 Physiochemical Properties of CECs (QSAR)

The American Chemical Society (ACS) maintains and catalogues an authoritative collection of disclosed chemical substance information in a registry by Chemical Abstracts Service Number, or CASN (ACS 2015; ChemAxon 2015). The CAS Registry is maintained by the ACS CAS Division. Currently, the CAS Registry identifies more than 81 million organic and inorganic substances, with physiochemical and/or structural characterization information about each substance. The registry is updated with approximately 15,000 additional new substances annually (ACS 2015). A tool for the molecular characterization of CECs, the CAS Registry maintains QSAR properties such as molecular weight, size, ionic charge, ionizing and partitioning coefficients, polarity, and solubility.

2.8.1.1 Molecular Weight

Molecular weight (MW) of a compound is the sum of the mass of each constituent atom. Atomic weight of a substance is the average atomic mass for an element. Atomic weights of the atoms are available from the periodic table and can be summed to obtain molecular weight. MW of a substance is measured in the unit grams/mole (g/mole).

2.8.1.2 Molecular Surface Area

Molecular and polar surface area are usually expressed in units of square angstroms ($Å^2$). Molecular surface area (MSA) can be defined as the surface area of a molecule that is accessible to a solvent (ChemAxon 2015). MSA was first described by Lee and Richards (1971) and is

sometimes called the Lee-Richards surface area. However, MSA is typically calculated using the "rolling ball" algorithm developed by Shrake and Rupley (1973).

2.8.1.3 Net Electrical Charge

The electrical charge of a CEC is generated when the compound of ions, atoms, or molecules includes a total number of electrons that is not equal to the total number of protons, giving the compound a net positive (+) or negative (-) electrical charge (ACS 2015). When the number of electrons and protons are in equilibrium, the compound has no charge and is referred to as neutral (0). Since all ions are charged, they are attracted to opposite electric charges and repelled by like charges. In chemical terms, if a neutral atom loses one or more electrons, it has a net positive charge. If an atom gains electrons, it has a net negative charge. The net charge of an ionizable atom is zero, or neutral, at a certain pH. This pH is referred to the isoelectric point (ChemAxon 2015).

2.8.1.4 Acid Dissociation Constant (pKa)

The Acid Dissociation Constant (pKa) value of a CEC is a quantitative measurement of a chemical compound's acidity in solution (Schwarzenbach et al. 2003; Benjamin and Lawler 2013). The pKa is derived from the equilibrium constant for the acid's dissociation reaction, Ka.

$$pKa = -\log_{10} Ka = pH + \log_{10} (\text{conjugate acid/conjugate base}) \qquad \text{Eq. (2.1)}$$

An organic conjugate acid is a species formed by the reception of a proton (e.g., hydrogen ion); conversely, an organic conjugate base is a species formed by the removal of a hydrogen ion from an acid. The lower the pKa value, the stronger the acid. The higher the pKa, the weaker the acid. Very strong acids have pKa values less than zero, while weak acids generally have pKa values between 0 and 9 (Schwarzenbach et al. 2003; Benjamin and Lawler 2013).

2.8.1.5 Octanol-Water Partition Coefficient

The octanol-water partition coefficient (K_{ow}) can been utilized to quantify the hydrophobicity of a CEC (Yangali-Quintanilla et al. 2011). Organic compound K_{ow} values are defined as the ratio of the compound's concentration in a known volume of n-octanol to its concentration in a known volume of water after the octanol and water have reached equilibrium (EPA 2015a). Expressed another way, K_{ow} is a dimensionless concentration ratio whose magnitude expresses the distribution of a compound between n-octanol (a non-polar solvent) and water (a polar solvent). The higher the K_{ow}, the more non-polar the compound. And, the lower the K_{ow}, the more polar the compound. Log K_{ow} values are generally inversely related to CEC solubility and directly proportional to MW (Schwarzenbach et al. 2003; Benjamin and Lawler 2013).

A high log K_{ow} is a relative indicator of the CEC tendency to come out of aqueous solution and adsorb to a solid medium such as a filter medium or membrane. Generally, CECs with log K_{ow} values less than 2.0 are considered hydrophilic (HL), or having a relatively high affinity for water, whereas CECs with log K_{ow} values greater than or equal to 2.0 are considered hydrophobic (HB), or having a relatively low affinity for water (Schwarzenbach et al. 2003; Yangali-Quintanilla et al. 2011; Benjamin and Lawler 2013).

2.8.1.6 Octanol-Air Partition Coefficient

The octanol–air partition coefficient, K_{oa}, is defined as the ratio of solute concentration in air versus octanol solvent when the octanol–air system is at equilibrium (Li et al. 2006). K_{oa} has been used extensively for describing the partitioning of organic compounds between air and solute organic phase. K_{oa} has a strong temperature dependence, which can be described by

$$\text{Log } K_{oa} = A + (\Delta H_{oa})/(2.303RT) \qquad \text{Eq. (2.2)}$$

where A is the intercept; ΔH_{oa} is the enthalpy change involved in octanol-to-air transfer of a chemical, R is the ideal gas constant, and T is absolute temperature (Schwarzenbach et al. 2003). This temperature dependence is important for assessing the potential long-range transport of CECs. As such, K_{oa} has been shown to be a key QSAR property pertinent to the long-term Great Lakes contamination potential of CECs, where relatively soluble CECs are subject to transport in colder climates (Wren 1991; Mac et al. 1993).

K_{oa} can also be expressed as a function of the K_{ow} and air-water partition constant (K_{aw}), known as Henry's law constant (Schwarzenbach et al. 2003).

$$K_{oa} = K_{ow} / K_{aw} \qquad \text{Eq. (2.3)}$$

Henry's law is one of the ideal gas laws formulated by the British chemist William Henry in 1803 and can be expressed for dilute solutions as a function of the solubility of a gas in a liquid and the partial pressure of the gas subjected to the liquid (Schwarzenbach et al. 2003; Benjamin and Lawler 2013). Various forms of Henry's law exist. For assessing the equilibrium distribution of a given CEC in an air-water system, the dimensionless form below will be assumed for standard atmospheric pressure and a given temperature.

$$K_{aw} = C_a/C_w = K_H/RT \qquad \text{Eq. (2.4)}$$

where C_a is the equilibrium concentration in the air phase and C_w is the equilibrium concentration in the water phase. Similar to K_{ow}, as discussed previously, the value of K_{aw} for a given CEC has been observed to generally decrease with increased water solubility (Yangali-Quintanilla et al. 2011).

2.8.1.7 Polarizability (α)

An induced dipole is generated by partial charges of a CEC molecule that has a tendency to alter the external electric field (Miller and Savchik 1979). This phenomenon is referred to as

polarizability, α. An empirical equation for the calculation of the average molecular polarizability, α, was developed by Miller and Savchik (1979):

$$\alpha = (4/N) [\Sigma_A r_A]^2 (Å^3) \qquad \text{Eq. (2.5)}$$

where r_A represents the sum of atomic hybrid components of α, N is the total number of electrons in the molecule, and A represents all atoms (A = 1, 2, 3…), and is expressed as cubed angstroms, $Å^3$. The ACS maintains polarizability values for each recorded chemical compound as a QSAR molecular property within the CAS Registry database (ACS 2015).

2.8.1.8 Water Solubility

The solubility of a CEC in water may be defined as the maximum amount, or concentration, of the compound that will dissolve in pure water at a specified temperature (EPA 2015a). Above this concentration, the water is considered a super-saturated aqueous solution. Generally speaking, water solubility is the extent to which a CEC will dissolve in water. Log water solubility (S_w) is typically inversely related to MW. Aqueous concentrations are usually stated in terms of mass per volume or weight ratios (e.g., mg/L, µg/L, or ηg/L).

2.8.2 Rejection Mechanisms

Bellona et al. (2004) conducted a comprehensive literature review of previous work to identify the rejection mechanisms and factors affecting rejection of organic solutes (i.e., CECs) by NF/RO membranes. The authors reported the following key CEC physical-chemical properties affect rejection:

1. Molecular weight (MW) and size (length and width)
2. Ionic charge (neutral, +, or -), as a function of the acid disassociation constant (pK_a)
3. Hydrophobicity (HB or HL), as a function of the octanol-water coefficient (log K_{ow})

Bellona also reported the following key membrane mechanisms affect rejection:

1. Steric exclusion (as a function of MWCO)
2. Electrostatic surface charge exclusion or adsorption (as a function of zeta potential)
3. Hydrophobic/hydrophilic adsorption, as a function of contact angle

The authors also concluded that tight NF membranes (with MWCO ≤ 200 Da) exhibit similar membrane rejection properties as RO and are preferred over open NF membranes (with MWCO >200 to 400 Da) for CEC control. Furthermore, the membrane skin for most TFC membranes is designed by the manufacturer to carry a negative charge to minimize fouling attributable to the adsorption of negatively charged solutes present in feed waters as it relates to the electrostatic charge rejection mechanism. This negative charge (i.e., zeta potential) for most membranes has been observed to become increasingly more negative as feed water pH is increased. Based on this phenomenon, the authors concluded that increased pH in the solute feed water led to increased rejection rate of ionic charged CECs with modern TFC membranes (Bellona et al. 2004).

Another study of CEC rejection phenomena by Linden et al. (2012) reported the key solute parameters that determine how effectively a membrane will reject a given CEC are its molecular weight, its dissociation constant (pK_a), its hydrophobicity (expressed as partitioning constant log K_{ow}), and its ionic charge (+, -, or neutral). Additional study determined the key rejection mechanisms of the membrane include the MWCO, pore size, surface charge (zeta potential), roughness, and hydrophobicity (Bellona et al. 2004).

Sanches et al. (2013) found that size exclusion (MWCO) and membrane surface charge (zeta potential) are the most relevant rejection mechanisms of select TFC NF membranes that impact CEC rejection efficiency with only minor contributions from hydrophobic interactions.

The CEC properties of MW, charge, and polarizability correlated best with the observed rejection. The research group observed the rejection of eight model CECs, including hormones and pesticides, in synthetic water with a bench-scale cross-flow test apparatus and commercially available GE Osmonics DK Series NF membranes with a MWCO range of 150-300 Da.

Kimura et al. (2003) reported negatively charged CECs are effectively rejected by NF and RO membranes because of electrostatic repulsion by the negatively charged membranes, whereas neutral CECs are removed based on the molecular size of the CEC and the MWCO of the membrane. This finding was based on the observed rejection potential of an NF membrane (zeta potential = -11mV: MWCO = 200 Da) and an RO membrane (zeta potential = -10mV; MWCO = 100 Da) for selected CECs. The cross-flow bench test apparatus included two commercially available membranes (NF: Hydranautics ESNA; RO: Dow Film-Tec XLE). Both membranes showed a >90% rejection for negatively charged CECs, whereas the RO membrane outperformed the NF membrane for neutral CECs, removing 99% of BPA. These experiments were conducted with three target CECs spiked in synthetic model waters in the absence of DOC from WRRF secondary effluent. When the authors lowered their model CEC concentrations in the laboratory prepared sample matrix to simulate the concentrations typically occurring in a WRRF secondary effluent matrix, the performance of both membranes declined but could not be explained by the molecular weights of the analytes. The authors further reported this work supports the need not only for membrane performance studies to be run at environmentally relevant levels of target CECs but also for further investigation into the combined effects of molecular size and membrane affinity (Kimura et al. 2003).

Ngheim et al. (2002) conducted research using a bench-scale experimental rejection program, apparatus, and membranes identical to Schafer et al. (2003). This study reported on the

variable effects of differing water matrices. In addition to matrix solutions of MilliQ DI water and carbonate buffer, matrix solutions were also supplemented separately with 10 mg/L doses of NOM, fulvic acid, and SE. The authors reported that the adsorption rejection mechanism was only slightly reduced due to the presence of competing organics in the matrix; however, the overall rejection remained high (80-100%) for estrone, thereby suggesting steric exclusion was the major rejection mechanism (Ngheim et al. 2002).

Yoon et al. (2006) utilized a bench-scale stainless steel dead-end stirred-cell filtration apparatus (SEPA ST, Osmonics) to study the NF rejection of 52 EDC and PPCP compounds in four lab spiked samples, one with DI matrix and three with source (not WRRF secondary effluent) water matrix. The three source water samples were pre-filtered to remove any particulate matter prior to spiking with the select CECs. The commercially available Hydraunatics ESNA NF membrane tested was reported with a MWCO of 600 Da and zeta potential of -10.6 mV. The 52 CECs were characterized for their QSAR properties of size, hydrophobicity, and polarity. Experiments were performed at environmentally relevant spiked CEC concentrations ranging typically from 2 to <250 ng/L. Results showed that the NF membrane rejection mechanisms were steric/size exclusion, hydrophobic adsorption, and electrostatic repulsion. The authors reported a general separation trend was observed due to hydrophobic adsorption as a function of octanol-water partition coefficient (log K_{ow}) between the hydrophobic CECs and hydrophobic membrane. Among the CECs observed with <100% rejection, the hydrophobic neutral CECs with log K_{ow} >2.8 generally exhibited <50% rejection, while hydrophobic neutral CECs with log K_{ow} <2.8 showed rejection of >75%. The authors also reported that NF rejection performance was observed to be better in the synthetic DI matrix than

the three source water matrix samples. This led to the author's hypothesis that the synthetic water had the least competition among CECs for membrane adsorption sites.

In follow-up to their 2006 study, Yoon et al. (2007) conducted additional research with the same SEPA dead-end bench-scale apparatus and Hydranautics NF membrane. The objective of this study was to further investigate the CEC-to-membrane hydrophobic relationship for 27 select CECs with a range of octanol-water partition coefficients (log K_{ow}) from -2.1 to 4.77. This study confirmed the hydrophobic adsorption relationship observed from the previous study in that CEC rejection by NF membranes generally increases with CEC log K_{ow} (or degree of hydrophobicity).

Dang et al. (2015) conducted follow-up research utilizing the bench-scale cross-flow experimental conditions identical to the previous paper (Dang et al. 2014). This study investigated the rejection of two biodegradable phytoestrogens: geneistein and formononetin. These lab-synthesized compounds were found to strongly adsorb initially to the membranes, but at steady-state conditions, the rejections reduced to less than 50% for the loose NF270 membrane. The authors reported that size exclusion, adsorption, and convection are key rejection mechanisms, while electrostatic repulsion was reported as the most significant rejection mechanism (Dang et al. 2015).

Schafer et al. (2003) researched rejection of the highly biodegradable natural hormone, estrone, by eight different NF and RO membranes from Koch and Trisep. Experiments were carried out in bench-scale batch mode with lab-synthesized samples of MilliQ DI and carbonate matrix with a target ethanol concentration of 100 ηg/L. Rejection by these membranes ranged from 80% for the XN-40 to 100% for all remaining membranes. The authors concluded that size

exclusion and adsorption are the major rejection mechanisms for both membrane types (Schafer et al. 2003).

Wintgens et al. (2002) studied 11 different bench-scale commercially available NF membranes for the rejection of bisphenol-A (BPA) and nonylphenol (NP) from a landfill leachate matrix following pretreatment by a membrane bioreactor (MBR). Observed rejection rates of the two CECs ranged from 70% to 100% for the 11 NF membranes. The authors confirmed membrane contact angle was an indicator for the hydrophobicity of a membrane, whose influence on NP rejection was evident. As reported, a membrane with low contact angle (<50º) is considered hydrophilic, while a membrane with a high contact angle (>50º) is considered hydrophobic. As observed for the study data set, rejection was greater with the hydrophilic membranes than with the hydrophobic membranes. (Wintgens et al. 2002).

To elucidate key factors governing the rejection of trace organic contaminants, the research team of Dang et al. (2014) reported the results of a bench-scale study on the removal of 16 hydrophilic and hydrophobic solutes, consisting of EDCs and PPCPs, by a MWCO = 300 NF membrane (Dow-Filmtec NF270) and LPRO (Hydranautics ESPA2) membrane using a SST cross-flow apparatus. Synthesized samples of the solutes at a target concentration of 25 µg/L were lab prepared with a matrix of methanol and DI water. Experiments were conducted at pH values of 4.7, 7, and 11. All tested pH values were above the isoelectric point of the membranes, which ranged from 3.5 to 4, indicating the membranes were negatively charged at all test conditions. The authors utilized the QSAR property Log D to correlate solute hydrophobicity rather than Log K_{ow}. A solute with a Log D value of 3 or higher was determined hydrophobic. In general, the rejection of charged compounds was better than neutral compounds at all tested pH conditions. However, 4-tert-butylphenol, bisphenol A, 4-tert-octylphenol, and triclosan were

rejected at less than 50% rejection which was attributed to adsorption and subsequent diffusion through the membrane. The cross-flow apparatus allowed mass balance calculation to estimate adsorption levels of the solutes. Adsorption levels of the hydrophobic solutes ranged 14% to 94% for the NF270 and 79% to 94% for ESPA2, whereas the hydrophilic solutes ranged 0 to 32% and 0 to 12%, respectively. A good correlation was observed between rejection and MW for hydrophilic neutral and charged species (Dang et al. 2014).

Several studies have reported a correlation between the rejection of hydrophobic CECs and their affinity for the membrane, expressed as log K_{ow} (Agenson et al. 2002; Agenson et al. 2003; Van der Bruggen et al. 2002). The authors reported that rejection of hydrophobic CECs by NF membranes increased linearly with increasing log K_{ow} values, indicating that hydrophobic interactions between the CEC and membrane were the dominant rejection mechanism for CECs with MW close to or less than the MWCO.

The phenomenon of low-molecular-weight solute rejection by porous and semi-porous membranes is well documented (Fane et al. 1983; Xu and Lebrun 1999). Dissolved organic matter has been experimentally shown to be a significant driver of MF and UF membrane fouling (Howe and Clark 2002). A well-known example of this phenomenon is the fouling of sterilization membranes in the pharmaceutical industry by product proteins that are smaller than the nominal membrane pore size. Adding hydrophilic coatings to MF membranes surfaces has been demonstrated to reduce the rate of protein fouling (Loh et al. 2009). For UF of organic protein solutions, investigations have concluded that by manipulating the electrostatic interactions between the low-MW organic solute and the charged membrane with solution pH, the membrane flux rate and subsequent protein rejection can be tuned (Musale and Kulkarni 1997). This tuning effect with variable solution pH can be amplified by membrane surface

doping. Acrylic acid nanobrushes grafted to NF membranes have been shown to improve the rejection of soluble sugars at pH greater than 7 (Himstedt et al. 2011). Recent testing with charged UF membranes indicated that rejection of reactive dye tracers is greatest with the most negatively-charged dye molecules (Chen et al. 2015). Thus, electrostatic interactions between charged solutes and membranes, as well as solution pH, can play a significant role in membrane fouling and solute rejection performance.

Feed water matrix composition can have a significant effect upon CEC rejection with NF and RO membranes (Schafer et al. 2001; Nghiem et al. 2002; Majewska-Nowak et al. 2002). Schafer and Ngheim reported that estrone samples prepared with a WRRF SE matrix showed poorer rejection rates from eight NF/RO membranes than the same estrone concentration samples prepared with synthetic matrix. The main driving mechanism for the removal estrone, which has a high log K_{ow} of 3.13, was determined hydrophobic sorption by the NF membrane. The authors concluded that the competition for adsorption sites by other CECs in the SE matrix resulted in the poorer rejection rates. Conversely, Majewska-Nowak et al. (2002) found that pesticides such as atrazine could adsorb to the organic matter in a WRRF secondary effluent matrix, thereby increasing the rejection rate of the NF as a result of increased size and electrostatic interaction.

Boussu et al. (2007) conducted a bench-scale cross-flow study of the rejection of 13 spiked CECs in synthetic matrix with three commercially available membranes manufactured by GE Osmonics and Nitto-Denko. The membranes were reported to have MWCOs of 200, 260, and 310 Da; with contact angles of 47, 44, and 70º; and with zeta potentials of -13, -17, and -15 mV, respectively. Two of the NF membranes were characterized as hydrophilic, while the other

NF membrane was characterized as hydrophobic. Based on the results, Boussu concluded the following:

1. CEC rejection was inversely related to MWCO.
2. Ionic charged CECs were best rejected by the membrane with the highest zeta potential.
3. Neutral charged CECs were best rejected by the hydrophilic membranes.

Yangali-Quintanilla (2010) studied the rejection of 17 model CECs with two Dow Film-Tec TFC NF membranes (NF-90: MWCO = 200 Da, contact angle = 58º, zeta = -48 mV; NF-200: MWCO = 300 Da, contact angle = 37.5º, zeta = -10.8 mV). Synthetic matrix test samples were spiked with stock solutions of CECs. To simulate environmentally relevant CEC concentrations reported in actual reuse water, the CEC concentration of the prepared feed water ranged from 6.5 to 65 µg/L. Rejection test runs were performed with two SEPA CF II (GE Osmonics) bench-scale stainless steel dead-end cells operated in parallel. Based on rejection results and correlation/modeling of the physical-chemical interactions between solute and membrane, the author concluded that the CEC rejection mechanisms of NF membranes are MWCO, surface charge, and hydrophobicity.

Sanches et al. (2013) reported that the use of synthetic waters is a suitable strategy to "unravel" the individual correlation of specific physical-chemical properties and membrane rejection mechanisms. However, this approach is not accurate enough to model the removal of CECs in actual natural matrices and recommended future study with actual reuse water.

In summary, research shows the predominant NF and RO mechanisms for rejection of CECs are steric exclusion, electrostatic interaction, and hydrophobicity.

2.9 NF Membrane Rejection Modeling

With an understanding of NF rejection theory gained from the previous section, this section shifts focus to the review of previous rejection modeling efforts. Emanating from this work, three different approaches are seen for the modeling of solute rejection by NF and RO membranes.

Plakas and Karabelas (2012) conducted a review of the removal of pesticides by NF and RO membrane processes starting from the early history to recent work on modeling the removal. The authors summarized the types of published models for solute rejection, including Spiegler-Kedem-based irreversible thermodynamic models, mass transport hydrodynamic Fick's-based models, and regression-based QSAR models along with their advantages and disadvantages in a simple tabular form, as provided below in Table 2-16. The authors concluded that all three considered modeling approaches could be utilized for the rejection of pesticides since membrane rejection is mostly attributable to size exclusion. However, the authors stated for predicting rejection of solutes smaller than membrane MWCO, the QSAR-based approach would be most suitable for modeling rejection mechanisms other than size exclusion. The authors cited other such rejection mechanisms included electrostatic interactions and hydrophobicity (Plakas and Karabelas 2012).

Table 2-16: NF/RO Models for Predicting Solute Rejection

Models	Advantages	Disadvantages
Irreversible film theory thermodynamics (Spiegler-Kadem)	1. No rejection mechanism or solute molecular structure input (membrane treated as a "black box"). 2. Ideal for RO desalination application.	1. Highly dependent on driving forces (pressure and concentration gradient), which restricts practical application. 2. Unrealistic assumptions must be made. 3. System must be in equilibrium to be applicable.
Mass transport hydrodynamic (Fick's Law)	1. Simple models provide estimates for technically demanding separations. 2. Linearization facilitates rapid calculations.	1. Valid only for high rejection membranes. 2. Variation of the solute mass transfer coefficients with different water qualities and operating conditions and intrinsic membrane properties constrains model portability to other systems. 3. Mainly applicable to single-solute compounds. 4. Solute mass transfer coefficients depend on the test unit scale, limiting the model accuracy in membrane scale-up.
QSAR-based regression	1. Easy to use. 2. No application of physical laws or transport phenomena, thus overcoming complexity. 3. Accurate statistics estimates based on mechanisms and solute properties. 4. Valid models regardless of rejection performance of membranes tested.	1. Specific; applicable in the range of experimental conditions employed for development. 2. Changes in membrane properties as a result of fouling, or swelling, influence model accuracy.

Source: Plakas and Karabelas 2012

Bellona et al. (2004) reported that many attempts have been made with little success to model the process performance of membrane separations in order to optimize membrane applications. To predict inorganic constituent (e.g. salts) mass transfer through high pressure membranes, the authors report modeling attempts have included irreversible thermodynamics, fate and transport, linear homogeneous solution-diffusion, film theory, and statistical-mechanical theory. One successful organic solute retention model, developed by Williams et al. (1999), utilized a modified solute-diffusion adsorption equation to describe the sorption and partitioning of chlorinated phenols in RO and NF membranes. The solution-diffusion equation, however, is not as applicable to newer generation TFC RO and NF membranes since the contribution of solute/membrane interaction is not considered nor is steric exclusion a primary rejection mechanism. Bellona (2004) reported that although past modeling theory has shown promise in describing the separation of components during specialized membrane processes, the need for a truly predictive rejection model based on membrane and solute properties is urgent. With their review of such properties, the authors created a rejection diagram to predict degrees of high pressure membrane rejection as high, moderate, or poor.

Ngheim et al. (2004) studied the rejection of estradiol, estrone, progesterone, and testosterone spiked at 100 ηg/L in a synthetic matrix. Two negatively charged TFC NF membranes (Dow/Filmtec NF270 and NF90) were utilized with the cross-flow bench-scale apparatus. They also developed mechanistic hydrodynamic (i.e. Fick's Law) models for predicting solute rejection. The authors acknowledged that the thermodynamic (i.e. SK) approach is more appropriate for modeling RO performance, but the hydrodynamic approach is better suited for modeling NF performance. Radiolabeled hormone samples were prepared in DI water from purchased stock solutions in ethanol and were measured using a scintillation counter

with a detection limit of 0.5 ηg/L. The pore radius of NF90 was determined to be 0.34 nm while the pore radius of NF270 was determined to be 0.42 nm. Based on the MW of the hormones tested (270 to 315 g/mol) the authors estimated a Stokes radius of 0.5 nm. The experimental results suggest (performed at pH 6) the steady state removal was as low as 90%, although initially the removal was 100%. The authors hypothesized that a combination of adsorption and steric exclusion caused the initial removal. However, with time, the adsorption mechanism was exhausted (much like carbon adsorption), leaving only steric exclusion. They also hypothesized that these hormones pass through the membranes by a diffusion mechanism via a sequence of "make and break" bonding (Ngheim et al. 2004).

Ahmad et al. (2009) presented results of experimental work and modeling performed to study rejection of atrazine and dimethoate by Dow/Filmtec NF90 polyamide nanofiltration membranes. The contaminant solutions were synthesized in the laboratory at mg/L level to simulate chemical spill conditions. No solvent matrix data were presented for the solutions. It is not clearly stated, but it seems a single solution was prepared that contained both pesticides. The membrane rejection tests were performed using a 300 mL stirred cell from Sterlitech SST bench-scale membrane coupon test apparatus. The experiments were performed in dead-end batch mode. The experimental data were used to derive fitting parameters for the SK thermodynamics model. For the SK model, the authors assumed that the retention of a solute through the membrane is a function of three parameters: specific hydraulic permeability (solvent flux), local solute permeability (solute flux), and reflection coefficient (a measure of portion of the membrane through which solute cannot be transferred). Rejection versus flux and rejection versus pressure data were presented in the paper along with prediction by SK model. Observed permeate flux versus pressure did not match the predicted values from SK model. There was

agreement between the model predictions and observed data; however, the model generated data was utilized to estimate the fitting parameters (Ahmad et al. 2009).

QSAR molecular properties based regression models are based on the assumption that similar molecules behave similarly (Silva et al. 2013). Li and Colosi (2012) proposed that a QSAR model could be used to predict the rejection of as-yet uncharacterized emerging contaminants of regulatory interest. Another study used a QSAR model to rank CECs found in environmental waters, including their parent compounds, metabolites, and transformation products, to select the most relevant compounds to be considered as monitoring indicators in drinking water treatment systems (Delgado et al. 2012).

Sanches et al. (2013) developed statistical, multivariate, regression-based models to describe the rejection of CECs by a commercially available TFC NF membrane. A group of 37 rejection values, generated from eight CEC profiles analyzed over five runs with three discounted anomalies, were utilized to develop the models. The models were developed to correlate rejection attained during NF membrane experiments with specific QSAR molecular property descriptors of the target CECs. Statistical regression analysis was applied to model rejection through best-fit linear correlations of the multiple input parameters. Specific input parameters considered were QSAR properties of the CECs: MW, log of the distribution coefficient at pH 7.4 (log D), dipole moment, pK_a, water solubility, molar volume, and polarizability. Additional CEC size parameters considered were molecular length, molecular width, and molecular depth as generated by 3-D visualization software for chemical structures (www.jmol.org). Iterative stepwise elimination (Boggia et al. 1997) and the Martens uncertainty test (Forina et al. 2004) were used to select the best-fit QSAR properties to model. The authors concluded that the developed models have good descriptive capability and contributed to an

overall comprehension of rejection of the CECs studied. Size exclusion and electrostatic interactions with minor contribution from hydrophobic interaction were the three modeled mechanisms. Since the models were calibrated with only eight CECs in synthetic matrix samples, the authors acknowledged that more comprehensive modeling with additional CECs in reuse matrix waters is necessary to extend this research (Sanches et al. 2013).

Yangali-Quintanilla (2010) utilized QSAR analysis to quantify compound rejection by a NF membrane in terms of CEC physical-chemical properties and membrane rejection mechanisms. The QSAR model was constructed using the internal experimental data described previously for synthetic waters. The model was internally validated using measures of goodness of fit and prediction, and subsequently was validated with external data. The QSAR model verified that steric exclusion and log K_{ow} are the most important variables that influence rejection. Using QSAR to describe CEC rejection was later improved and extended with the use of non-linear artificial neural network (ANN) models. Use of ANN models based on QSAR equations was an important tool to predict rejection of neutral CECs by NF and RO membranes with standard errors of estimation close to 5% and regression coefficients, R^2, of 0.97. The ANN-QSAR models demonstrated that rejection of neutral CECs by NF and RO membranes is controlled more by size exclusion and less by hydrophobic interaction.

Fujioka et al. (2014a,b) developed and validated a mathematical model based on irreversible thermodynamic principles (SK) for predicting removal of N-nitrosamines by spiral-wound RO membrane. The modeling approach included subdividing the membrane surface into layers and determining rejection behavior for each section similar to a finite element approach. Pilot testing was conducted using a three-stage membrane pilot using ESPA2-4040 elements from Hydranautics. The pilot was operated in a loop where the concentrate stream and the

permeate streams were returned to the feed tank. The feed solution was made using DI matrix spiked with stock solutions of nitrosamines, NaCl, CaCl2, and HCO3 were added to simulate treated wastewater conditions. Three different fluxes were tested (10, 20, and 30 l/m^{2}h). The rejection of higher molecular weight nitrosamines were 90% or higher at all fluxes. The rejection of the lower molecular weight nitrosamines varied with flux and ranged from 31% to 54%. A strong correlation was observed between boron removal and NDMA removal thereby suggesting boron could be a potential surrogate indicator for nitrosamines. Elevated temperature was reported to lower the removal of NDMA. However, pH was not found to have a strong effect on removal of NDMA. The authors reported model predicted rejections correlated well with observed rejection results (Fujioka et al. 2014a,b).

Shamansouri and Bellona (2013) conducted research to develop and validate a model for predicting rejection of a study set of 67 nonionic (i.e., neutral charged) CECs by Dow/Filmtec NF270 NF membranes. Predictive models explored for best fit with the observed rejection data were an SK irreversible thermodynamic transport model and a hybrid QSAR-based regression model with fitting parameters for flux and CEC diffusion. The test apparatus utilized for the experimental work was a bench-scale cross-flow configuration. Test conditions included constant temperature (18 C), pH (6.3), and steady-state influent flow rate. Solute sample matrix was synthesized with DI water. Pressure was varied between 10 and 200 psi to produce 5 incremental flux conditions ranging from 10-120 l/m^{2}h. Sixteen of the 67 compounds tested showed significant deterioration of rejection performance between the 2 hour and 24 hour run times, indicating adsorption saturation. These 16 compounds were scrubbed from the data set for model development. Eighty percent of the remaining results were used to develop the model while the other 20% (11 CECs) were used for internal model validation. The SK model could not

be validated to produce acceptable predictive results. The SK approach was determined to not correlate well ($R^2 < 0.8$) with CECs rejected by mechanisms other than steric exclusion. The hybrid QSAR model proved to correlate well ($R^2 > 0.9$) between predicted and observed rejection of the validation set of 11 CECs (Shamansouri and Bellona 2013).

Mohammad et al. (2015) conducted a comprehensive review on recent advancements in NF membranes that characterized the latest commercially available models from GE Osmonics, Dow-Filmtec, Koch, Nitto-Denko, TriSep, Synder, and Toray. The authors provided discussion on predictive modeling, fabrication, applications, operations, fouling, and future prospects for NF membranes. The research team stated that

> the overwhelming majority of NF predictive rejection models to date are inadequate because they have been developed with idealized solutions typically containing only 2, 3, or sometimes 4 solutes. If accurate modeling of concentrated multi-solute solutions realistic of industrial processing is to become commonplace then more effort needs to be placed into modeling systems of real industrial relevance (Mohammad et al. 2015).

2.10 Needed Study

There are three primary areas of needed study:

1. Determine the recalcitrant CECs in typical WRRF SE.
2. Determine NF and RO rejection efficacies for the recalcitrant CECs in SE matrix.
3. Develop a practical predictive modeling tool to assist regulators, engineers and PWS managers with CEC control for I/DPR applications.

Whether planned or unplanned, IPR is in practice world-wide. DPR systems are currently operating in Africa and Texas. Many state water plans have identified billions of dollars in capital infrastructure for the implementation of I/DPR systems over the next decade. As PWS portfolios take on more reuse water, conventional treatment barriers may prove deficient and the upcycling of CECs could be harmful to human health if more effective and robust treatment

barriers are not in place. PWS managers are looking for guidance from regulators and industry. For now, EPA has opted to leave it to the states for that guidance. State regulators are looking to industry advisory committees to provide the knowledge and tools to identify what CECs to monitor and what barrier treatment technologies to implement for CEC control. This need is critical and immediate.

With the lack of knowledge, the default approach can be an overly-conservative and cost-prohibitive design. RO is trending in planned and recently implemented DPR systems as the default FAT barrier for CEC control. NF has many advantages over RO including lower system pressure, less energy consumed, and less waste generated. An extensive literature review performed by EPA in 2014 of over 400 publications on control of CECs found zero full-scale and only 13 bench-scale NF studies from which to gather knowledge. Review of the 13 and subsequent studies revealed the NF rejection study of spiked CECs in lab-synthesized matrix solutions. Although this approach may provide a fundamental understanding of rejection theory, it is not representative of I/DPR conditions for NF rejection of recalcitrant CECs occurring in WRRF effluent matrices.

To achieve the study objectives of this research, PE and SE samples will be collected from WRRFs in Texas and Oklahoma. SE samples will be processed by bench-scale commercially available TFC NF and RO membranes in parallel. All samples will be analyzed by a CCL EPA-certified lab for the Norman 96 set of CECs. The Norman 96 CECs will be characterized by intended use and physiochemical properties. Results will be analyzed to verify rejection performance and develop a practical QSAR-based predictive modeling tool.

CHAPTER 3 - METHODS

3.1 Overview

Research was conducted to develop a practical modeling tool for regulators and PWS managers to predict the rejection of recalcitrant CECs from typical municipal WWRF secondary effluents for I/DPR applications by commercially available NF.

To determine membrane rejection for the recalcitrant CEC trace residual following secondary treatment, actual SE was collected from three full-scale operating WRRFs. The collected SE samples were processed through bench-scale dead-end TFC NF and RO membranes, and analyzed by a certified laboratory to ascertain actual occurring CECs in the WRRF effluent and their respective rejection coefficients across the membranes. Prior to and concurrent with processing the collected SE through the membranes, the CEC concentrations were determined for the SE of each of the three WRRF biological treatment systems. The membranes evaluated under this research represent tertiary, or advanced, treatment unit processes that could potentially be implemented downstream of a secondary activated sludge biological process for reuse application.

Ultimately, the reduction (e.g., rejection coefficient) of recalcitrant CECs that can be effectively removed from actual SE by TFC NF membrane processes with a MWCO of 200 and negative surface charge was determined. The observed NF rejection coefficients were then correlated with researched molecular properties of the CECs and membrane removal mechanisms to develop a QMPM to predict organic solute rejection from secondary effluents with similar TFC NF membranes for planned I/DPR applications.

3.2 WRRF Descriptions

Actual municipal WRRF secondary effluent was collected from the following three facilities downstream of the respective biological process but upstream of any disinfection or tertiary treatment.

3.2.1 North Texas (NTX) WRRF

The City of Garland, Texas, owns and operates two tertiary WRRFs (Rowlett Creek and Duck Creek) to treat flows from their Dallas/Fort Worth suburb population of 235,000 residents (Sober 2016). Secondary effluent for this research was collected from the Rowlett Creek WRRF, a fixed-film trickling filter and suspended-growth activated sludge (TF/AS) facility, permitted to treat 24 MGD. The TCEQ administers a Texas Pollutant Discharge Elimination System (TPDES) permit which dictates the monthly average effluent limits from Rowlett Creek to a carbonaceous biochemical oxygen demand (cBOD) of 10 mg/L, total suspended solids (TSS) of 15 mg/L, and seasonal ammonia nitrogen limits of 5 mg/L (December through March) and 2 mg/L (April through November). Effluent is discharged to the East Fork of the Trinity River and ultimately to the Trinity River. There is no reuse practice at this time for the NTX facility. However, during dry summer months and periods of drought, the river flow consists primarily of WRRF effluent. As such, the performance of the Rowlett Creek WRRF is critical to the Trinity's health and usefulness as a drinking water source for those downstream.

Figure 3-1 illustrates the NTX process flow diagram (PFD) of the Rowlett Creek facility, which consists of influent screening, grit removal, primary clarification, trickling filters, intermediate clarification, activated sludge, final clarification, tertiary traveling bridge sand filters, chlorine disinfection, and effluent pumping.

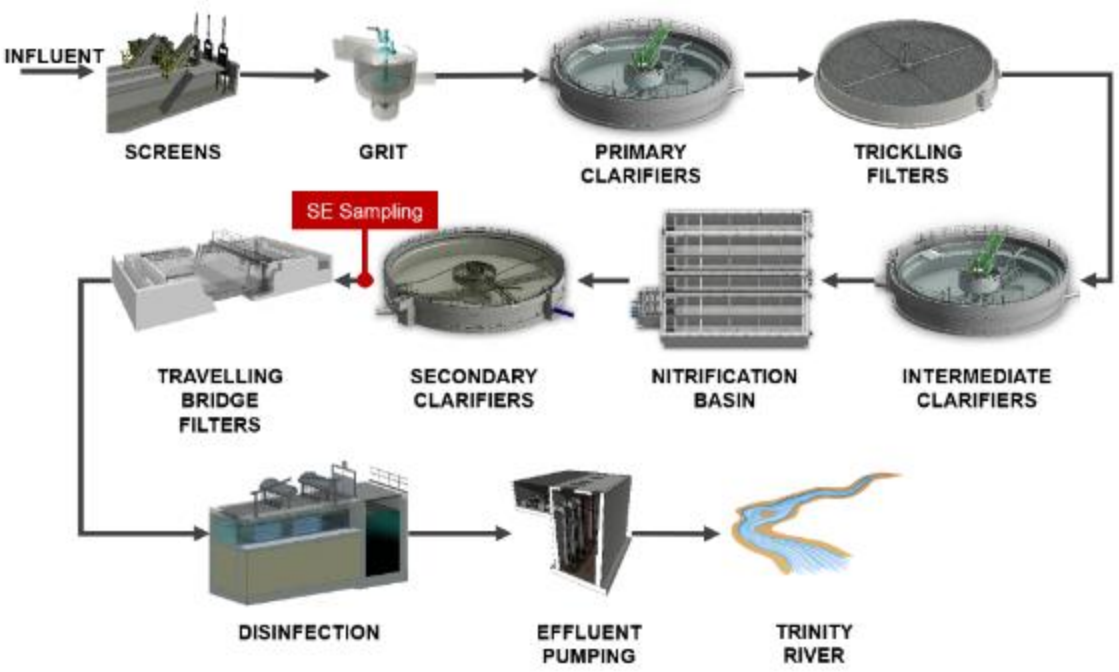


Figure 3-1: NTX PFD

3.2.2 Southwest Oklahoma (SOK) WRRF

The City of Lawton, Oklahoma, owns and operates a tertiary TF/AS plant to treat flows from their southwest Oklahoma population of 85,872 residents (Graves et al. 2015). The Lawton WRRF currently treats an average daily flow of 10 MGD with average daily effluent water quality of 3 mg/L cBOD, 9 mg/L TSS, and 0.2 mg/L ammonia nitrogen. Effluent is discharged to Nine Mile Creek in the Red River watershed; however, up to 5 MGD is dedicated for reuse by the Public Service Company of Oklahoma (PSO) for their industrial cooling towers.

Figure 3-2 illustrates the PFD of the Lawton facility, which consists of influent screening, grit removal, primary clarification, trickling filters, intermediate clarification, activated sludge, final clarification, UV disinfection, and tertiary anthracite filtration.

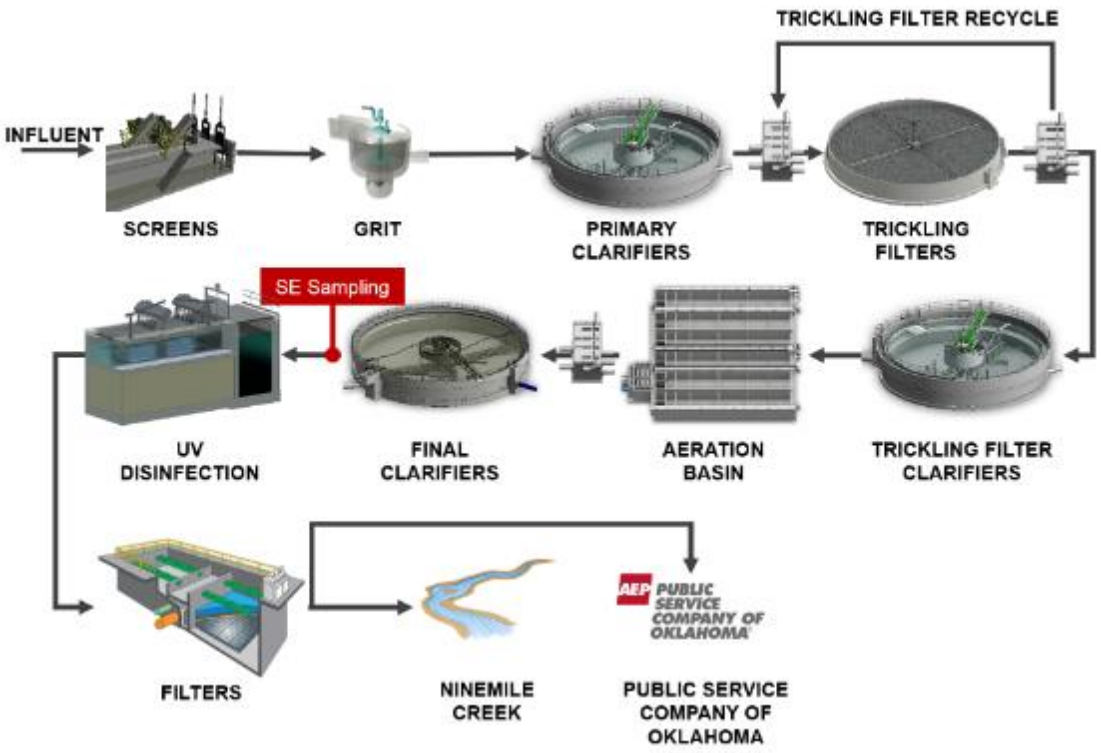


Figure 3-2: SOK PFD

3.2.3 Central Oklahoma (COK) WRRF

The City of Norman, Oklahoma, owns and operates a WRRF to treat flows from their Oklahoma City suburb and major University population of over 100,000 residents (Kruger et al. 2013). The Norman WRRF is a conventional suspended-growth activated sludge (AS) facility, permitted to treat 12 MGD. The ODEQ administers an Oklahoma Pollutant Discharge Elimination System (OPDES) permit which dictates the monthly average effluent limits from the WRRF to a cBOD of 13 mg/L, TSS of 30 mg/L, and ammonia nitrogen limits of 4.1 mg/L. Effluent is discharged to the Canadian River in the Arkansas River watershed. The Norman WRRF provides seasonal reuse to the University of Oklahoma for irrigation of the Jimmie Austin Golf Course.

Figure 3-3 illustrates the PFD of the Norman facility, which consists of influent screening, grit removal, primary clarification, conventional activated sludge, final clarification, UV disinfection, and post aeration.

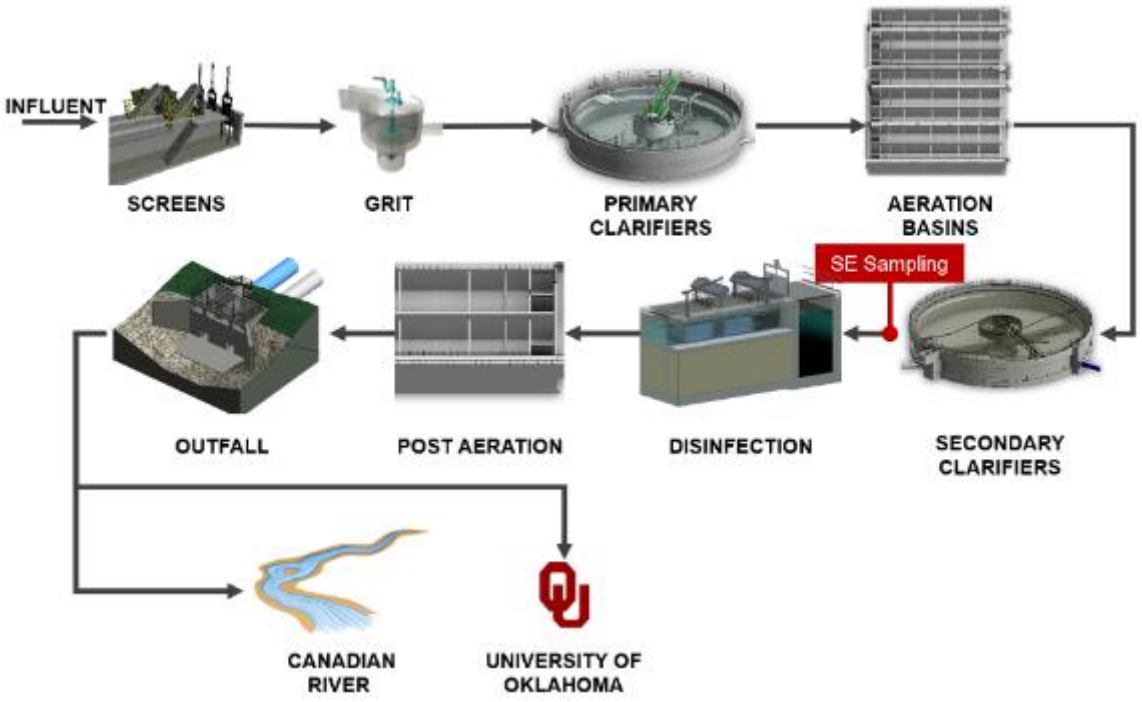


Figure 3-3: COK PFD

3.2.4 WRRF Operational Data

Where available, monthly operating reports (MORs) were collected during the sampling interval. Notably, MOR data collected at the WRRFs such as cBOD, TSS, ammonia nitrogen, and total phosphorus were typically measured on a 24-hour composite sample and reported weekly. CEC research samples were taken on the same day as the MOR composite samples if the WRRF staff did not measure it daily. Typical MOR data included DO, pH, cBOD/COD, TSS/VSS, and ammonia nitrogen. Also, where available, additional standard operating procedure (SOP) data relative to the WRRF secondary process was collected during the sample period such

as solids retention time (SRT) and mixed liquor suspended solids (MLSS). Collected WRRF operational data is provided in Appendix B.

3.3 Sampling Program

During 18 sampling events in the summer months, 108 samples were collected from the three WRRFs. Sampling program tasks involved collecting, preserving, packaging, and shipping samples for analysis. Primary objectives of the sampling program included:

- Collecting representative I/DPR source water samples from full-scale WRRFs
- Collecting multiple samples over time during base-flow dry-weather conditions when CEC concentrations are generally greatest
- Collecting samples to assess actual recalcitrant CEC remaining in the SE following full-scale WRRF biological degradation
- Collecting SE samples for bench-scale NF and RO membrane rejection analysis of the recalcitrant CECs

3.3.1 Sampling Schedule and Target Conditions

To capture base-flow, dry-weather conditions, the sampling period occurred during the summer of 2014 over six weeks from July through August. Samples were collected weekly if target conditions were acceptable for sample collection. If target conditions were not ideal, sampling was deferred to the following week. The target conditions for sampling were as follows:

- Plant flow of no more than average day
- No storm event within seven days
- Not during a daily diurnal peak
- Sample on or near the day that samples were taken for regulatory reporting

3.3.2 WRRF Sampling Locations

Sampling locations for each WRRF represented the combined effluent from all operating liquid process trains downstream of the biological process. The SE samples were collected from combined final clarifier effluents, but prior to any tertiary treatment or disinfection. Sampling locations were illustrated previously in the WRRF PFDs (Figures 3-1, 3-2, and 3-3) and are also shown on the plant site aerials in Figures 3-4, 3-5, and 3-6.

Figure 3-4: NTX WRRF Site Aerial (Google Maps)

Figure 3-5: SOK WRRF Site Aerial (Google Maps)

Figure 3-6: COK WRRF Site Aerial (Google Maps)

3.3.3 Sample Collection, Preservation, and Handling

As defined in this section, sample collection, preservation, and handling protocol was followed in accordance with guidelines provided by the following references: Snyder et al. 2003; ASTM 2006; Rice and Bridgewater 2012; Vanderford et al. 2012. Grab samples were collected in amber glass bottles with preservatives, chilled to target temperature below 6°C but above freezing, and analyzed within 30 days of sampling.

3.3.3.1 Collection Protocol

Grab sampling was the site collection method utilized for this research. Sampling equipment included a 950 ml wide-mouth amber glass packer attached to an 8-24 ft. telescoping fiberglass swing pole. Collection equipment was cleaned thoroughly before use with non-antibacterial detergents and rinsed well with lab-provided Type 1 (ASTM D1193) laboratory reagent grade DI water after detergent wash. No wetted collection equipment was made of Tygon, polyethylene, or other such plastics. Notably, detergents and plastics can be a source of interference in the analysis of CECs. The final rinse of collection samplers was with a methanol rinse. The collection bottle was submerged into the SE collection boxes to mid-depth and filled completely. Care was taken that the mouth of the bottle did not come into contact with anything other than the sample water. Collected SE in the glass packer was transferred to the lab-provided amber glass bottles. Using indelible ink, all samples were clearly marked with appropriate identifying information as provided in Appendix B.

3.3.3.2 Preservation Protocol

As samples were transferred to the amber glass bottles provided by the laboratory, sodium omadine and ascorbic acid were utilized to inhibit CEC biodegradation and oxidation between sampling and analysis. The samples were refrigerated until ready for shipping overnight

to the membrane bench-test facility or to the laboratory for CEC analysis. Ice or gel packs were utilized to target a temperature below 6°C during shipping. Sample collection data forms, kit order forms, and chain-of-custody forms were prepared for shipping, placed in sealed bag, and placed in the shipping cooler on top of the packing material as identified in Appendix B. Samples were shipped via FedEx next day service. Samples were promptly removed from the coolers and refrigerated below 6°C, but above freezing, until analysis. All lab analyses were performed within 30 days of sampling.

3.3.3.3 Handling Protocol

Analytes being measured at ηg/L (i.e., parts per trillion) levels are prone to contamination (or interference) from handling. Nitrile gloves were worn at all times when handling samples. Gloves were changed between each sample location. Care was taken not to touch or breathe directly into samples or equipment. On the day of sampling, contact with pharmaceuticals, pesticides, or personal care products that may contaminate samples was avoided. A field control blank sample of DI water was collected, shipped, and analyzed. Potential sample interference from mishandling could occur from any one or more of the following common utilized substances:

1. Soaps and detergents, including antibacterial cleansers
2. DEET (insect repellent)
3. Weed killers
4. Fragrances (perfume, cologne, after shave, etc.)
5. Caffeine and sweeteners
6. Prescription and over-the counter medications
7. Tobacco
8. Sunscreen

Table 3-1 identifies the 108 samples that were collected and shipped to the destinations as identified in Appendix B for testing and analysis.

Table 3-1: Sample Shipping List

WRRF	No. of Sampling Events	40 ml SE samples to Laboratory (EEA)	1 liter samples to NF/RO Testing (GE Osmonics	40 ml NF/RO permeate samples to Laboratory (EEA)
SOK	6	12	12	12
COK	6	12	12	12
NTX	6	12	12	12
TOTAL	**18**	**36**	**36**	**36**

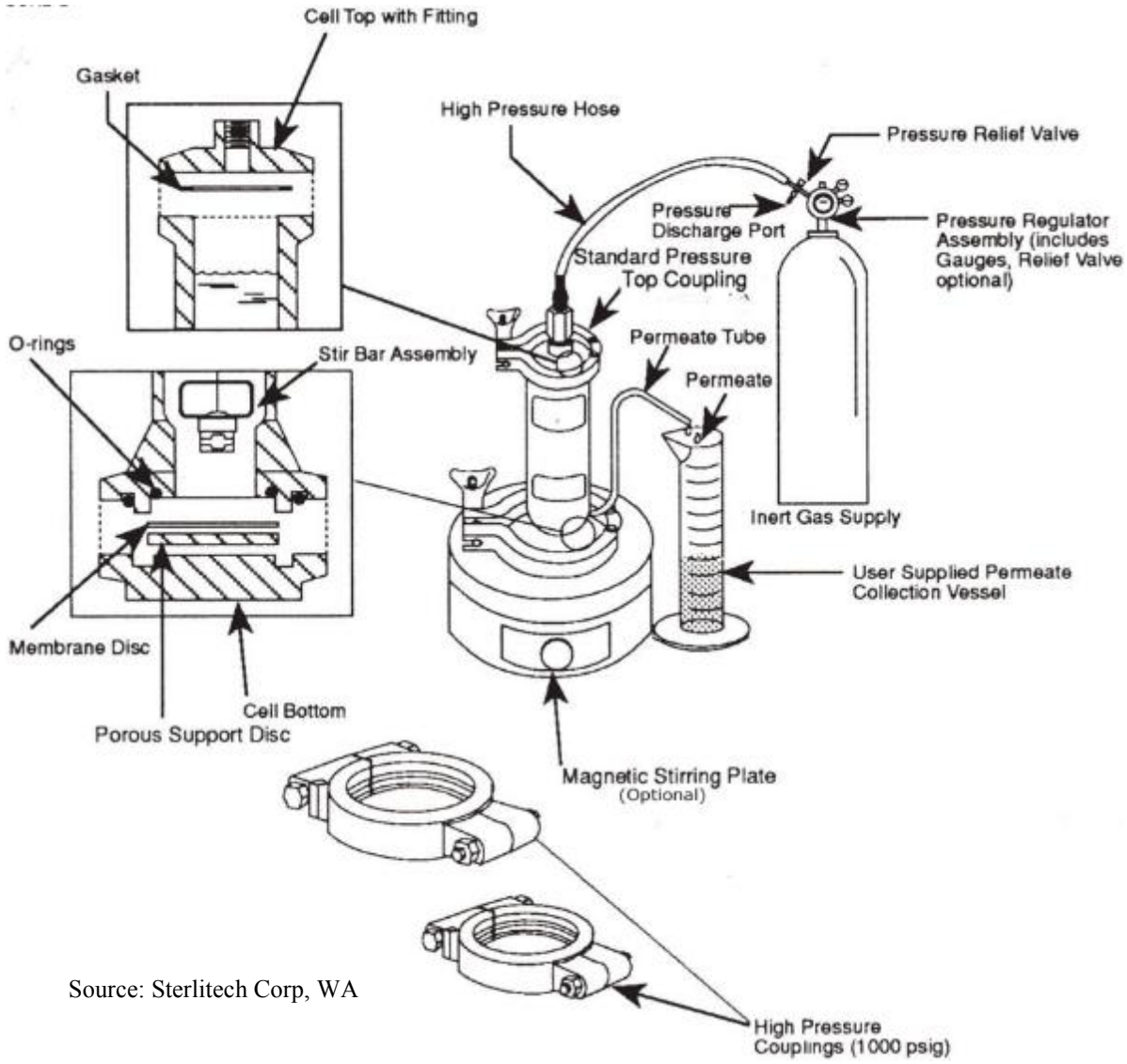
3.4 Bench Scale Testing

SE samples collected from the three study WRRFs were dead-end bench-tested with NF and RO membranes at GE Osmonics' purpose-built test laboratory facility in Minnetonka, Minnesota. SE and NF/RO permeate samples were analyzed for CEC content by Eurofins Eaton Analytical (EEA) of Monrovia, California.

3.4.1 Test Apparatus

Figure 3-7 illustrates that the bench-scale testing apparatus consisted of flat-sheet membrane coupons secured in stirred dead-end permeation cells. Figure 3-8 depicts three SEPA ST (Sterlitech Corp., Kent, Wash.) model HP4750, 316 stainless steel, high-pressure stirred cells that operated in parallel for each permeate process run. Regulated high-pressure high-purity

nitrogen (>99.9%) gas was utilized for driving head. Table 3-2 shows the apparatus specifications.



Source: Sterlitech Corp, WA

Figure 3-7: Membrane Bench Test Apparatus – Schematic

Figure 3-8: Membrane Bench Test Apparatus – As Tested

Table 3-2: Test Apparatus Specifications

Parameter	Specification
Membrane Coupon Diameter[a]	49 mm (1.93 in)
Active Membrane Area[a]	14.6 cm^2 (2.26 in^2)
Batch Process Volume[a]	300 mL
Constant TMP (Pressure Head)[a]	DK: 65 psi; AG: 145 psi
Specific Flux Range[a]	10 -12 GFD
Sample Temperature[a]	20°C ± 0.5
Sample pH[a]	7.0 – 7.5 (no sample adjustment)
Pressure Inlet	1/4 inch FNPT
Permeate Outlet	1/8 inch 316SST tubing
Wetted Materials of Construction:	316 SST
Cell Body	Buna-N
O-Rings and Gaskets	PTFE-coated magnet
Stir Bar	
Cell Dimensions:	
Body Diameter	5.1 cm (2.0 in)
Top Width (w/ clamp)	10.2 cm (4.0 in)
Bottom Width (w/ clamp)	13.3 cm (5.25 in)
Height	22.1 cm (9.5 in)

Sources: GE Osmonics; Sterlitech
[a] *As tested & verified*

3.4.2 Membrane Properties

Two commercially available polyamide TFC membranes (GE Osmonics) were selected for this research: DK Series (manufactured in California) and AG Series (manufactured in Minnesota). The TFC laminate for both membranes includes a polyester backing, a polysulfone UF layer, a proprietary layer to adjust Zeta potential, and an engineered steric exclusion polyamide NF or RO layer (Abolmaali et al. 2015). For this research, flat sheet coupons were cut from this TFC laminate and utilized in the bench-scale testing, whereas for full-scale application modules, this TFC laminate is spiral wound with a feed spacer mesh and impermeable envelope.

The selection of the test membranes was based on: (1) a qualitative steric rejection assessment of CECs with a MW of more than 150 g/mol by membranes with a MWCO between 100 and 200 Daltons, and (2) their established performance in full-scale applications. Appendix B provides manufacturer data sheets for both commercially available full-scale membrane modules. In addition to membrane data provided by the manufacturer, membrane physical property testing was performed by the National Science Foundation (NSF) Membrane Applied Science and Technology (MAST) Research Center at the University of Arkansas (Fayetteville) Cato Springs Laboratory (Wickramasinghe R. 2015). Appendix B provides MAST lab results. Table 3-3 provides the relevant test membrane properties as required for QSAR analyses and the rejection modeling of the recalcitrant CEC residual that was performed subsequently in Chapter 4. Both test membranes were found to have contact angles less than 90º and are thereby considered hydrophilic (Yangali-Quintanilla 2010).

Table 3-3: Test Membrane Properties

Test Membrane	MWCO (Da)	Zeta Potential[a] (mV)	Contact Angle (degrees)
AG Series RO	100	-20	23
DK Series NF	200	-12	20

Sources: GE Osmonics, NSF MAST Research Center at University of Arkansas
[a] Zeta Potential at neutral pH

3.4.3 Membrane Testing Protocol

Permeate runs were processed in parallel for all three WRRF SE sample events with the select DK (RO) membrane coupons. Subsequently, permeate runs were processed in parallel for all three WRRF SE sample events with the select AG (NF) membrane coupons. This process operating sequence was repeated for all sample events. Each permeate run was eight hours in duration. A total of 18 membrane permeate runs were processed. Table 3-4 details the batch process operating sequence for each permeate run.

Table 3-4: Bench-Scale Batch Process Operating Sequence

Process Sequence	Procedure
Rinse and load	Rinse SEPA cells with DI water and load fresh membrane coupons.
Conditioning	Load 300 ml of standard salt solution (2,000 mg/L NaCl for AG and 2,000 mg/L MgSO4 for DK) and process 100 ml of permeate to waste (225 psi for AG and 110 psi for DK).
Pre-compaction	Rinse SEPA cells with DI, load 300 ml of DI and process 100 ml permeate to waste (225 psi for AG and 110 psi for DK).
Ripening	Load 300 ml of SE sample and process 150 ml permeate to waste at standard operating conditions: constant-rate TMP (145 psi for AG and 65 psi for DK); declining-rate flux (12-10 GFD).
Verification	Verify membrane operation over batch ripening run is within specification. Record volume or weight collected every 10 g/10 ml to verify flux is within specification. Collect 5-10 ml of permeate in graduated cylinders and record run time to determine flux.
Rinse	Rinse SEPA cells with DI, load 300 ml DI, and process 20 ml permeate to waste.
Permeate Run	Load 300 ml of SE sample and process to 100 ml permeate at standard operating conditions for TMP (145 or 65 psi) and flux (12-10 GFD): 1. Waste first 20 ml permeate (verify flux is within specification as defined above), 2. Collect next 40 ml permeate sample for CEC analysis (verify flux is within specification as defined above), 3. Collect last 40 ml permeate sample for CEC analysis (verify flux is within specification as defined above).
Breakdown/Clean	Remove membrane coupons and rinse cells with methanol and DI.
Package and Ship	Prepare samples, label, package, complete manifests, and ship for CEC analysis by EEA as detailed previously.

Sources: Abolmaali et al. 2015

3.5 Analytics

Collected WRRF SE samples, as well as the NF and RO permeate test samples, were analyzed for CEC content at EEA of Monrovia, California.

3.5.1 Laboratory

As shown in Appendix B, EEA is certified by EPA and 46 states as an accredited lab for Test Methods 539 and 1964 (US EPA 2010; US EPA 2007). Furthermore, EEA recently served as a co-principal investigator on a Water Research Foundation project that evaluated over 20 analytical methods for CEC analysis in water (Vanderford et al. 2012). That research validated US EPA Methods 539 and 1964 as the best overall methods for precision and accuracy of CEC analysis. Subsequently, the EPA requires these validated methods for analysis and reporting of CECs as required by the UCMR3 program.

3.5.2 Analytical Methods and Equipment

Methods 539 and 1964 provided quantitative data on the suite of 96 CECs being investigated for this research. These methods involved online pre-concentration followed by liquid chromatograph separation and series mass spectrometry (LS-MS-MS) with electrospray ionization (ESI) in positive and negative modes. Instrumentation included an atmospheric pressure ionization API 5000 LC-MS-MS in connection with a Dionex Ultimate 3000 HPLC system.

For the utilized methods, Eaton and Haghani report:

> Appropriate mass transitions for each CEC analyte were determined by direct infusion of each analyte. Multiple mass transitions were used for each analyte to ensure unequivocal compound identification. A sample was injected into the HPLC through a ten port switching valve. Analytes were concentrated onto an Oasis HLB solid phase extraction column and the matrix diverted to waste. The valve position was then changed and the target analytes were refocused on an analytical column and then separated and eluted into the mass spectrometer, using an acidic eluent for positive mode and basic eluent for negative mode to gain

sensitivity on the mass spectrometry. Measurements of mass intensity were then determined using ESI in positive and negative mode, depending on whether the CEC has an affinity to protonate or de-protonate in high voltage creating an ionized adduct specie with negative or positive charge to be guided by electrical gradient through the MS filter quads. In general, a CEC containing nitrogen (N) will trend toward ESI positive, whereas a CEC with a carboxylic group (COOH) will trend toward ESI negative. All standards, test samples, and quality control (QC) samples were processed in the same manner. (Eaton and Haghani 2012)

3.5.3 Minimum Reportable Levels

Minimum reportable levels (MRLs) represent the lowest calibration point for the test method, typically limited by the instrumentation. The utilized test methods MRL for the subject 96 CECs ranged from 5 to 100 ηg/L. The test suite of 96 CECs with corresponding analytical LC-MS-MS ESI mode and MRL is provided in Table 3-5.

Table 3-5: CEC Test Suite Analytical Mode and Minimum Reportable Level

CEC	Analytical Mode	MRL (ηg/L)	CEC	Analytical Mode	MRL (ηg/L)
1,7-Dimethylxanthine	ESI +	10	Ibuprofen	ESI -	10
2,4-D	ESI -	5	Iohexal	ESI -	10
4-nonylphenol	ESI -	100	Iopromide	ESI -	5
4-tert-Octylphenol	ESI -	50	Isobutylparaben	ESI -	5
Acesulfame-K	ESI -	20	Isoproturon	ESI +	100
Acetaminophen	ESI +	5	Ketoprofen	ESI +	5
Albuterol	ESI +	5	Ketorolac	ESI +	5
Amoxicillin	ESI +	20	Lidocaine	ESI +	5
Andorostenedione	ESI +	5	Lincomycin	ESI +	10
Atenolol	ESI +	5	Linuron	ESI +	5
Atrazine	ESI +	5	Lopressor	ESI +	20
Azithromycin	ESI +	20	Meclofenamic Acid	ESI +	5
Bendroflumethiazide	ESI -	5	Meprobamate	ESI +	5
Bezafibrate	ESI +	5	Metazachlor	ESI +	5
Bisphenol-A (BPA)	ESI -	10	Methylparaben	ESI -	20
Bromacil	ESI +	5	Naproxen	ESI -	10
Butalbital	ESI -	5	Nifedipine	ESI +	20
Butylparaben	ESI -	5	Norethisterone	ESI +	5
Caffeine	ESI -	5	Oxolinic acid	ESI +	10
Carbadox	ESI +	5	Pentoxifylline	ESI +	5
Carbamazepine	ESI +	5	Phenazone	ESI +	5
Carisoprodol	ESI +	5	Primidone	ESI +	5
Chloramphenicol	ESI -	10	Progesterone	ESI +	5
Chloridazon	ESI +	5	Propazine	ESI +	5
Chlorotoluron	ESI +	5	Propylparaben	ESI -	5
Cimetidine	ESI +	5	Quinoline	ESI +	5
Clofibric Acid	ESI -	5	Simazine	ESI +	5
Cotinine	ESI +	10	Sucralose	ESI -	100
Cyanazine	ESI +	5	Sulfachloropyridazine	ESI +	5
DACT	ESI -	5	Sulfadiazine	ESI +	5
DEA	ESI +	5	Sulfadimethoxine	ESI +	5
DEET	ESI +	10	Sulfamerazine	ESI +	5
Dehydronifedipine	ESI +	5	Sulfamethazine	ESI +	5
DIA	ESI +	5	Sulfamethizole	ESI +	5
Diazepam	ESI +	5	Sulfamethoxazole	ESI +	5
Diclofenac	ESI -	5	Sulfathiazole	ESI +	5
Dilantin	ESI +	20	TCEP	ESI +	10
Diuron	ESI +	5	TCPP	ESI +	100
Erythromycin	ESI +	10	TDCPP	ESI +	100
Estradiol	ESI -	5	Testosterone	ESI +	5
Estrone	ESI -	5	Theobromine	ESI +	10
Ethinyl Estradiol - 17 alpha	ESI -	5	Theophylline	ESI +	20
Ethylparaben	ESI -	20	Triclosan	ESI -	10
Flumeqine	ESI +	10	Trimethoprim	ESI +	5
Fluoxetine	ESI +	10	Warfarin	ESI -	5
Gemfibrozil	ESI -	5			

MRL = Minimum reportable level
EPA Analytical Method: MS/MS/LS-ESI (+ or -)
Source: Eurofins Eaton Analytical, Inc.

3.6 Data Analysis

Each of the selected CECs was classified by use and cataloged by their quantitative chemical properties, cited from literature and scientific databases as identified in Chapter 4. Rejection coefficients ($R = 1 - C/C_0$) were also determined for each of the 940 discrete generated data events (CECs measured).

With the end-goal to develop a novel, but practical, CEC rejection model for the studied commercially available NF membrane, this research program was designed to elucidate the vital predictive variables influencing the rejection of CECs in municipal reclaimed secondary effluent samples. As such, a multi-level, multi-variable model was developed to predict the probable rejection coefficient (R) of each CEC with the studied NF membrane. The model was developed from predictor variables selected for their association with known membrane removal mechanisms for organic solutes (size-exclusion, electro-static interactions, hydrophobicity, etc.), CEC-specific chemical properties based on QSAR, and wastewater quality characteristics of the actual SE matrix. R statistics software version 3.1.3 was utilized for property collinearity analysis, outlier analysis, and regression modeling. The Pearson correlation method was utilized to select the most vital predictor variables for modeling. The resulting QMPM, as presented in Chapter 4, was then successfully developed to predict the NF rejection of more than 90 CECs. Furthermore, the QMPM was verified against a CEC rejection dataset published by an independent study for a similar commercially available NF membrane (Yangali-Quintanilla 2010).

CHAPTER 4 - RESULTS AND MODELING

4.1 Overview

The rejection of CECs by NF or RO membranes is a developing reuse treatment application to remove trace anthropogenic, recalcitrant organic contaminants from WRRF secondary effluents. As described previously in Chapter 2, many laboratory studies to date have identified rejection mechanisms for CECs across RO membranes that can be classified by either steric exclusion or surface interactions. A 2007 laboratory-scale, stirred-membrane-cell study identified hydrophobic adsorption and size exclusion as the predominant mechanisms for NF membrane rejection of 27 different CECs (Yoon et al. 2007). However, multiple studies have found solution matrix pH, and consequently electrostatic attraction/repulsion, are the most important predictors for CEC rejection by NF and RO membranes (Lin and Lee 2014; Yangali-Quitanilla 2010; Ozaki et al. 2008).

Recognizing the inherent complexity of CEC membrane rejection models, this research program was designed to elucidate the vital predictive variables influencing the rejection of more than 90 CECs in municipal reclaimed secondary effluent samples. Each of the selected CECs was cataloged by their intended use and QSAR properties (cited from literature and scientific databases) and measured in treated effluent samples (taken over multiple weeks) from three WRRFs in Texas and Oklahoma. These effluent samples were then filtered in bench-scale, stirred, dead-end membrane test cells with commercially available water treatment industry specified NF (DK) and RO (AG) membranes as provided by GE Osmonics (Minnetonka, Minnesota). As detailed in Chapter 3, the manufacturer-specified MWCO for the NF and RO test membranes were 200 and 100 Daltons, respectively. Both membranes were also analyzed by

atomic force microscopy (AFM) and determined to be hydrophilic with negative zeta potential surface charges of -12 and -20 mV, respectively (Wickramasinghe 2015).

A multi-level, multi-variable model was developed to predict the probable rejection coefficient ($R_p = 1 - C/C_0$) of a CEC in reclaimed secondary effluent with the studied industry-specified commercially available thin-film composite NF (MWCO 200) membrane. The model was developed from predictor variables selected for their association with known membrane removal mechanisms for dissolved organic solutes (size-exclusion, electro-static interactions, hydrophobicity, etc.), CEC-specific chemical properties based on QSAR properties, and matrix characteristics of the treated samples. The developed QMPM was then successfully applied to an independent database to verify the modeled mechanisms governing the rejection (by NF) of the selected CECs.

4.2 QSAR Properties Characterization

The study set of 96 CECs was classified in Chapter 2 by the seven intended use classifications of EDCs, pharmaceuticals, stimulants, preservatives, artificial sweeteners, pesticides, and flame retardants. Within each intended use classification, each of the 96 CECs is characterized as follows by the physical-chemical QSAR properties: MW, PSA, ionic charge at neutral pH, partitioning constants (e.g., pK_a, K_{ow}, K_{oa}), polarizability (α), and solubility (S_w). Based on these QSAR properties, each of the 96 CECs was further classified as hydrophobic-neutral (HB-N), hydrophobic-ionic (HB-I), hydrophilic-neutral (HL-N), or hydrophilic-ionic (HL-I).

4.2.1 Endocrine Disrupting Compounds

EDCs can be defined as both natural and synthetic exogenous estrogens, anti-androgens, and agents that interfere with the production, release, transport, metabolism, action or otherwise

elimination of natural hormones in the body responsible for the maintenance of homeostasis and the regulation of developmental processes (Spellman 2014). Disrupting the endocrine system can occur in various ways. Some chemicals can mimic a natural hormone, "fooling" the body into over-responding to the stimulus (e.g., a growth hormone that results in increased muscle mass) or responding at inappropriate times (e.g., producing insulin when it is not needed). Other EDCs can block the effects of a hormone from certain receptors. Still others can directly stimulate or inhibit the endocrine system, causing overproduction or underproduction of hormones.

Significant published literature has suggested that wildlife species have suffered adverse health effects after exposure to EDCs in the aquatic environment. Examples include reproductive problems in wood ducks from Bayou Meto, Arkansas (White and Hoffman 1995); embryonic deformities in Great Lakes fish-eating birds (i.e., gulls, terns, and cormorants) (Peakall and Fox 1987); feminization and embryonic mortality in lake trout and salmonids in the Great Lakes (Mac and Edsall 1991; Mac et al. 1993; Leatherland 1993); developmental effects in Great Lakes snapping turtles (Bishop et al. 1991); abnormalities of sexual development in Lake Apopka alligators (Guilette et al. 1995); reproductive failure in mink and otter from the Great Lakes area (Wren 1991); and reproductive impairment in the Florida Panther (Facemire et al. 1995). In each of these cited cases, detectable concentrations of EDCs were reported in the animals or in their environment.

Characterization of the CEC study set reveals 10 CECs that can be classified as EDCs. Table 4-1 provides a review of the CAS Registry for the subject EDCs identified the QSAR properties.

Table 4-1: EDC QSAR Properties

CEC	CASN	MW (g/mol)	PSA ($Å^2$)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	α ($Å^3$)	Sw (mg/L)	Hydro Class[a]
Androstenedione ($C_{19}H_{26}O_2$)	63-05-8	286.4	34.14	0		2.75	8.57	32.71	65.97	HB-N
Norethisterone ($C_{20}H_{26}O_2$)	68-22-4	298.4	37.30	0		3.22	10.6	34	7.04	HB-N
Progesterone ($C_{21}H_{30}O_2$)	57-83-0	314.5	34.14	0		4.15	9.45	36.4	8.81	HB-N
Testosterone ($C_{19}H_{28}O_2$)	58-22-0	288.4	37.30	0		3.37	10.16	33.26	23.4	HB-N
4-Nonylphenol ($C_{15}H_{23}KO$)	25154-52-3	220.5	23.06	0	10.3	5.74	8.62	27.21	7	HB-N
4-tert-Octylphenol ($C_{14}H_{22}O$)	140-66-9	206.3	20.23	0	10.2	4.69	9.02	25.63	31.63	HB-N
Bisphenol-A ($C_{15}H_{16}O_2$)	80-05-7	228.3	40.46	0	9.78	4.04	12.75	26.59	120	HB-N
Estradiol ($C_{18}H_{24}O_2$)	50-28-2	272.4	40.46	0	10.3	3.75	12.84	31.31	3.9	HB-N
Estrone ($C_{18}H_{22}O_2$)	53-16-7	270.4	37.30	0	10.3	4.31	10.94	30.76	30	HB-N
17 α -Ethinyl Estradiol ($C_{20}H_{24}O_2$)	57-63-6	296.4	40.46	0	10.3	3.9	13.16	33.9	11.3	HB-N

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

Table 4-1 QSAR properties show that all studied EDCs have a MW greater than 200 g/mol, MSA greater than 400 $Å^2$, a neutral charge, α ranging from 26 to 36 $Å^3$, and tend to be basic in nature with high pKa values greater than 9. In addition, the studied EDCs appear to have a relatively low affinity for water with a high (> 2.0) partitioning constant (log K_{ow}) and low water solubility. As such, the ten analyzed EDCs can be classified as HB-N.

4.2.2 Pharmaceuticals

Characterization of the CEC study set reveals 49 of the 96 are classified as pharmaceuticals, representing the largest use classification. Abundant study over the last 10 years shows the bioaccumulation and toxicity of fisheries in WRRF effluent-dominated Texas streams with pharmaceutical exposure at or below 1 µg/L, a common trigger for environmental assessments (Brooks 2014; Brooks et al. 2005).

Review of the CAS Registry reveals the QSAR properties characterization for the 49 pharmaceuticals as provided in Table 4-2. The analyzed pharmaceutical CECs were found to be both neutral and ionic charged (positive and negative). The 20 neutral charged pharmaceutical CECs, shown in Table 4-2a, consist of a wide range of medicinal applications: pain relief, anti-seizure, muscle relaxers, anxiety suppressors, antidepressants, cardiovascular, radiocontrast tracers, and anti-inflammatory. The neutral charged pharmaceutical CECs also possess high variability in size, solubility, polarity, and hydrophobicity.

Table 4-2a: Pharmaceuticals (neutral charge) QSAR Properties

CEC	CASN	MW (g/mol)	PSA (Å^2)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	α (Å^3)	Sw (mg/L)	Hydro Class[a]
Acetaminophen ($C_8H_9NO_2$)	103-90-2	151.2	49.33	0	9.46	0.27	11.04	15.82	30,400	HL-N
Butalbital ($C_{11}H_{16}N_2O_3$)	77-26-9	224.3	75.27	0	8.48	1.59	12.46	22.56	1,700	HL-N
Carbamazepine ($C_{15}H_{12}N_2O$)	298-46-4	236.3	46.33	0	15.96	2.45	10.81	26.95	17.66	HB-N
Carisoprodol ($C_{12}H_{24}N_2O_4$)	78-44-4	260.3	90.65	0	15.06	2.36	9.90	26.69	201	HB-N
Dehydronifedipine ($C_{17}H_{16}N_2O_6$)	67035-22-7	344.3	108.63	0	3.47	3.15	14.51	34.67	5.56	HB-N
Diazepam ($C_{16}H_{13}ClN_2O$)	439-14-5	284.7	32.67	0	2.92	2.82	9.65	30.32	50	HB-N
Dilantin ($C_{15}H_{12}N_2O_2$)	57-41-0	252.3	58.20	0	9.47	2.47	11.85	27.12	178.6	HB-N
Fluoxetine ($C_{17}H_{18}F_3NO$)	54910-89-3	309.3	21.26	0		3.93	9.26	30.44	60.28	HB-N
Gemfibrozil ($C_{15}H_{22}O_3$)	25812-30-0	250.3	46.53	0	4.42	4.39	11.08	27.93	4.96	HB-N
Iohexal ($C_{19}H_{26}I_3N_3O_9$)	66108-95-0	821.1	199.89	0	11.73	-1.95	23.91	57.82	106.5	HL-N
Iopromide ($C_{18}H_{24}I_3N_3O_8$)	73334-07-3	791.1	168.66	0	11.1	-0.44	24.34	55.37	23.75	HL-N
Ketoprofen ($C_{16}H_{14}O_3$)	22071-15-4	254.3	54.37	0	3.88	3.61	12.18	28.01	51	HB-N
Ketorolac ($C_{15}H_{13}NO_3$)	74103-06-3	255.3	59.30	0	3.84	2.28	13.18	26.84	572.3	HB-N
Meprobamate ($C_9H_{18}N_2O_4$)	57-53-4	218.3	104.64	0		0.93	8.82	21.22	4,700	HL-N
Naproxen ($C_{14}H_{14}O_3$)	22204-53-1	230.3	46.53	0	4.19	2.99	11.04	26.39	15.9	HB-N
Nifedipine ($C_{17}H_{18}N_2O_6$)	21829-25-4	346.3	107.77	0		1.82	13.73	33.98	357.5	HL-N
Pentoxifylline ($C_{13}H_{18}N_4O_3$)	6493-05-6	278.3	75.51	0		0.23	11.93	27.12	7,700	HL-N
Phenazone ($C_{11}H_{12}N_2O$)	60-80-0	188.2	23.55	0	0.37	1.22	7.95	20.89	10,000	HL-N
Primidone ($C_{12}H_{14}N_2O_2$)	125-33-7	218.3	58.20	0	11.5	1.12	9.01	23.07	500	HL-N
Warfarin ($C_{19}H_{16}O_4$)	81-81-2	308.3	63.60	0	5.63	3.52	9.65	33.26	17	HB-N

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

The 11 positive charged pharmaceutical CECs, shown in Table 4-2b, consist of a narrower range of medicinal applications: respiratory, antibiotics, cardiovascular, anxiety, gastrointestinal, and local anesthetic. The antibiotic CECs of this class are uniquely characterized as relatively large with MW greater than 400 g/mol, low solubility, highly polar, and

hydrophobic with log K_{ow} values less than 2.0. Conversely, the remaining positive charged pharmaceutical CECs are generally characterized with MW in the 200-400 g/mol range, high solubility, and hydrophyllic.

Table 4-2b: Pharmaceuticals (positive charge) QSAR Properties

CEC	CASN	MW (g/mol)	PSA (Å2)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	α (Å3)	Sw (mg/L)	Hydro Class[a]
Albuterol ($C_{26}H_{44}N_2O_{10}S$)	51022-70-9	72.72	406.0	1	10.12	0.64	14.22	26.58	300,000	HL-I
Atenolol ($C_{14}H_{22}N_2O_3$)	29122-68-7	84.58	440.4	1	14.08	0.16	16.41	29.09	13,300	HL-I
Azithromycin ($C_{38}H_{72}N_2O_{12}$)	83905-01-5	180.08	1284.6	1.8		4.02	30.68	79.01	0.06	HB-I
Bendroflumethiazide ($C_{15}H_{14}F_3N_3O_4S_2$)	73-48-3	118.36	505.9	0.1	9.04	1.7	11.54	35.91	108	HL-I
Cimetidine ($C_{10}H_{16}N_6S$)	51481-61-9	88.89	369.6	0.3		0.4	13.81	25.89	10,500	HL-I
Diltiazem ($C_{22}H_{26}N_2O_4S$)	42399-41-7	59.08	612.2	0.604	8.18	2.79	17.15	44.82	12.3	HB-I
Erythrommycin ($C_{37}H_{67}NO_{13}$)	114-07-8	193.91	1222.4	1.2	8.38	3.06	29.71	75.76	0.52	HB-I
Lidocaine ($C_{14}H_{22}N_2O$)	137-58-6	32.34	424.0	1	7.75	2.84	10.71	27.64	4,100	HB-I
Lincomycin ($C_{18}H_{37}ClN_2O_7S$)	154-21-2	122.49	624.5	1	7.97	-0.3	21.11	41.49	92.19	HL-I
Lopressor ($C_{15}H_{25}NO_3$)	51384-51-1	50.72	474.7	1	9.67	1.76	13.12	30.34	16,900	HL-I
Trimethoprim ($C_{14}H_{18}N_4O_3$)	738-70-5	105.51	431.2	0.6	7.16	1.28	12.92	29.76	400	HL-I

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

The 18 negative charged pharmaceutical CECs, shown in Table 4-2c, consist mostly of antibiotics but also anti-inflammatory and respiratory medicinal metabolites. The negative CECs of this pharmaceutical class are characterized as relatively small with MW less than 400 g/mol, moderate solubility, polar, and mostly HL-I.

Table 4-2c: Pharmaceuticals (negative charge) QSAR Properties

CEC	CASN	MW (g/mol)	PSA (Å^2)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	α (Å^3)	Sw (mg/L)	Hydro Class[a]
Amoxicillin ($C_{16}H_{25}N_3O_8S$)	26787-78-0	365.4	132.96	-0.33	3.23	0.87	19.86	35.52	3,433	HL-I
Bezafibrate ($C_{19}H_{20}ClNO_4$)	41859-67-0	361.8	75.63	-1	3.83	4.25	17.31	36.89	1.22	HB-I
Carbadox ($C_{11}H_{10}N_4O_4$)	6804-07-5	262.2	100.56	-0.02	0.78	-1.37	19.36	25.35	14,800	HL-I
Chloramphenicol ($C_{11}H_{12}Cl_2N_2O_5$)	56-75-7	323.1	112.70	-0.25	7.59	0.88	17.17	27.82	2,500	HL-I
Diclofenac ($C_{14}H_{11}C_{12}NO_2$)	15307-86-5	296.1	49.33	-1	4	4.26	14.22	29.03	2.37	HB-I
Flumequine ($C_{14}H_{12}FNO_3$)	42835-25-6	261.3	57.61	-1	6	1.6	12.56	24.74	2,186	HL-I
Ibuprofen ($C_{13}H_{18}O_2$)	15687-27-1	206.3	37.30	-1	4.85	3.84	9.18	23.65	21	HB-I
Meclofenamic ($C_{14}H_{11}Cl_2NO_2$)	644-62-2	296.1	49.33	-1	3.7	6.09	15.30	28.93	30	HB-I
Oxolinic acid ($C_{13}H_{11}NO_5$)	14698-29-4	262.2	76.07	-1	5.58	1.35	14.71	24.68	3.2	HL-I
Sulfachloropyridazine ($C_{10}H_9ClN_4O_2S$)	80-32-0	284.7	97.97	-1	6.6	0.85	10.39	26.59	7,000	HL-I
Sulfadiazine ($C_{10}H_{10}N_4O_2S$)	68-35-9	250.3	97.97	-0.65	6.99	0.39	8.1	24.59	77	HL-I
Sulfadimethoxine ($C_{12}H_{14}N_4O_4S$)	122-11-2	310.3	116.43	-0.58	6.91	1.26	13.9	29.7	343	HL-I
Sulfamerazine ($C_{11}H_{12}N_4O_2S$)	127-79-7	264.3	97.97	-0.59	6.99	0.52	8.29	26.35	202	HL-I
Sulfamethazine ($C_{12}H_{14}N_4O_2S$)	57-68-1	278.3	97.97	-0.51	6.99	0.65	8.29	28.1	1,500	HL-I
Sulfamethizole ($C_9H_{10}N_4O_2S_2$)	144-82-1	270.3	97.97	-0.65	6.71	0.21	12.51	25.13	1,050	HL-I
Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$)	723-46-6	253.3	98.22	-1	6.16	0.79	11.30	24.16	610	HL-I
Sulfathiazole ($C_9H_9N_3O_2S_2$)	72-14-0	255.3	85.08	-0.54	6.93	0.98	11.67	24.19	373	HL-I
Theophylline ($C_7H_8N_4O_2$)	58-55-9	180.2	69.30	-0.1	7.82	-0.77	10.12	16.13	7,360	HL-I

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

4.2.3 Stimulants

Characterization of the CEC study set reveals the QSAR properties for four stimulants as provided in Table 4-3. The analyzed stimulants include caffeine and metabolites of caffeine, nicotine, and chocolate. This group of CECs is readily classified as small with MW less than 200, low polarity, high solubility, and HL-N.

Table 4-3: Stimulants QSAR Properties

CEC	CASN	MW (g/mol)	PSA (Å^2)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	α (Å^3)	Sw (mg/L)	Hydro Class[a]
1,7-Dimethylxanthine ($C_7H_8N_4O_2$)	611-59-6	180.2	67.23	0	10.76	-0.39	9.76	16.06	4,149	HL-N
Caffeine ($C_8H_{10}N_4O_2$)	58-08-2	194.2	58.44	0		-0.07	8.77	17.87	2,632	HL-N
Cotinine ($C_{10}H_{12}N_2O$)	486-56-6	176.2	33.20	0		0.07	9.94	19.11	999,000	HL-N
Theobromine ($C_7H_8N_4O_2$)	83-67-0	180.2		0	9.28	-0.77	8.40	16.05	330	HL-N

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

4.2.4 Preservatives

Characterization of the CEC study set reveals the QSAR properties for eight preservatives as provided in Table 4-4. This group of CECs includes preservatives for food and personal care products and can be generally characterized as relatively small with MW less than 400, low polarity, moderately soluble, and mostly HB-N.

Table 4-4: Preservatives QSAR Properties

CEC	CASN	MW (g/mol)	PSA (Å^2)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	α (Å^3)	Sw (mg/L)	Hydro Class[a]
Quinoline (C9H7N)	91-22-5	129.2	12.89	0	4.5	2.13	6.2	17.08	6,110	HB-N
Butylparaben (C11H14O3)	94-26-8	194.2	46.53	0	8.5	3	10.0	20.88	207	HB-N
Ethylparaben (C9H10O3)	120-47-8	166.2	46.53	0	8.5	2.03	9.18	17.2	885	HB-N
Isobutylparaben (C11H14O3)	4247-02-3	194.2	46.53	0	8.5	2.92	9.86	20.88	224	HB-N
Methylparaben (C8H8O3)	99-76-3	152.2	46.53	0	8.5	1.67	8.79	15.37	2,500	HL-N
Propylparaben (C10H12O3)	94-13-3	180.2	46.53	0	8.5	2.55	9.62	19.04	500	HB-N
Triclocarban (C13H9Cl3N2O)	101-20-2	315.6	41.13	0	11.42	4.93	13.63	29.78	0.65	HB-N
Triclosan (C12H7Cl3O2)	3380-34-5	289.5	29.46	-0.14	7.68	4.98	11.45	26.96	10	HB-I

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

4.2.5 Artificial Sweeteners

Characterization of the CEC study set reveals the QSAR properties for two artificial sweeteners as provided in Table 4-5. This group of CECs includes widely utilized products (e.g., Splenda) by the food and beverage industry for low to no-calorie consumption. As evidenced by the relatively high concentrations seen in Table 4-5, these products are resistant to bio-degradation in WRRF biological processes. This group is characterized as small with MW less than 400, highly soluble, and HL-N.

Table 4-5: Artificial Sweeteners QSAR Properties

CEC	CASN	MW (g/mol)	PSA ($Å^2$)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	α ($Å^3$)	Sw (mg/L)	Hydro Class[a]
Acesulfame-K ($C_4H_4KNO_4S$)	55589-62-3	201.2	78.79	0	2	-0.69	ND	13.29	1,000,000	HL-N
Sucralose ($C_{12}H_{19}Cl_3O_8$)	56038-13-2	397.6	128.84	0	11.9	-0.47	15.79	32.65	22,800	HL-N

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

4.2.6 Pesticides

Characterization of the CEC study set reveals the QSAR properties for 18 pesticides as provided in Table 4-6. This group generally includes agents designed to inhibit, incapacitate, or otherwise terminate plant and animal life (Spellman 2014). As such, this group of CECs is of particular concern in public water supplies for human consumption. All 18 of the analyzed pesticides can be characterized to be relatively small with MW less than 300 g/mol, low to moderate solubility, and hydrophobic neutral. Five of the 18 pesticides, however, can be characterized as chloraminated (NHCl) compounds with high solubility and are HL-N.

Table 4-6: Pesticides QSAR Properties

CEC	CASN	MW (g/mol)	PSA (Å^2)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	A (Å^3)	Sw (mg/L)	Hydro Class[a]
Atrazine ($C_8H_{14}ClN_5$)	1912-24-9	215.7	62.73	0		2.61	9.63	21.19	214	HB-N
Bromacil ($C_9H_{13}BrN_2O_2$)	314-40-9	261.1	49.41	0	9.95	2.11	10.39	21.65	815	HB-N
Chloridazon ($C_{10}H_8ClN_3O$)	1698-60-8	221.7	58.69	0		1.14	9.0	21.65	3,585	HL-N
Chlorotoluron ($C_{10}H_{13}ClN_2O$)	15545-48-9	212.7	32.34	0	13.53	2.41	10.64	21.83	329	HB-N
Cyanazine ($C_9H_{13}ClN_6$)	21725-46-2	240.7	86.52	0		2.22	12.20	22.91	170	HB-N
DACT ($C_3H_4ClN_5$)	3397-62-4	145.6	90.71	0	3.58	0.32	8.11	12.11	42,000	HL-N
DEA ($C_6H_{10}ClN_5$)	6190-65-4	187.6	76.72	0	3.38	1.51	8.71	17.55	2,593	HL-N
DEET ($C_{12}H_{17}NO$)	134-62-3	191.3	20.31	0		2.18	8.25	22.29	666	HB-N
DIA ($C_5H_8ClN_5$)	1007-28-9	173.6	76.72	0	3.41	1.15	8.47	15.73	6,160	HL-N
Diuron ($C_9H_{10}Cl_2N_2O$)	330-54-1	233.1	32.34	0	13.18	2.68	10.37	22.02	42	HB-N
Isoproturon ($C_{12}H_{18}N_2O$)	34123-59-6	206.3	32.34	0	13.5	2.57	11.2	23.63	65	HB-N
Linuron ($C_9H_{10}Cl_2N_2O_2$)	330-55-2	249.1	41.57	0	11.94	2.68	9.79	22.77	75	HB-N
Metazachlor ($C_{14}H_{16}ClN_3O$)	67129-08-2	277.8	38.13	0	1.84	2.98	9.77	28.81	430	HB-N
Metolachlor ($C_{15}H_{22}ClNO_2$)	51218-45-2	283.8	29.54	0		3.45	9.33	30.46	530	HB-N
Propazine ($C_9H_{16}ClN_5$)	139-40-2	229.7	62.73	0	3.17	2.61	9.66	23.02	8.6	HB-N
Simazine ($C_7H_{12}ClN_5$)	122-34-9	201.7	62.73	0	3	1.78	9.59	19.37	6.2	HL-N
2,4-D ($C_8H_6Cl_2O_3$)	94-75-7	221.0	46.53	0	2.81	2.5	8.65	19.13	677	HB-N
Clofibric Acid ($C_{10}H_{11}ClO_3$)	882-09-7	214.6	46.53	0	3.37	2.9	8.6	20.8	583	HB-N

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

4.2.7 Flame Retardants

This group of CECs that have been detected in secondary effluents include chlorinated alkyl-phosphates that are typically applied to manufactured textiles, such as clothing and linens, in order to inhibit, suppress, or prevent the spread of fire. While the eco-toxic and human health effects of aqueous flame retardants are not clear, California has listed tris-2-chloroethyl phosphate (TCEP) among carcinogens and reproductive toxins since 1992 (CAEPA 2006).

Flame retardants have been shown to resist biodegradation and oxidation in treated effluents (Westerhoff et al. 2005). With their resistance to conventional WRRF treatment processes and relative abundance in the hydrosphere, it is apparent that alternative treatments for control of this group of CECs is required (Watts and Linden 2009).

Characterization of the CEC study set reveals the QSAR properties for three flame retardants as provided in Table 4-7. This group of CECs as relatively large (with MW > 350 g/mol) and neutral. Although log K_{ow} values slightly greater than 2.0 are reported by ACS for this group of CECs, solubility is reported as moderate to high.

Table 4-7: Flame Retardants QSAR Properties

CEC	CASN	MW (g/mol)	PSA (Å^2)	Charge pH 7.0 (mV)	pKa	log Kow	log Koa	A (Å^3)	Sw (mg/L)	Hydrophobicity Class[a]
TCEP (C6H12Cl3O4P)	115-96-8	285.49	44.76	0		2.11	5.31	23.06	7,000	HB-N
TCPP (C9H18Cl3O4P)	13674-84-5	327.6	44.76	0		3.36	8.20	28.46	1,200	HB-N
TDCPP (C9H15Cl6O4P)	13674-87-8	430.9	44.76	0		4.28	10.62	34.29	7	HB-N

Compiled from: ACS 2015, ChemAxon 2015

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charge*

4.3 Rejection Analysis

For the study set of 96 CECs, 82 were detected above the corresponding MRL in the primary effluent. The 14 undetected CECs either did not exist at measurable concentration in the WRRF influent or were effectively removed by the WRRF primary treatment gravity separation barriers. Most relevant to this DPR research, 18 of the studied 96 CECs were 100% removed by full-scale WRRF biological treatment. Conversely, 64 of the 96 studied CECs were found to exist in the secondary effluent at recalcitrant residual concentrations above MRL.

Of the 3,456 discrete analytic events, CEC detections above MRL were discovered in almost a third of the data set, as provided in Appendix C, or a total of 926 discrete occurrences.

Table 4-8 provides the distribution of CEC detections. This distribution clearly reveals a high to low profile across samples, thereby indicating a cursory assessment of the relative effectiveness of WRRF biological, bench-scale NF, and bench-scale RO as absolute barriers for the removal of CECs from the potential reuse supply.

Table 4-8: CEC Detections

Sample	COK	SOK	NTX
PE	158	142	144
SE	111	116	127
NF	36	27	48
RO	8	1	8

PE = primary effluent, SE = secondary effluent, NF = Nanofiltration permeate, RO = reverse osmosis permeate

For each of the 482 discrete SE to permeate events, observed rejection coefficients, R, were calculated across corresponding treatment barrier samples according to the following formula:

$$R = 1 - (C_p/C_o) \qquad \text{Eq. (4.1)}$$

C_p = concentration of CEC in membrane permeate sample

C_0 = concentration of CEC in SE sample

In most cases, a CEC detected in SE samples was not detected in permeate. In these cases, Cp was taken to be zero, yielding R = 100%. This was interpreted as 100% removal of a detectable chemical (concentrations greater than its MRL, in ηg/L). Recalcitrant CECs were, in most cases, rejected by NF and to a greater degree by RO as indicated in the following discussion for each of the CEC intended use classifications.

4.3.1 Observed Rejection

Rejection analyses of the EDCs, as indicated in Table 4-9, revealed that most natural human hormones existing in the primary effluent samples were readily removed to below MRL by the WRRF biological processes. Estrone was the only natural human hormone not fully biodegraded; NF effectively rejected approximately half the remaining fraction and RO rejected all remaining fraction. The other two recalcitrant EDCs were 4-tert-Octylphenol (surfactant) and BPA (plasticizer), for which both membranes were found to be very effective barriers. All three EDCs detected in NF permeate samples have a MW just above the NF MWCO and are classified HB-N, suggesting steric exclusion and hydrophobic sorption as the predominant rejection mechanisms. 17α-Ethinyl Estradiol (contraceptive) was not detected in the primary effluent samples, while 4-Nonylphenol (surfactant) was discounted from the dataset due to lab interference as detected in control blanks.

Table 4-9: EDC Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
4-tert-Octylphenol ($C_{14}H_{22}O$)	206	HB-N	88%	92%	90%	100%	100%	100%
4-Nonylphenol ($C_{15}H_{23}KO$)	221	HB-N	Discounted due to lab interference					
Bisphenol-A ($C_{15}H_{16}O_2$)	228	HB-N	95%	95%	95%	100%	100%	100%
Estrone ($C_{18}H_{22}O_2$)	270	HB-N	38%	62%	46%	100%	100%	100%
Estradiol ($C_{18}H_{24}O_2$)	272	HB-N	100% removed by WRRF biological treatment					
Androstenedione ($C_{19}H_{26}O_2$)	286	HB-N	100% removed by WRRF biological treatment					
Testosterone ($C_{19}H_{28}O_2$)	288	HB-N	100% removed by WRRF biological treatment					
17 α -Ethinyl Estradiol ($C_{20}H_{24}O_2$)	296	HB-N	Not detected in primary effluent					
Norethisterone ($C_{20}H_{26}O_2$)	298	HB-N	100% removed by WRRF biological treatment					
Progesterone ($C_{21}H_{30}O_2$)	315	HB-N	100% removed by WRRF biological treatment					

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

All but one of the 20 studied neutral-charged pharmaceuticals were detected in SE samples at concentrations above MRL. Phenazone (analgesic) was not detected in the primary effluent samples. Table 4-10a shows that both NF and RO were very effective barriers for the rejection of this group of CECs. With a neutral charge, this group of CECs is likely rejected by steric exclusion and some hydrophobic sorption, although the 100% exclusion of Acetaminophen (MW = 151 g/mol) by the NF test membrane suggests molecular PSA may be a better QSAR indicator than MW for steric exclusion. Table 4-2a also indicates that Acetaminophen has a molecular PSA of 223$Å^2$.

Table 4-10a: Pharmaceuticals (neutral) Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
Acetaminophen ($C_8H_9NO_2$)	151	HL-N	100%	100%	100%	100%	100%	100%
Phenazone ($C_{11}H_{12}N_2O$)	188	HL-N	Not detected in primary effluent					
Meprobamate ($C_9H_{18}N_2O_4$)	218	HL-N	89%	100%	99%	100%	100%	100%
Primidone ($C_{12}H_{14}N_2O_2$)	218	HL-N	100%	100%	100%	100%	100%	100%
Butalbital ($C_{11}H_{16}N_2O_3$)	224	HL-N	100%	100%	100%	100%	100%	100%
Naproxen ($C_{14}H_{14}O_3$)	230	HB-N	85%	100%	98%	100%	100%	100%
Carbamazepine ($C_{15}H_{12}N_2O$)	236	HB-N	85%	97%	94%	100%	100%	100%
Gemfibrozil ($C_{15}H_{22}O_3$)	250	HB-N	100%	100%	100%	100%	100%	100%
Dilantin ($C_{15}H_{12}N_2O_2$)	252	HB-N	100%	100%	100%	100%	100%	100%
Ketoprofen ($C_{16}H_{14}O_3$)	254	HB-N	100%	100%	100%	100%	100%	100%
Ketorolac ($C_{15}H_{13}NO_3$)	255	HB-N	100%	100%	100%	100%	100%	100%
Carisoprodol ($C_{12}H_{24}N_2O_4$)	260	HB-N	100%	100%	100%	100%	100%	100%
Pentoxifylline ($C_{13}H_{18}N_4O_3$)	278	HL-N	100%	100%	100%	100%	100%	100%
Diazepam ($C_{16}H_{13}ClN_2O$)	285	HB-N	100%	100%	100%	100%	100%	100%
Warfarin ($C_{19}H_{16}O_4$)	308	HB-N	100%	100%	100%	100%	100%	100%
Fluoxetine ($C_{17}H_{18}F_3NO$)	309	HB-N	63%	100%	89%	100%	100%	100%
Dehydronifedipine ($C_{17}H_{16}N_2O_6$)	344	HB-N	100%	100%	100%	100%	100%	100%
Nifedipine ($C_{17}H_{18}N_2O_6$)	346	HL-N	100%	100%	100%	100%	100%	100%
Iopromide ($C_{18}H_{24}I_3N_3O_8$)	791	HL-N	100%	100%	100%	100%	100%	100%
Iohexal ($C_{19}H_{26}I_3N_3O_9$)	821	HL-N	100%	100%	100%	100%	100%	100%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

All but one of the 11 studied positive-charged pharmaceuticals were detected above MRL in secondary effluent samples. With characteristically high MW (e.g., antibiotics) and positive-

charge, as seen in Table 4-10b, this group of CECs was highly rejected by both tested membranes by steric and electrostatic exclusion.

Table 4-10b: Pharmaceuticals (positive) Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
Lidocaine ($C_{14}H_{22}N_2O$)	234	HB-I	100%	100%	100%	100%	100%	100%
Albuterol ($C_{26}H_{44}N_2O_{10}S$)	239	HL-I	100%	100%	100%	100%	100%	100%
Cimetidine ($C_{10}H_{16}N_6S$)	252	HL-I	78%	100%	97%	100%	100%	100%
Atenolol ($C_{14}H_{22}N_2O_3$)	266	HL-I	90%	100%	98%	100%	100%	100%
Lopressor ($C_{15}H_{25}NO_3$)	267	HL-I	100%	100%	100%	100%	100%	100%
Trimethoprim ($C_{14}H_{18}N_4O_3$)	290	HL-I	94%	100%	99%	100%	100%	100%
Diltiazem ($C_{22}H_{26}N_2O_4S$)	415	HB-I	100%	100%	100%	100%	100%	100%
Bendroflumethiazide ($C_{15}H_{14}F_3N_3O_4S_2$)	421	HL-I	Not detected in primary effluent					
Lincomycin ($C_{18}H_{37}ClN_2O_7S$)	461	HL-I	100%	100%	100%	100%	100%	100%
Erythrommycin ($C_{37}H_{67}NO_{13}$)	734	HB-I	100%	100%	100%	100%	100%	100%
Azithromycin ($C_{38}H_{72}N_2O_{12}$)	749	HB-I	92%	100%	99%	99%	100%	100%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

The group of 18 negative-charged pharmaceuticals was found with the most variable occurrence of the studied CECs. Table 4-10c indicates that eight were not detected in primary effluent samples and two were fully removed through WRRF biological treatment. The seven recalcitrant negative-charged pharmaceuticals were found to be highly rejected by both test membranes, via steric and electrostatic exclusion. Only the hydrophilic Sulfamethoxazole (antibiotic) was detected in any membrane permeate samples.

Table 4-10c: Pharmaceuticals (negative) Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
Theophylline ($C_7H_8N_4O_2$)	180	HL-I	100%	100%	100%	100%	100%	100%
Ibuprofen ($C_{13}H_{18}O_2$)	206	HB-I	100% removed by WRRF biological treatment					
Sulfadiazine ($C_{10}H_{10}N_4O_2S$)	250	HL-I	100%	100%	100%	100%	100%	100%
Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$)	253	HL-I	83%	98%	91%	99%	100%	100%
Sulfathiazole ($C_9H_9N_3O_2S_2$)	255	HL-I	100%	100%	100%	100%	100%	100%
Flumequine ($C_{14}H_{12}FNO_3$)	261	HL-I	Not detected in primary effluent					
Carbadox ($C_{11}H_{10}N_4O_4$)	262	HL-I	Not detected in primary effluent					
Oxolinic acid ($C_{13}H_{11}NO_5$)	262	HL-I	Not detected in primary effluent					
Sulfamerazine ($C_{11}H_{12}N_4O_2S$)	264	HL-I	Not detected in primary effluent					
Sulfamethizole ($C_9H_{10}N_4O_2S_2$)	270	HL-I	Not detected in primary effluent					
Sulfamethazine ($C_{12}H_{14}N_4O_2S$)	278	HL-I	Not detected in primary effluent					
Sulfachloropyridazine ($C_{10}H_9ClN_4O_2S$)	285	HL-I	Not detected in primary effluent					
Meclofenamic ($C_{14}H_{11}Cl_2NO_2$)	296	HB-I	Not detected in primary effluent					
Diclofenac ($C_{14}H_{11}C_{l2}NO_2$)	296	HB-I	100%	100%	100%	100%	100%	100%
Sulfadimethoxine ($C_{12}H_{14}N_4O_4S$)	310	HL-I	100%	100%	100%	100%	100%	100%
Chloramphenicol ($C_{11}H_{12}Cl_2N_2O_5$)	323	HL-I	100% removed by WRRF biological treatment					
Bezafibrate ($C_{19}H_{20}ClNO_4$)	362	HB-I	100% removed by WRRF biological treatment					
Amoxicillin ($C_{16}H_{25}N_3O_8S$)	365	HL-I	100%	100%	100%	100%	100%	100%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

Representing caffeine and associated degradates of caffeine, nicotine, and chocolate, the stimulants group was somewhat surprisingly found to be recalcitrant. All studied stimulants were characterized previously as HL-N with relatively low molecular weights, thereby suggesting a possible challenge for NF membrane rejection. However, as indicated below in Table 4-11, the stimulants group were highly rejected by both test membranes with only one NF permeate

sample indicating an 11 ηg/L occurrence of caffeine, albeit considerably below the MRL of 500 ηg/L.

Table 4-11: Stimulants Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
Cotinine ($C_{10}H_{12}N_2O$)	176	HL-N	100%	100%	100%	100%	100%	100%
Theobromine ($C_7H_8N_4O_2$)	180	HL-N	100%	100%	100%	100%	100%	100%
1,7-Dimethylxanthine ($C_7H_8N_4O_2$)	180	HL-N	100%	100%	100%	100%	100%	100%
Caffeine ($C_8H_{10}N_4O_2$)	194	HL-N	70%	100%	97%	100%	100%	100%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

The preservatives group of CECs were QSAR-characterized as having relatively low MW and mostly HB-N. Generally, such properties suggest the predominant membrane rejection mechanism for this group may be more sorption and less exclusion.

Notably, as evidenced in Table 4-12, five of the eight studied preservatives were found to be 100% removed by WRRF biological treatment. Of the three recalcitrant preservatives, results indicated the two largest, Triclocarban and Triclosan, were highly rejected by both test membranes, with the ionic analyte in the group (Triclosan) fully rejected. The other recalcitrant preservative, Quinoline, represents the smallest analyte (MW = 129 g/mol) in the study set of 96 CECs. Rejection analysis revealed moderate (89%) removal of Quinoline by both membranes.

Table 4-12: Preservatives Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
Quinoline (C_9H_7N)	129	HB-N	56%	100%	89%	56%	100%	89%
Methylparaben ($C_8H_8O_3$)	152	HL-N	100% removed by WRRF biological treatment					
Ethylparaben ($C_9H_{10}O_3$)	166	HB-N	100% removed by WRRF biological treatment					
Propylparaben ($C_{10}H_{12}O_3$)	180	HB-N	100% removed by WRRF biological treatment					
Butylparaben ($C_{11}H_{14}O_3$)	194	HB-N	100% removed by WRRF biological treatment					
Isobutylparaben ($C_{11}H_{14}O_3$)	194	HB-N	100% removed by WRRF biological treatment					
Triclosan ($C_{12}H_7Cl_3O_2$)	290	HB-I	100%	100%	100%	100%	100%	100%
Triclocarban ($C_{13}H_9Cl_3N_2O$)	316	HB-N	80%	100%	95%	63%	100%	93%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

Table 4-13 shows that the artificial sweeteners study group included two HL-N CECs. This group of CECs was found to be fully recalcitrant in the WRRF SE. Results indicated the larger sweetener, Sucralose, was highly rejected by both test membranes by steric exclusion. However, the smaller Acesulfame-K (MW = 201) was only rejected at 56% by the NF membrane.

Table 4-13: Artificial Sweeteners Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
Acesulfame-K ($C_4H_4KNO_4S$)	201	HL-N	8%	98%	56%	100%	100%	100%
Sucralose ($C_{12}H_{19}Cl_3O_8$)	398	HL-N	99%	100%	99%	100%	100%	100%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

Similar to artificial sweeteners, the flame retardants were found to be highly recalcitrant in the WRRF SE. Table 4-14 shows that this group of CECs is QSAR-characterized as moderate

size and HB-N. Mean rejection by NF of this group ranged from 55% for the smallest, TCEP, to 89% for the largest, TDCPP, whereas the tighter RO test membrane proved to be a highly effective barrier to this group of CECs.

Table 4-14: Flame Retardants Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
TCEP ($C_6H_{12}Cl_3O_4P$)	285	HB-N	8%	97%	55%	95%	100%	99.5%
TCPP ($C_9H_{18}Cl_3O_4P$)	328	HB-N	29%	100%	81%	100%	100%	100%
TDCPP ($C_9H_{15}Cl_6O_4P$)	431	HB-N	77%	100%	89%	100%	100%	100%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

Table 4-15 identifies that the pesticides group of 18 CECs were QSAR-characterized as relatively low to moderate in size, with MW ranging from 146 to 284 g/mol, and of neutral charge. Three of the 18 were not detected in the primary effluent, while 2 of the pesticides were found to be fully removed by the WRRF biological processes. The remaining 13 pesticides were found to be recalcitrant CECs in the secondary effluents. With the exception of Atrazine, the NF test membrane proved to be most effective (92-100%) for rejection of the nine hydrophobic pesticides and slightly less effective (74-89%) for rejection of the four hydrophilic species. Notably, the tighter RO membrane was found to fully reject all recalcitrant pesticides regardless of hydrophobicity.

Table 4-15: Pesticides Rejection

CEC	Molecular Weight (g/mol)	Hydro Class[a]	Nanofiltration			Reverse Osmosis		
			Min R	Max R	Mean R	Min R	Max R	Mean R
DACT ($C_3H_4ClN_5$)	146	HL-N	18%	100%	84%	100%	100%	100%
DIA ($C_5H_8ClN_5$)	174	HL-N	20%	100%	74%	100%	100%	100%
DEA ($C_6H_{10}ClN_5$)	188	HL-N	13%	100%	80%	100%	100%	100%
DEET ($C_{12}H_{17}NO$)	191	HB-N	84%	100%	97%	100%	100%	100%
Simazine ($C_7H_{12}ClN_5$)	202	HL-N	76%	100%	89%	100%	100%	100%
Isoproturon ($C_{12}H_{18}N_2O$)	206	HB-N	Not detected in primary effluent					
Chlorotoluron ($C_{10}H_{13}ClN_2O$)	213	HB-N	100% removed by WRRF biological treatment					
Clofibric Acid ($C_{10}H_{11}ClO_3$)	215	HB-N	100% removed by WRRF biological treatment					
Atrazine ($C_8H_{14}ClN_5$)	216	HB-N	10%	89%	68%	100%	100%	100%
2,4-D ($C_8H_6Cl_2O_3$)	221	HB-N	64%	100%	92%	100%	100%	100%
Chloridazon ($C_{10}H_8ClN_3O$)	222	HL-N	Not detected in primary effluent					
Propazine ($C_9H_{16}ClN_5$)	230	HB-N	Not detected in primary effluent					
Diuron ($C_9H_{10}Cl_2N_2O$)	233	HB-N	100%	100%	100%	100%	100%	100%
Cyanazine ($C_9H_{13}ClN_6$)	241	HB-N	100%	100%	100%	100%	100%	100%
Linuron ($C_9H_{10}Cl_2N_2O_2$)	249	HB-N	100%	100%	100%	100%	100%	100%
Bromacil ($C_9H_{13}BrN_2O_2$)	261	HB-N	100%	100%	100%	100%	100%	100%
Metazachlor ($C_{14}H_{16}ClN_3O$)	278	HB-N	100%	100%	100%	100%	100%	100%
Metolachlor ($C_{15}H_{22}ClNO_2$)	284	HB-N	100%	100%	100%	100%	100%	100%

[a] *Hydrophobicity Class: HL = Hydrophilic, HB = Hydrophobic, N = Neutral, I = Ionic charged*

4.3.2 NF Rejection Coefficient Outliers

Under the assumption that every non-complete CEC removal (R < 100%) by the NF test membrane was statistically an outlier for the general data population, rejection (R), as a function of a CEC and its properties, is not a normally-distributed dataset; thus, subpopulations of the CEC rejection data were further analyzed for statistical outliers. Subsets of the data were populated for each of the selected CECs. Standard boxplot analysis for each such CEC are shown

in Appendix C. This analysis demonstrated that rejection was consistent throughout the dataset (with well-defined lower- and upper-quartiles) for most CECs. This is to be expected. The fundamental assumption of QSAR is that the behavior of an analyte (in this case, rejection by NF membranes) will be a function of the properties of that analyte; therefore, each CEC should have a repeatable rate of rejection with repeated membrane filtration testing. However, for 12 cases of CEC detection, removal varied significantly despite the analyte and membrane properties remaining constant. Table 4-16 shows a complete list of the identified statistical outliers.

Table 4-16: Identified Outliers for Observed NF Rejection of CECs

OUTLIER	ANALYTE	SAMPLE SOURCE	OBSERVED REJECTION
1	2,4-D	Lawton	64%
2	Atrazine	Garland	9%
3	BPA	Garland	-13%
4	Caffeine	Garland	70%
5	Cimetidine	Garland	78%
6	DACT	Garland	18%
7	DEA	Lawton	13%
8	DIA	Garland	35%
9	Fluoxetine	Norman	63%
10	Quinoline	Garland	56%
11	Triclosan	Garland	-8%
12	Triclosan	Norman	-7%

In three of the 12 outlier cases, the reported analyte concentration was greater in the membrane permeate than in the secondary effluent, resulting in negative coefficients. Subsequently, outliers, negative coefficients, and cases where a chemical was not detected in

secondary effluent (i.e., R = 100% through WRRF primary and secondary treatment) were removed for development of the NF rejection model.

4.4 Nanofiltration Rejection Model

A multi-level, multi-variable model was developed to predict the probable rejection of a CEC in reclaimed secondary effluent with the studied NF membrane. The model was developed from predictor variables selected for their association with known membrane removal mechanisms for dissolved organic solutes, CEC-specific chemical properties based on QSAR properties, and matrix characteristics of the secondary effluent. The developed QMPM was then successfully applied to an independent CEC rejection database for model validation.

4.4.1 Pearson Correlation Analysis

As previously discussed, three predominant mechanisms for rejection of organic solutes by nano-porous membranes are steric (size) exclusion, electrostatic repulsion, and hydrophobic sorption. A variety of potential predictors for CEC rejection by NF was tested in categories according to descriptors for matrix quality and CEC-specific QSAR-based chemical properties.

Chemical properties were selected for analysis for their potential relationship to these known removal mechanisms for the rejection of dissolved organic compounds by NF membrane filtration, including:

1. Electrostatic surface interactions
2. Size-exclusion
3. Hydrophobicity/Hydrophilicity

Table 4-17 lists the variables tested for significance in predicting the rejection of CECs by NF. Values for each chemical-specific property were compiled from existing online databases (US EPA EPI Suite v.2, *ChemAxon*: www.chemicalize.org).

Table 4-17: QSAR Properties Tested for Predicting the Rejection of CECs by NF

	Properties	Relevant Rejection Mechanisms
Phase Partitioning	K_{ow}	Hydrophobicity
	K_{aw}	
	K_{oa}	
Water Solubility	Solubility, S	Hydrophobicity
Surface Charge	Molecular Charge at Neutral pH (7)	Electro-Static Interactions
Molecular Size	Molecular Weight	Steric Exclusion
	Polar Surface Area	Steric Exclusion Hydrophobicity
	Polarizability, a	

Previous efforts to build predictive models for regulated pesticide rejection by NF of drinking waters (Sanches et al. 2013) have highlighted the complexity of the underlying phenomena governing micropollutant rejection, requiring multivariate statistical analysis. Each of the listed predictor variables in Table 4-17 were evaluated individually for statistical significance in predicting the rejection of the 96 CEC study set. Initially, each variable was systematically compared to another to determine incidences of collinearity. Figure 4-1 is a graphical representation of a Pearson Correlation Matrix for the predictor variables evaluated from Table 4-17.

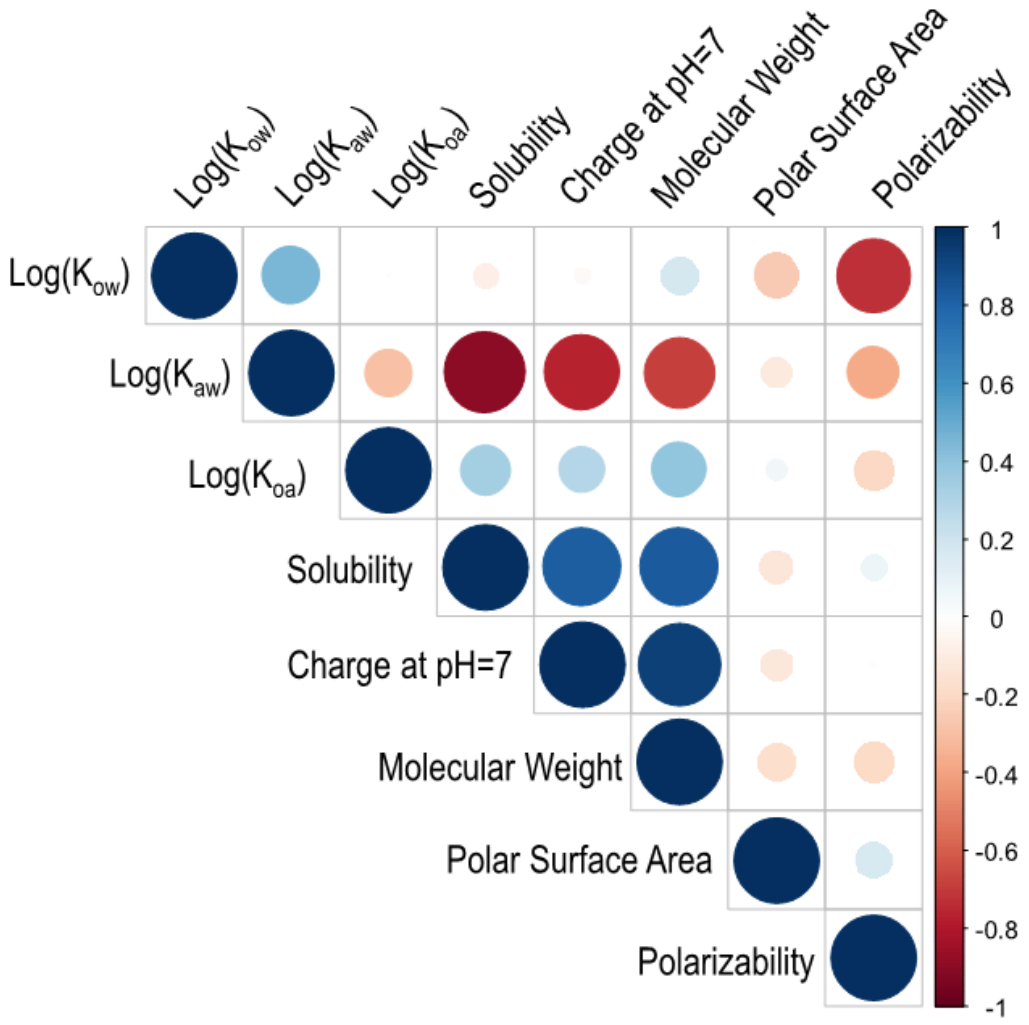


Figure 4-1: Pearson Correlation Matrix for QSAR Properties of the Examined CECs

The color intensity and the size of the circles, represented in Figure 4-1, are proportional to the Pearson correlation coefficients. Large, dark blue circles are indicative of strong, positive correlations between variables. Large, dark red circles are indicative of strong, negative (or inverse) correlations between variables. Examining the correlation coefficients among the partitioning coefficients, the value of K_{ow} is collinear with K_{aw}, while independent of K_{oa} in the CEC study dataset. This was somewhat surprising given that K_{oa} also describes the ratio of K_{ow}/K_{aw}. As expected, K_{aw} displays some collinearity and dependence with K_{oa}. Therefore, for

the purposes of developing a QMPM, both K_{ow} and K_{oa} (K_{ow}/K_{aw}) were evaluated as potential predictors of CEC selectivity with NF.

Steric measures (molecular size descriptors) also correlated with three of the four partitioning properties, thereby demonstrating that the size and shape of an organic molecule does have a significant impact on the partitioning behavior of that molecule. CEC polar surface area (PSA), a measure of the molecular surface area occupied by polar atoms (e.g., O and N for many CECs), revealed limited collinearity with K_{oa} (K_{ow}/K_{aw}) and therefore is an independent predictor. Nevertheless, MW was preserved for QMPM development in order to evaluate the potential MWCO of the studied NF membrane.

Parameters that can be used to describe the polarity of the studied CECs, charge at neutral pH and solubility constant (S) in water, were determined to be independent of the partitioning coefficient K_{ow}. Molecular polarizability (α) was also found to have limited association with either solubility or charge at neutral pH.

From the Pearson Correlation analysis, an initial set of independent QSAR parameters was selected for model development:

1. Log K_{ow}
2. Log K_{oa} (K_{ow}/K_{aw})
3. Molecular Charge at Neutral pH
4. Molecular Weight
5. Polar Surface Area
6. Polarizability

4.4.2 Model Predictor Variables

The following predictor variables had the lowest mutual dependence and best collinearity with the predominant rejection mechanisms of the NF test membrane: size exclusion, hydrophobic sorption, and electrostatic surface interactions.

4.4.2.1 Molecular Weight

As previously discussed, one approach to assessing the absolute MWCO of a membrane is to plot the rejection coefficients of many solutes of varying molecular weight.

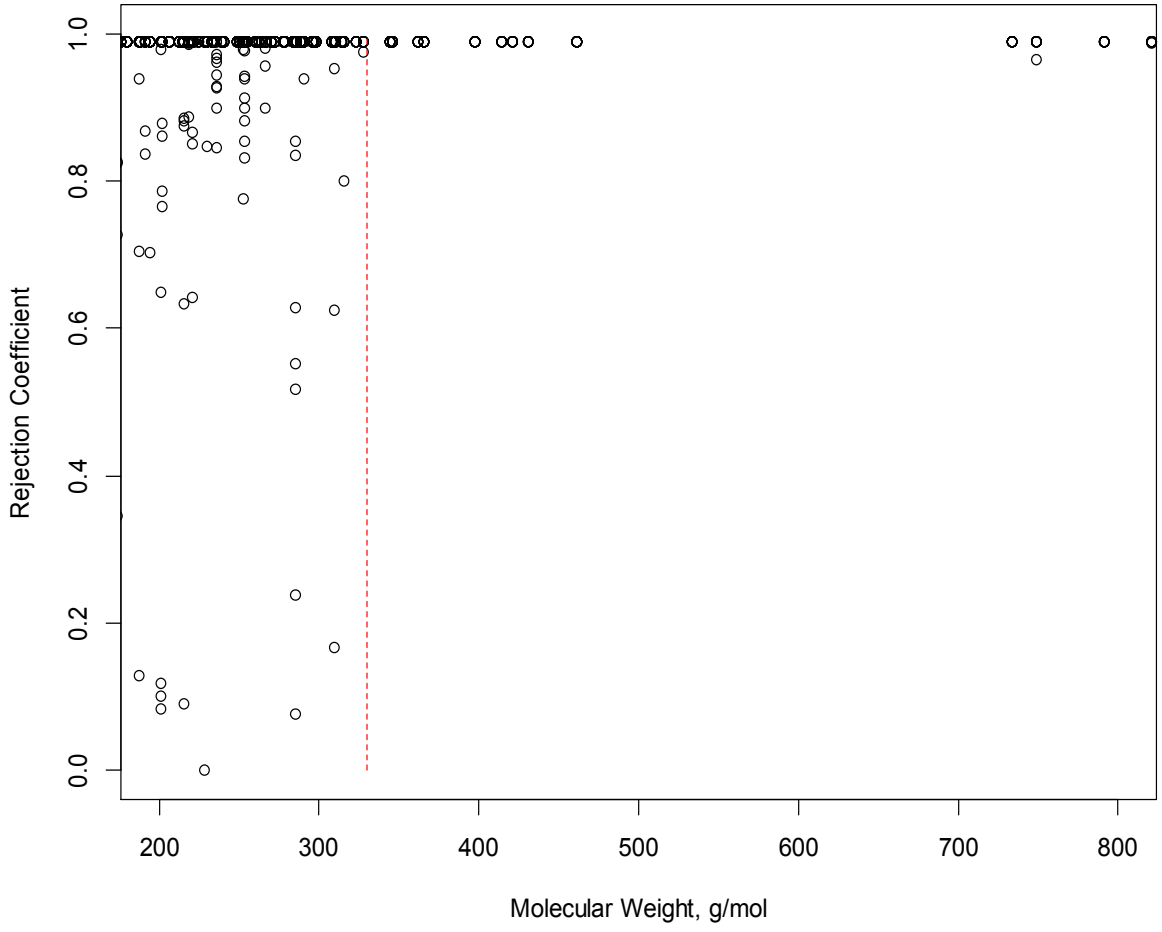


Figure 4-2: MW versus Observed Rejection

In Figure 4-2, the dashed line represents the observed molecular weight rejection threshold for the studied NF membrane above which nearly complete rejection of CECs was observed. For smaller molecular weight CECs (< 330 g/mol), observed rejection ranged from 0 to 100%. With a clear molecular weight rejection cutoff established for the tested membrane, it was apparent that a QSAR-based CEC rejection model would be most useful in predicting the variability in rejection of the smaller CECs (with molecular weight < 330 g/mol).

4.4.2.2 Molecular Charge at Neutral pH

Electrostatic repulsion and attraction of dissolved CECs by the charged membrane surface (with a negative zeta potential) can be described by the molecular charge at the neutral pH of the sampled matrix (for the purposes of safe stream discharge or water reuse, typical reclaimed municipal effluents will have a pH between 7 and 8). By plotting the molecular surface charge density (C/m^2) of each CEC versus its observed rejection coefficient, a clear delineation can be observed in Figure 4-3 between the rates of rejection of charged and neutral species. With the exception of four observations, charged CECs (positive or negative) at neutral pH were removed by 90% or more (for greater than 1-log rejection). However, neutral CECs (solutes with zero surface charge density at pH =7) could potentially see less efficient rejection by the tested NF membrane. As recently observed by Chen et al. (2015), the CECs furthest away from their isoelectric point in neutral pH reclaimed waters have the greatest probability of NF rejection.

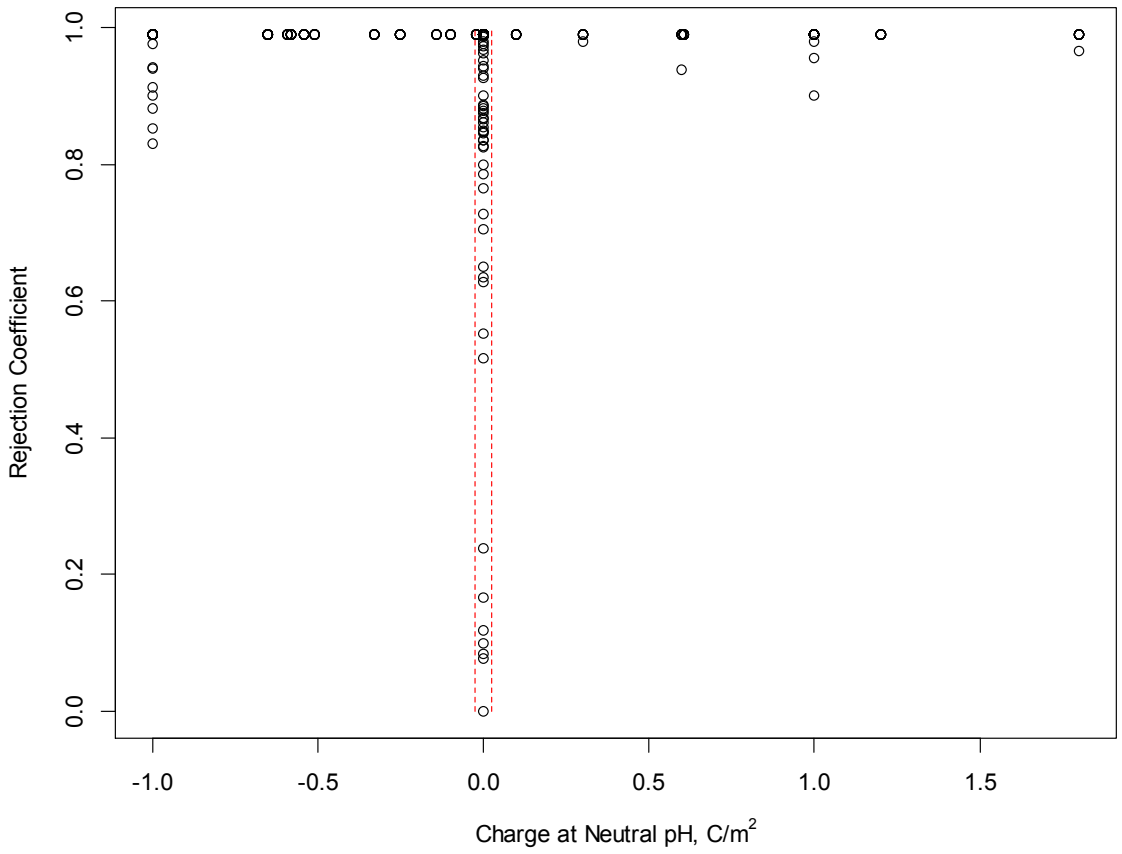


Figure 4-3: Surface Charge Density versus Observed Rejection

To assess the expected percent rejection of charged/ionic CECs, frequency distributions were plotted for observed NF rejection (excluding observations for nonionic, or neutral, CECs). Figure 4-4 shows the frequency of observed rejection coefficients for negatively charged CECs. With few exceptions, negatively charged CECs were rejected fully (R = 1.00) by the NF test membrane, and the 1st-quartile, median, and 3rd-quartile observed R were all 1.00 for these compounds.

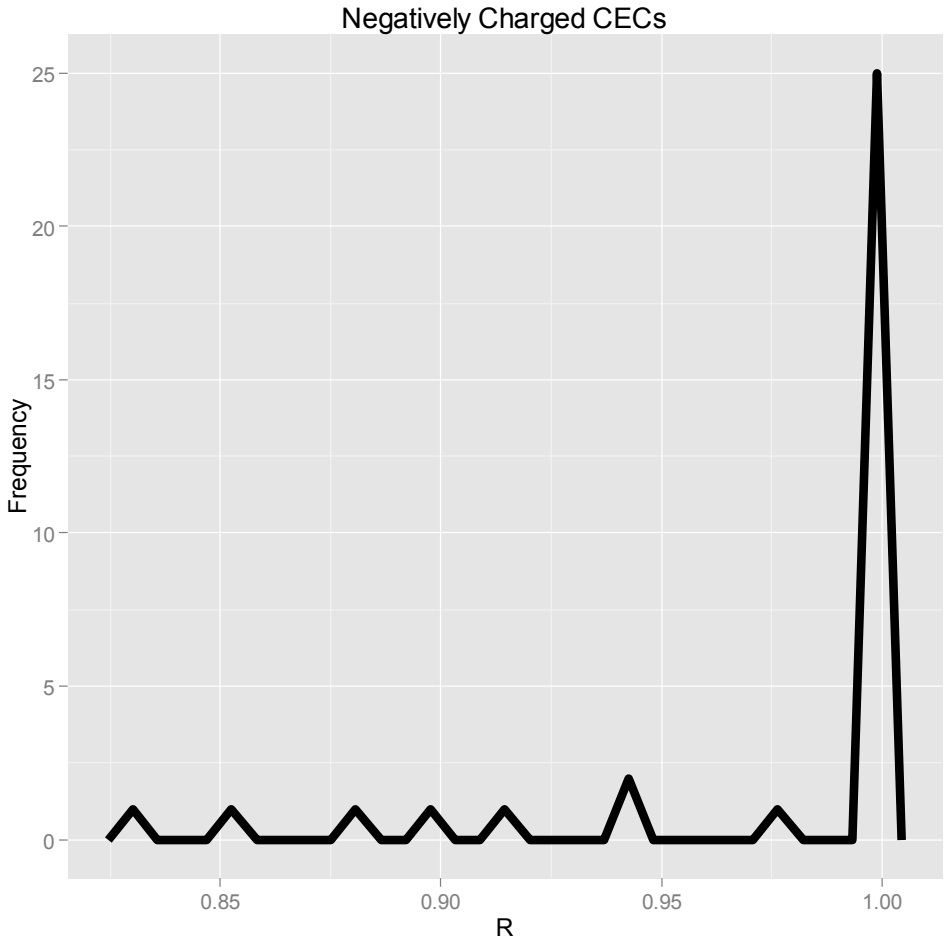


Figure 4-4: Frequency Distribution of NF Rejected Negative CECs

Similarly, positive-charged CECs were also rejected fully (R = 1.00) by the NF test membrane, and the 1st-quartile, median, and 3rd-quartile observed R were all 1.00 for these compounds. Figure 4-5 illustrates the frequency of observed R for positively charged CECs.

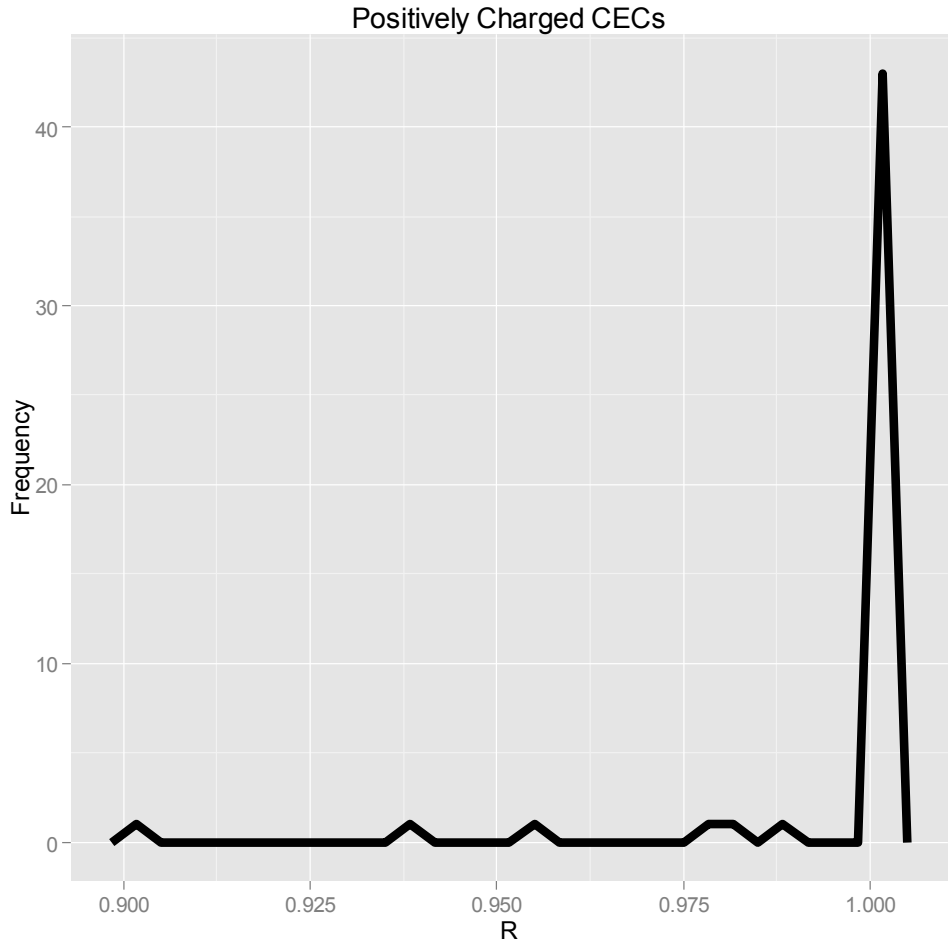


Figure 4-5: Frequency Distribution of NF Rejected Positive CECs

4.4.2.3 Phase Partitioning

Having identified that the greatest variation in observed NF rejection could be explained by small molecular weight CECs with neutral surface charges at pH =7, hydrophobic sorption was next examined as potential predictors. Solute hydrophobicity has been previously described by phase partition coefficients like K_{ow}. However, for this dataset, neither K_{ow} nor the log of K_{ow} was found to be a statistically significant predictor, in itself, of CEC rejection by NF.

Other phase partitioning constants, either empirical or model-derived, were considered as well, including the air-water partitioning coefficient (K_{aw}). Individually, these partitioning

coefficients were also ruled out as strong predictors of CEC rejection coefficients due to lack of correlation with the observed rejection dataset. However, an obvious trend was identified when the ratio of log K_{ow} to log K_{aw} was examined for its relationship to observed CEC rejection. As evidenced by Figure 4-6, for log K_{ow}/K_{aw} greater than 17, all cases had an observed rate of rejection greater than 100%.

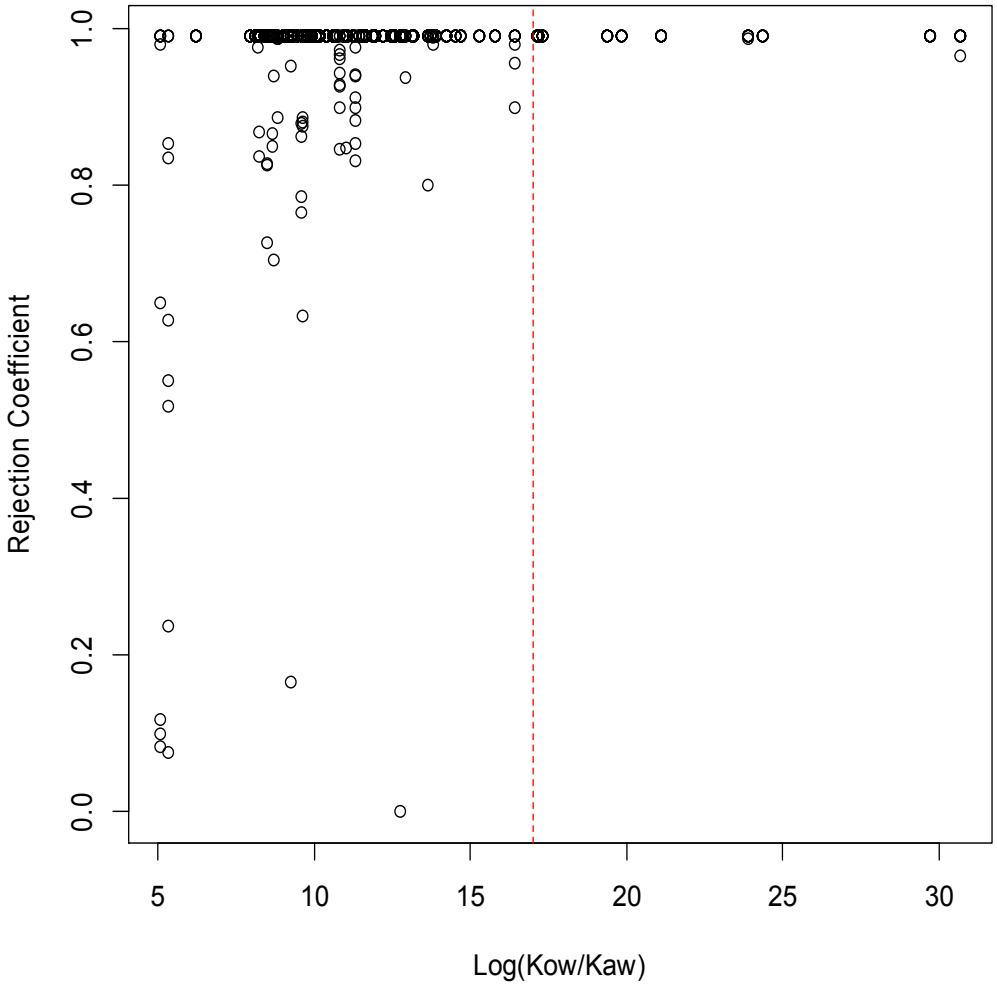


Figure 4-6: NF Rejection as a Function of log (K_{ow}/K_{aw})

Applying linear regression to the observed CEC rejection coefficients when MW<330 g/mol, ionic (i.e., charged) CECs at pH =7, and log (K_{ow}/K_{aw}) > 17, the resulting model for

rejection coefficients as a function of CEC log (K_{ow}/K_{aw}) has a negligible slope, and an intercept of 0.99. Thus, the minimum predicted rejection with NF of smaller, charged CECs with log (K_{ow}/K_{aw}) > 17 is expected to be 100%.

4.4.3 NF Rejection Model

Having characterized the variability in CEC rejection by NF as a function of small molecular weight, neutrally charged at pH =7, and having a log K_{ow}/K_{aw} less than 17, a clear taxonomy for CEC selectivity with NF was formed. Figure 4-7 allows for classification of the likelihood for CEC rejection by NF by steric, electrostatic, and hydrophobic/hydrophilic mechanisms.

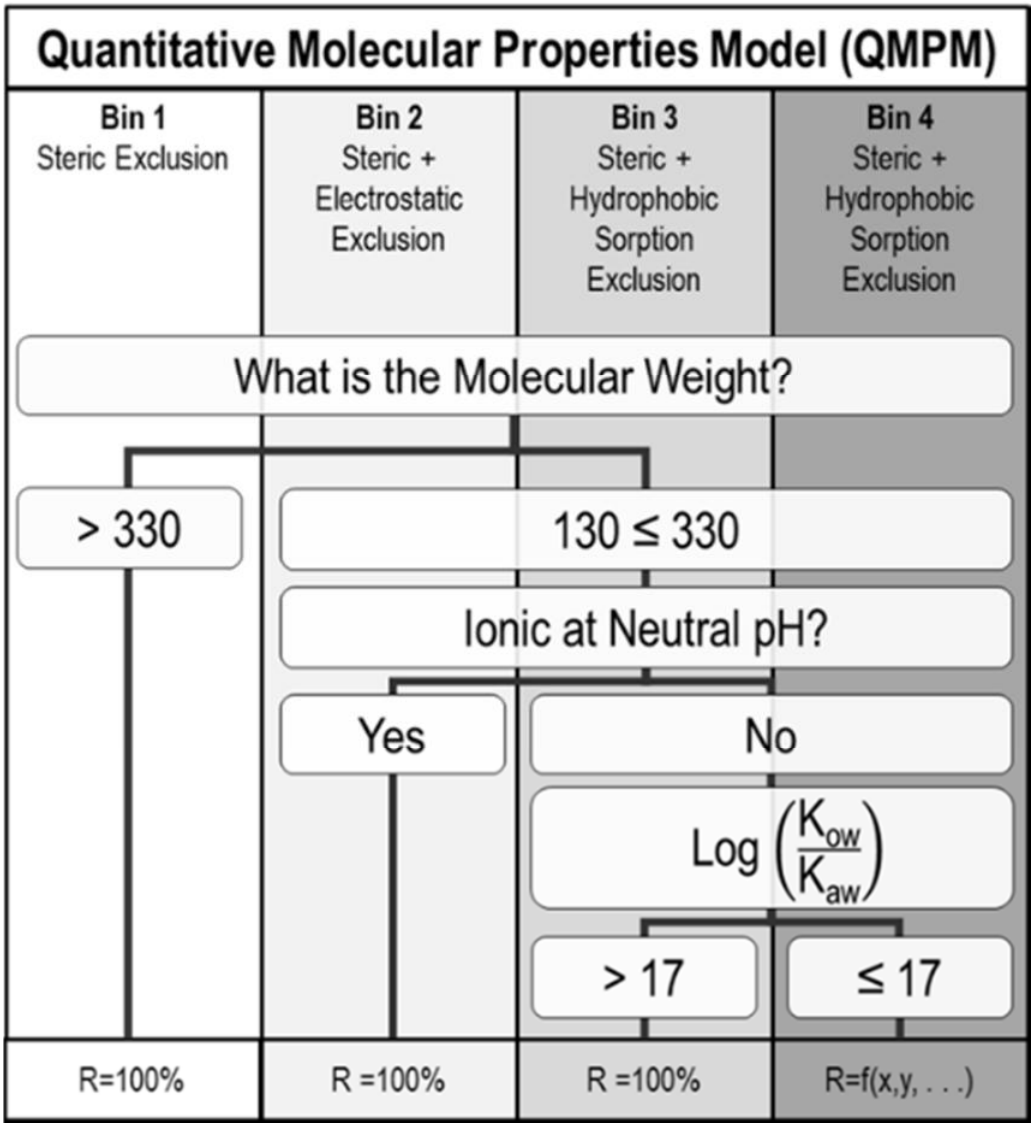


Figure 4-7: Quantitative Molecular Properties Model

As defined, the Bin 4 CECs (i.e., small, neutral, hydrophilic) had the greatest variability in observed rejection coefficients with the tested NF membrane. However, as seen in Figure 4-8, this subset of data remains heavily weighted by occurrences of complete, or nearly complete, rejection.

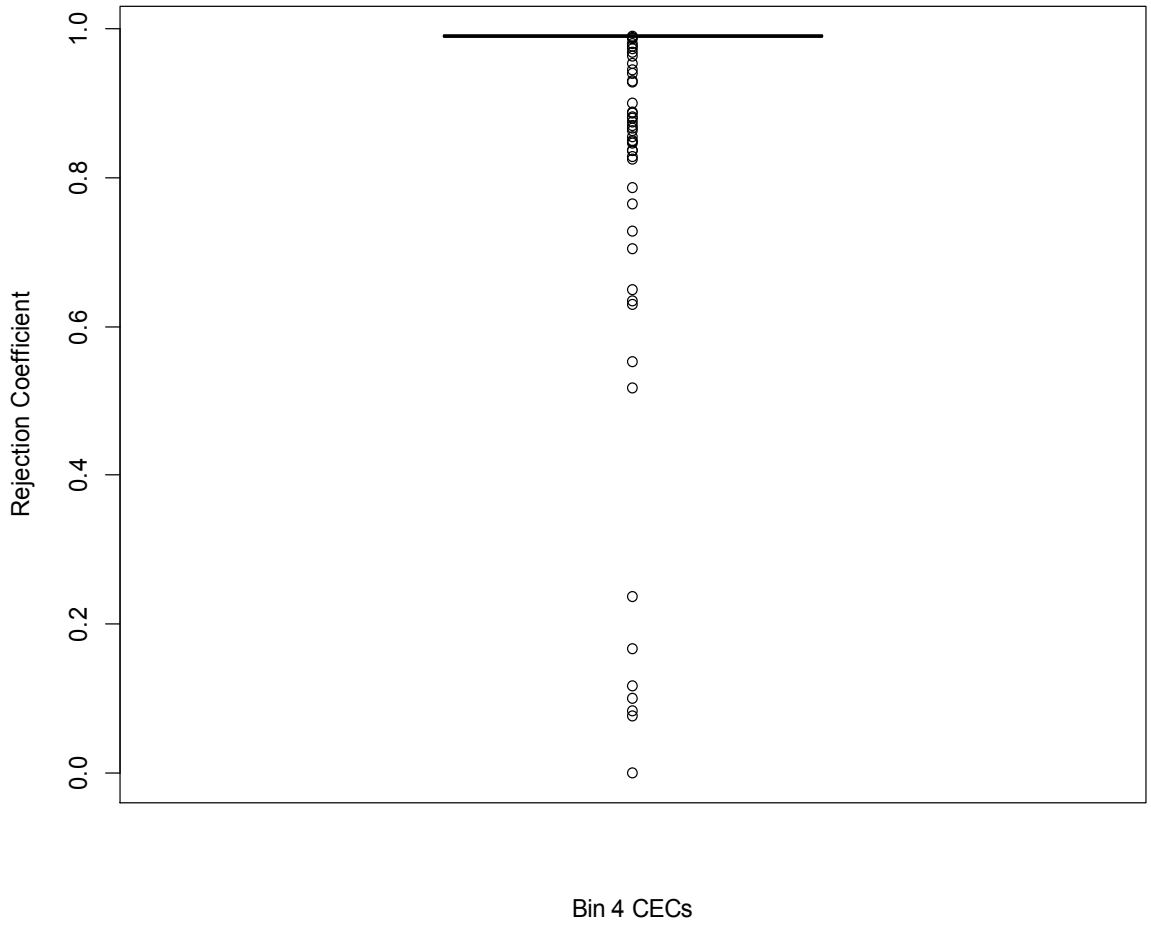


Figure 4-8: Distribution of Bin 4 CEC Rejection Coefficients

To better predict the rate of rejection of CECs that are less selective for NF, a regression model was fit to the subset of Bin 4 data where R<99% (excluding cases of 100% rejection). The resulting model applies the variable function log (K_{ow}/K_{aw}) to quantify the trend in increasing CEC rejection by NF with increasing K_{ow}/K_{aw}. Notably, the Bin 4 equation includes both hydrophobic and steric rejection functions.

$$\boldsymbol{R} = \begin{cases} \boldsymbol{\beta_1 log(\frac{K_{ow}}{K_{aw}}) + \beta_2 log(PSA)}, \ \boldsymbol{log\left(\frac{K_{ow}}{K_{aw}}\right) \leq 17} \\ \boldsymbol{100\%}, \ \boldsymbol{log\left(\frac{K_{ow}}{K_{aw}}\right) > 17} \end{cases} \quad \text{Eq. (4.2)}$$

Where:

β_1, β_2 = model coefficients

PSA = polar surface area

R = predicted CEC rejection by NF

The best-fit model parameter and corresponding summary statistics for the Bin 4 linear regression model are provided in Table 4-18 below. Summary statistics were calculated using statistical software (*R v.3.1.1*). Table 4-18 lists the estimated parameter coefficients and standard errors. The p-value was the test statistic used to assess the significance of the estimated mean in relationship to the null hypothesis (that the true mean is actually 0). A p-value less than 0.05 was considered highly significant, with 95% confidence.

Table 4-18: Summary Statistics for Bin 4 Equation

Parameter	Estimated Mean	Standard Error	p-value
β_1	0.05301	0.01520	0.0011
β_2	0.16502	0.07720	0.0380

4.4.4 Model Validation

With a predictive NF rejection model for Bin 4 CECs, a comparison of the predicted NF rejection of incompletely removed (Bin 4) CECs to observed NF rejection is a useful exercise for assessing model validity. Figure 4-9 shows a side-by-side comparison of observed Bin 4 CECs rejection, with the studied NF membrane, and model-predicted rejection.

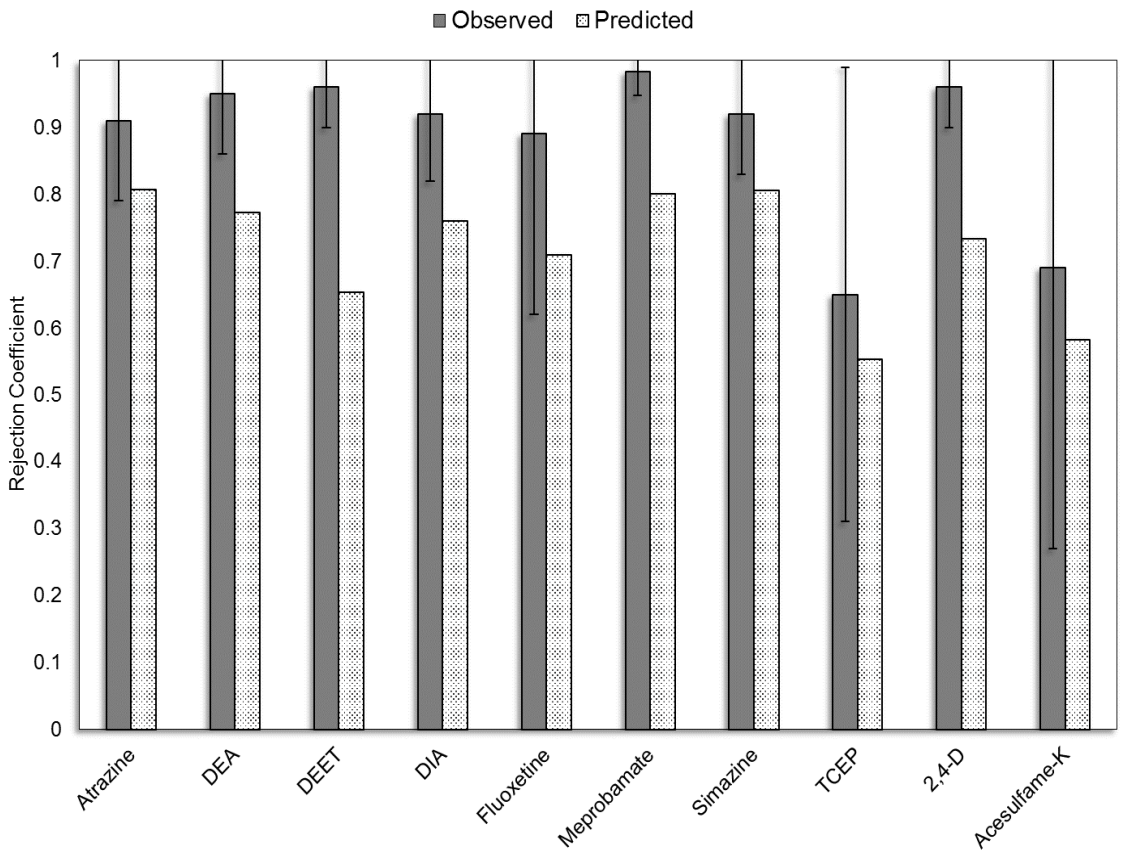


Figure 4-9: Observed (mean) Rejection for 10 Bin 4 CECs vs. Model Predicted

For all ten Bin 4-CECs examined, the QMPM slightly under-predicts the rate of NF rejection. This result was expected, considering the mean observed CEC rejection includes cases where rejection was 99% or more. The average under-prediction for each of the 10 CECs was 20% of the observed mean rejection coefficient. From a design and treatment selection perspective, this consistent under-prediction by the QMPM provides a necessary factor-of-safety when assessing the viability of NF to meet potential treatment and regulatory requirements for filtrate concentrations of monitored CECs.

4.5 Model Verification

The close proximity of modeled and observed CEC rejection for the Bin 4 CECs highlights the potential utility of this predictive QMPM model. For further validation, an

independent dataset for bench-scale NF rejection testing of CECs in purified water was selected for comparison. Yangali-Quintanilla published a dataset in 2010 that was collected from a similar bench-scale, membrane pressure cell testing apparatus. Although, a continuous cross-flow was applied to the membrane coupon, rather than dead-end operation. The NF membrane utilized by Yanagali-Quintanilla was very similar to the GE Osmonics DK membrane used for this research: commercially available (Dow-Filmtec NF-90), thin-film polyamide composite hydrophilic membrane with MWCO of 200 Da and negative zeta potential. However, relative to this thesis research, Yangali-Quintanilla's NF rejection study represents an idealized system for observing CEC rejection. The relative purity of the Yangali-Quintanilla water matrix makes it an applicable test case for the universality of the QMPM.

Yangali-Quintanilla's (2010) data set included the following QMPM Bin 4 CECs:

- **Phenacetin** (log K_{ow}/K_{aw}=9.6)
- Atrazine (log K_{ow}/K_{aw}=9.6)
- **Metronidazole** (log K_{ow}/K_{aw}=9.14)
- Caffeine (log K_{ow}/K_{aw}=8.77)
- Phenazone (log K_{ow}/K_{aw}=7.95)
- 4-Nonylphenol (log K_{ow}/K_{aw}=9.37)
- Ibuprofen (log K_{ow}/K_{aw}=9.18)

The constituents highlighted in **bold** were not present in the study set of 96 CECs analyzed in samples from Garland, Lawton, and Norman. For comparison, Figure 4-10 plots the observed CEC rejection with NF by Yangali-Quintanilla and subsequent predicted CEC rejection for these Bin 4 constituents.

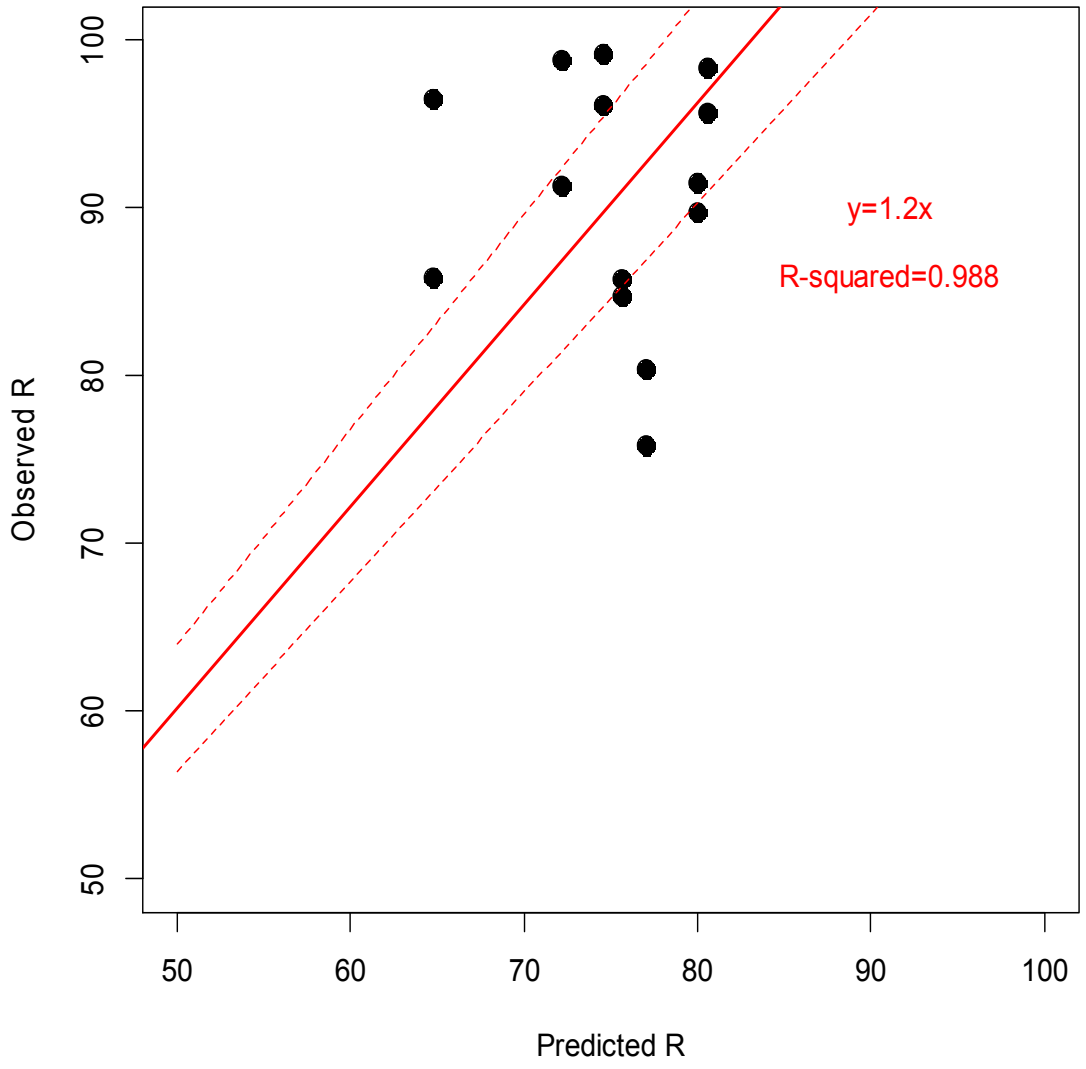


Figure 4-10: Observed Bin 4 CEC rejection (by NF) versus model-predicted CEC rejection for Yangali-Quintanilla (2010) data set. Red dashed lines depict upper and lower 95% confidence intervals on the regression line.

Despite testing the NF membrane in a different filtration mode (cross-flow vs. dead-end) with artificially spiked CECs in ideal, laboratory-grade water, the QMPM also under-predicts Yangali-Quintanilla's observed Bin 4 CEC rejection coefficients by 20%. As previously discussed, CECs that would be classified as Bin 4 according to QSAR are the most challenging to remove by tight TFC NF membranes. As such, some factor of safety (FOS) would be prudent. The utility of a predictive rejection model which provides a FOS for the most poorly rejected Bin

4 CECs is that it provides a conservative tool for assessing NF as treatment technology for potable reuse applications where numerical criteria for CECs in produced water are a likely eventual reality.

As opposed to *a priori* models of NF rejection, the QMPM is independent of membrane- or solution-specific properties. Thus, the developed model can be used to screen or select CECs that could be classified as Bin 4 contaminants and therefore most challenging to NF filtration. For I/DPR applications of NF, the window of CECs that must be analyzed for prior to design and monitored for during full-scale operation is reduced to the Bin 4 CECs that resist WRRF removal and are known to exist in the treated effluent water matrix.

The conservatism of the developed QMPM can be attributed to discounting the 100% NF rejection observations in the modeled data set for Bin 4 CECs. While it can be argued that this approach artificially lowers the predicted rejection of CECs by NF, the goal of this work was not to develop a multi-parameter, membrane-specific, fundamental mechanism model (which would provide inherently greater prediction precision), but to synthesize a simple, universal, CEC rejection prediction and screening tool. The ultimate success of the QMPM will depend on future application and improvement through NF pilot- and full-scale testing, and consequently the adoption of the QMPM by engineers and regulators for screening and selection of CECs for NF process monitoring during potable reuse water production.

As previously discussed, the QMPM is a departure from fundamental, first-principles-based solute rejection models for RO. Models based on SK theory and Fick's Law have been proven useful for developing a complete mass-balance of single solutes in an idealized membrane filtration system, typical of RO desalination applications. The complexity of predicting rejection of a mixed-liquor of trace organic solutes (i.e., CECs) in a constantly-

changing water matrix such as a reclaimed wastewater requires a more robust, universal modeling approach than fixed-film theory can provide. The Yangali-Quintanilla data set was purposely selected to validate the universality of the QMPM for conservative prediction of observed CEC rejection. By selecting chemical-specific QSAR prediction parameters, rather than membrane-specific properties, the QMPM can consistently predict the minimum rejection coefficient for recalcitrant trace organic wastewater contaminants regardless of the quality of the water matrix being filtered. While the QMPM is not a 'black box' solution and can be adapted to predict NF rejection of future CECs after identifying the solute's bin classification based on QSAR properties, it does not consider changes in membrane properties, such as irreversible fouling and swelling, due to aging and continued use. As such, the best application of the QMPM will be as a decision science screening tool for developing a priority list of CECs for testing and monitoring during NF application for I/DPR.

CHAPTER 5 - CONCLUSIONS AND FUTURE WORK

The objective of this research was to elucidate the recalcitrant CEC rejection performance of a commercially available tight thin-film composite (GE Osmonics DK) NF membrane in parallel with and relative to a typical water industry specified (GE Osmonics AG) RO membrane with actual secondary effluents from three WRRFs where the PWS managers are currently considering the addition of reuse water to their water supply portfolio. And, ultimately, the objective was to conceive and develop a novel but practical decision science tool, derived from CEC QSAR properties and membrane rejection mechanisms, for regulators, PWS managers, and designers to utilize when selecting barrier treatment technologies for the implementation of potable reuse systems.

5.1 Rejection Conclusions

Nanofiltration of WRRF SE was observed to meet published and regulated human health criterion for the CEC study set. As provided in Table 5-1, a factor of safety (FOS) greater than 30 was achieved for all CEC analytes. The FOS for CECs regulated by the US EPA NPDWR for potable water supply ranged from 125 to 2,059. The following discussion summarizes the observed rejection coefficients by CEC intended use classification.

Table 5-1: Human Health Criterion Factor of Safety with NF

CEC	Human Health Criterion[a] (ηg/L)	Observed NF Reuse Supply			NF Factor of Safety
		Minimum (ηg/L)	Mean (ηg/L)	Maximum (ηg/L)	
Ethinyl estradiol	5	Not detected in PE			--
17-β-estradiol	5	Not detected in SE			--
Estrone	320	ND	ND	ND	64
Cotinine	1,000	ND	ND	ND	100
Primidone	10,000	ND	ND	ND	2,000
Dilantin	2,000	ND	ND	ND	100
Meprobamate	200,000	ND	< 5	9	22,222
Atenolol	4,000	ND	< 5	27	148
Carbamazepine	10,000	5	12	19	526
Sucralose	150,000,000	ND	< 100	160	937,500
TCEP	5,000	ND	92	160	31
DEET	200,000	ND	< 5	21	9,524
Triclosan	50,000	ND	9	35	1,429
2,4-D	MCL: 70,000	ND	6	34	2,059
Atrazine	MCL: 3,000	ND	11	24	125
Simazine	MCL: 4,000	ND	11	31	129

[a]Adapted from NWRI, US EPA NPDWR.
MCL = maximum contaminant level. ND = not detected. PE = primary effluent. SE = secondary effluent.

For the study set of 96 CECs, 82 were detected above the corresponding MRL in the primary effluent. The 14 undetected CECs either did not exist at measurable concentration in the WRRF influent or were effectively removed by the WRRF primary treatment gravity separation barriers. Of significant relevance for potable reuse applications, 18 of the studied 96 CECs were fully (100%) removed by full-scale WRRF biological treatment. Conversely, 64 of the 96 studied

CECs were found to exist in the SE at recalcitrant residual concentrations above MRL. Of the recalcitrant CECs, mean rejection by the tested NF was 90% or higher for 53 of the 64. The other 11 CECs were rejected at a range from 46% to 89%. Notably, the tested RO membrane fully (100%) rejected all but 2 of the 64 recalcitrant CECs: Quinoline (89%) and Triclocarban (93%).

Rejection analyses of the EDCs revealed that most natural human hormones were readily removed to below MRL by the WRRF biological processes. Estrone was the only natural human hormone not fully biodegraded, and NF effectively rejected approximately half the remaining fraction. The other two recalcitrant EDCs were 4-tert-Octylphenol (surfactant) and BPA (plasticizer), for which the NF membrane was found to be a very effective barrier rejecting 90% to 95%. All three EDCs detected in NF permeate samples have a MW above the NF MWCO and are classified hydrophobic neutral, suggesting steric exclusion and hydrophobic sorption as the predominant rejection mechanisms.

NF proved very effective for the rejection (84% to 100%) of neutral-charged pharmaceuticals. With a neutral charge, this group of CECs is likely rejected by steric exclusion and some hydrophobic sorption, although the 100% exclusion of Acetaminophen (MW = 151 g/mol) by the NF test membrane was evidence molecular PSA may be a better QSAR indicator than MW for steric exclusion. With characteristically high MW (e.g., antibiotics) and ionic charge, the positive-charged pharmaceuticals were highly rejected (97% to 100%) by the tested NF membrane by steric and electrostatic exclusion. The recalcitrant negative-charged pharmaceuticals were also found to be highly rejected (97% to 100%) by the NF test membranes, via steric and electrostatic exclusion.

Representing caffeine and associated degradates of caffeine, nicotine, and chocolate, the stimulants group was somewhat surprisingly found to be in recalcitrant non-biodegraded trace

occurrence in secondary effluent samples. All studied stimulants were characterized as hydrophilic-neutral with relatively low molecular weights, thereby suggesting a possible challenge for NF membrane rejection. However, all stimulants but caffeine (97%) were rejected fully by the NF test membranes.

The preservatives group of CECs were QSAR characterized as relatively low MW and mostly hydrophobic neutral. Generally, such properties suggest the predominant membrane rejection mechanism for this group may be more sorption and less exclusion. Five of the eight studied preservatives were found to be 100% removed by WRRF biological treatment. Of the three recalcitrant preservatives, results indicated the two largest, Triclocarban and Triclosan, were highly rejected (95 to 100%) by the NF test membrane, with the ionic analyte (Triclosan) fully rejected. The third recalcitrant preservative, Quinoline, represented the smallest analyte (MW = 129 g/mol) in the study set of 96 CECs. Rejection analysis revealed good (89%) removal of Quinoline by the NF membrane.

The studied artificial sweeteners group included two hydrophilic neutral CECs. As suspected, this group of CECs was found to be resistent to biodegradation by the WRRFs and fully recalcitrant. Results indicated the larger sweetener, Sucralose, was highly rejected (99 to 100%) by the NF test membrane by steric exclusion. However, the smaller Acesulfame-K was rejected at 56%.

Similar to artificial sweeteners, the flame retardants were found to be highly recalcitrant in the WRRF secondary effluents. This group of CECs is QSAR characterized as moderate size and hydrophobic neutral. Mean rejection by NF of this group ranged from 55% for the smallest to 89% for the largest analyte.

The pesticides group of 18 CECs were QSAR characterized as relatively low to moderate in size, with MW ranging from 146 to 284 g/mol, and of neutral charge. Three of the 18 were not detected in the primary effluent, while two of the pesticides were found to be fully removed by the WRRF biological processes. The remaining 13 pesticides were found to be recalcitrant CECs in the secondary effluents. With the exception of Atrazine, the NF test membrane proved to be highly effective (92-100%) for rejection of the nine hydrophobic pesticides and slightly less effective (74-89%) for rejection of the four hydrophilic species.

5.2 Modeling Conclusions

A multi-level, multi-variable model was developed to predict the probable rejection coefficient ($R = 1 - C/C_0$) of recalcitrant CECs in secondary effluent with the studied NF membrane. The model was developed from predictor variables selected for their association with known membrane rejection mechanisms for organic solutes (size-exclusion, electro-static interactions, and hydrophobicity), CEC-specific chemical properties based on QSAR, and wastewater matrix characteristics of the samples. The resulting QMPM, as presented in Figure 5-1, was then successfully applied and verified to evaluate the mechanisms governing the rejection (by NF) of the studied recalcitrant CECs.

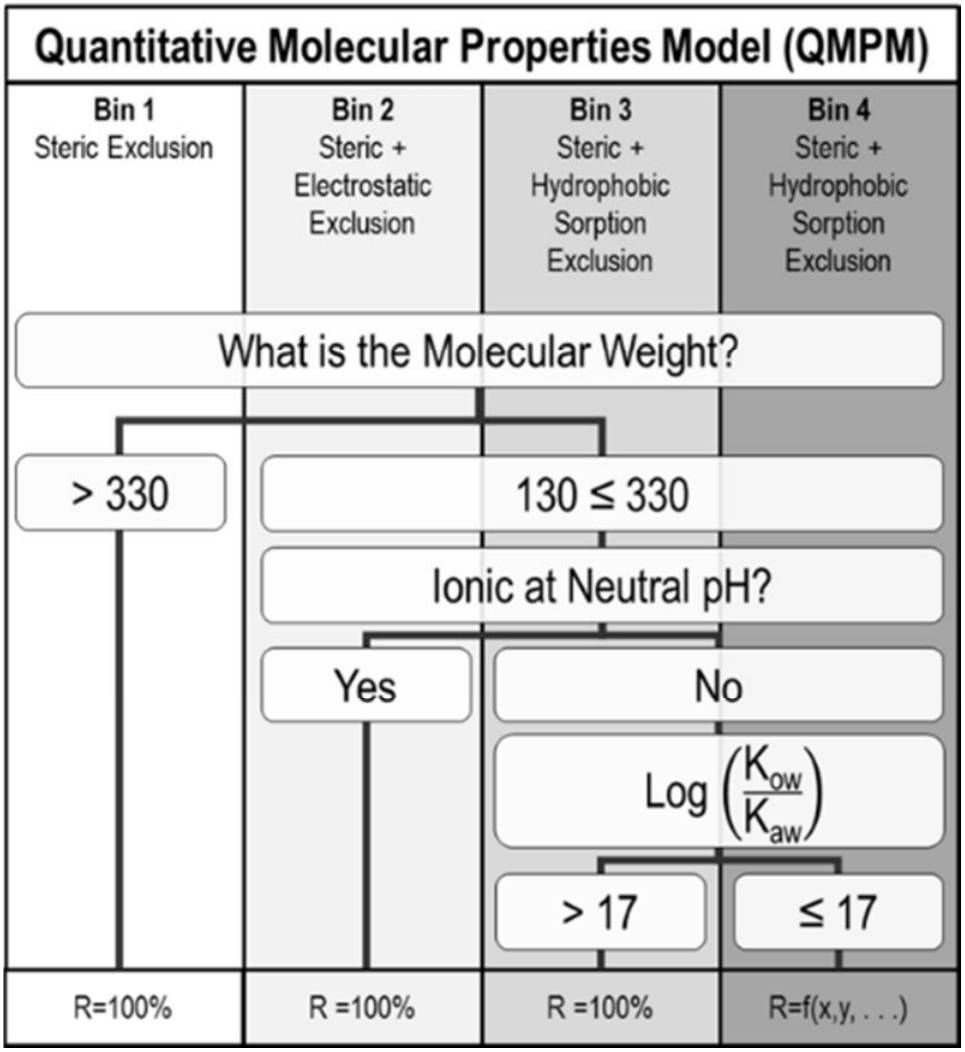


Figure 5-1: NF Quantitative Molecular Properties Model (QMPM)

Similar to other decision science tools released by the EPA for compliance with rules of the SDWA (e.g. SWTR, DBPR), a "bin" approach was adopted for development of the QMPM. Each of the four bins represents a unique set of conditions consisting of CEC QSAR properties and membrane rejection mechanisms. Figure 2 shows the respective bin classifications for the Norman 96.

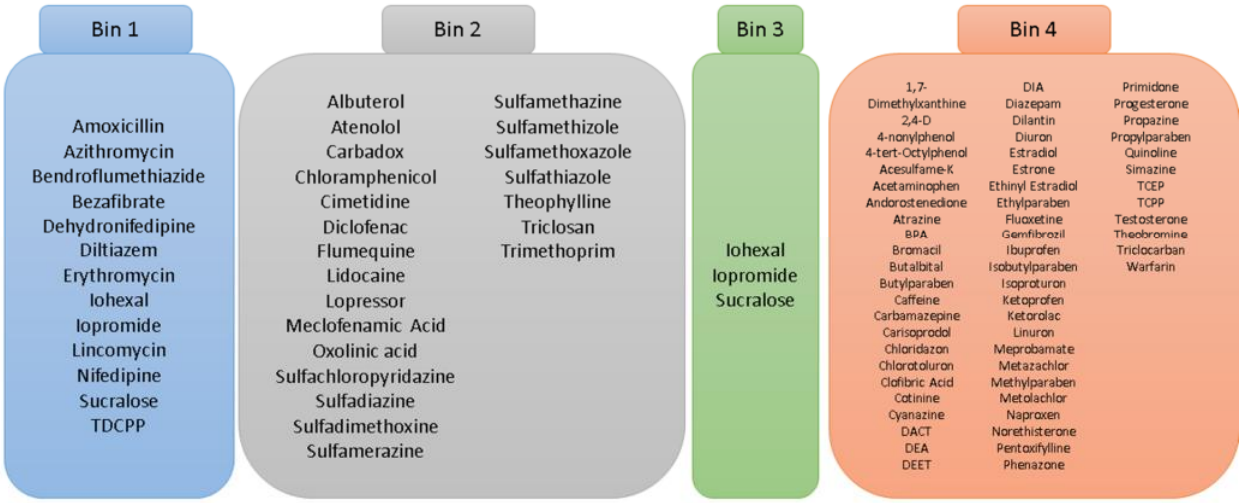


Figure 5-2: Bin Classification of Norman 96

For Bin 1, steric exclusion represents the predominant NF rejection mechanism. The model predicts 100% rejection of the larger CECs with a MW greater than or equal to 330 g/mol. A total of 10 CECs from the study set fell in Bin 1. Examples of large CECs captured by Bin 1 include antibiotics from the pharmaceuticals classification. With Bin 2, steric and electrostatic exclusion are the predominant rejection mechanisms. From the study set, a total of 30 CECs with a MW ranging 130-330 g/mol and an ionic charge (positive or negative) at neutral pH were fully rejected in Bin 2. These CECs consisted of the ionic pharmaceuticals and the preservative Triclosan.

For Bins 3 and 4, including over half the CEC study set, steric exclusion and hydrophobic sorption are the rejection mechanisms. The model predicts neutral charged CECs with a MW ranging 130-330 g/mol and hydrophobic, log (K_{ow}/K_{aw}) > 17, in nature will be rejected fully (100%) in Bin 3 by the hydrophilic NF test membrane, whereas the Bin 4 hydrophilic-neutral CECs with log (K_{ow}/K_{aw}) ≤ 17 were not fully rejected in many cases by the tested NF membrane.

As such, the QMPM predicts Bin 4 CECs are rejected at a rate as determined by the Equation 5.1.

$$R = 0.05301 \log (K_{ow}/K_{aw}) + 0.16502 \log (PSA) \qquad \text{Eq (5.1)}$$

Where:

PSA = polar surface area

R = Bin 4 predicted CEC rejection by NF

The QMPM-predicted rejection coefficients were validated against the observed data set. Furthermore, the QMPM was verified against the hydrophilic-neutral CEC data set reported by Yangali-Quintanilla in 2010. CECs that would be classified as Bin 4 according to QSAR are the most challenging to remove by tight TFC NF membranes. As such, some FOS would be prudent. A predictive rejection model which provides a FOS for the less highly rejected Bin 4 CECs is useful because it provides a conservative tool for assessing NF as treatment technology for I/DPR applications where numerical criteria for CECs in produced water are a likely eventual reality.

5.3 Future Work

The exhaustive literature review performed by EPA in 2014 of over 400 publications shows that zero full-scale and only 13 bench-scale NF membrane units were found from which to report CEC rejection. With the lack of knowledge, the default approach can be an over-conservative and cost-prohibitive design. Currently, RO in existing I/DPR treatment facilities is the default FAT barrier for CEC control. RO represents a major capital and O&M expense not seen with conventional technologies. Further, an RO system produces a brine reject waste that can represent new treatment/disposal challenges. However, the default RO approach to CEC control may be questioned if we consider new commercially available tight (i.e., MWCO ≤ 200

Da) TFC NF membranes. Tight NF membranes may provide suitable CEC rejection efficacies for less capital, O&M, power, and waste generated. Clearly, more research is required to ascertain if tight NF membranes can be acceptable FAT barriers for CEC control in potable reuse systems.

More research is required to assess the NF membrane sorption rejection mechanism of recalcitrant hydrophilic-neutral CECs in actual secondary effluents. Some bench-scale research has reported that NF membrane rejection can be overestimated if the sorption mechanism of a fresh membrane is not allowed to reach equilibrium (Kimura et al. 2003). Other bench-scale research has studied the sorption equilibrium effect and reported only nominal differences (i.e., <1 to 5%) in CEC rejection with and without adsorption equilibrium (Yangali-Quintanilla 2010). This researcher also reported a fouled NF membrane could produce higher hydrophilic-neutral CEC rejection coefficients than a fresh membrane. For bench-scale testing, a cross-flow apparatus must be utilized if the sorption mass is to be determined. However, bench-scale testing cannot simulate the sorption rejection recovery effect of a pilot or full-scale NF membrane following backwash, maintenance clean, or clean-in-place. As such, NF pilot or full-scale testing to research the rejection of recalcitrant hydrophilic-neutral CECs is recommended.

Regarding future work in NF predictive modeling, Mohammad and his research team reported that

> … the overwhelming majority of NF predictive rejection models to date are inadequate because they have been developed with idealized solutions typically containing only 2, 3, or sometimes 4 solutes. If accurate modeling of concentrated multi-solute solutions realistic of industrial processing is to become common place then more effort needs to be placed into modeling systems of real industrial relevance. (Mohammad et al. 2015)

As such, future work is recommended with WRRF secondary effluent matrices (not synthetic lab solutions) and recalcitrant occurring (not spiked) CECs at environmentally relevant ηg/L concentrations.

And finally, more work is required to determine human health criterion based MCLs for high-risk CECs. Treatment goals should be based on human health, rather than setting treatment goals as full (100%) rejection of MRL as established by the latest analytical methods. Complete removal of all chemicals is impractical (Tchobanoglous et al. 2015).

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APPENDIX A

A-1: Recommended CEC Control Indicators for DPR Systems

A-2: UCMR3 NCOD Summary

A-3: USEPA Draft CCL4 List of 100

Table A-1: Recommended CEC Control Indicators for DPR Systems

CEC	Criterion	Rationale
Atazine	3 ug/L	NPDWS MCL
2,4-D (dichlorophenooxyacetic)	70 ug/L	
Methoxychlor	40 ug/L	
Simazine	4 ug/L	
Perfluorooctanoic acid	0.4 ug/L	U.S. EPA health advisory
Perfluorooctane sulfonate	0.2 ug/L	
Perchlorate	6 ug/L	CDPH MCL
1,4-Dioxane	1 ug/L	CSWRCB notification
Ethinyl estradiol	None yet, but MCL will approach MRL (low ng/L)	Evaluate presence in source water
17β-estradiol		
Cotinine	1 ug/L	Surrogate for low MW CECs
Primidone	10 ug/L	
Phenyltoin	2 ug/L	
Meprobamate	200 ug/L	Occurs frequently at ng/L level
Atenolol	4 ug/L	
Carbamazepine	10 ug/L	Unique structure
Estrone	320 ng/L	Surrogate for steroids
Sucralose	150,000 ug/L	Surrogate for neutral solutes w/ moderate MW
Tris (2-Carboxyethyl phosphine) hydrochloride	5 ug/L	MDH 2015 guidance value
N,N-diethyl-meta-toluamide	200 ug/L	
Triclosan	2,100 ug/L	NRC 2012 risk-based action level

Source: WRRF 2015; NWRI 2013

Table A-2: UCMR3 NCOD Summary (U.S. EPA, June 2015)

Contaminant	MRL[1]	Reference Concentration [1]	Total number of results	Number of results ≥MRL	Number of results >Reference Concentration	% of total results >Reference Concentration	Total number of PWSs with results	Number of PWSs with results ≥MRL	Number of PWSs with results >Reference Concentration	% of PWSs with results >Reference Concentration
1,2,3-trichloropropane	0.03	0.0004 / 0.04[2]	28,901	217	217 / 168[2]	0.8% / 0.6%[2]	4,398	59	59 / 50[2]	1.3% / 1.1%[2]
1,3-butadiene	0.1	0.0103 / 1.03[2]	28,901	1	1 / 0[2]	0.003% / 0%[2]	4,398	1	1 / 0[2]	0.02% / 0%[2]
Chloromethane	0.2	2.69 / 269[2]	28,899	209	18 / 0[2]	0.06% / 0%[2]	4,398	108	7 / 0[2]	0.2% / 0%[2]
1,1-dichloroethane	0.03	6.14 / 614[2]	28,900	686	1 / 0[2]	0.003% / 0%[2]	4,398	209	1 / 0[2]	0.02% / 0%[2]
Bromomethane	0.2	140	28,900	98	0	0%	4,398	45	0	0%
HCFC-22	0.08	N/A	28,901	661	--	--	4,398	245	--	--
Halon 1011	0.06	90	28,901	539	0	0%	4,398	260	0	0%
1,4-dioxane	0.07	0.35 / 35[2]	28,702	3,350	882 / 0[2]	3.1% / 0%[2]	4,394	943	294/ 0[2]	6.7% / 0%[2]
Vanadium	0.2	21	49,219	29,617	1,402	2.8%	4,413	3,185	145	3.3%
Molybdenum	1	40	49,230	20,473	121	0.2%	4,413	2,261	31	0.7%
Cobalt	1	70	49,216	722	3	0.006%	4,413	215	3	0.07%
Strontium	0.3	1,500	49,157	48,982	1,312	2.7%	4,413	4,412	247	5.6%
Chromium	0.2	100	49,094	24,791	1	0.002%	4,413	3,220	1	0.02%
Chromium-6	0.03	N/A	49,159	36,992	--	--	4,425	3,899	--	--
Chlorate	20	210	49,172	27,459	7,574	15.4%	4,412	2,994	1,590	36%
PFOS	0.04	0.2	29,076	234	31	0.1%	4,418	87	17	0.4%
PFOA	0.02	0.4	29,075	287	0	0%	4,418	94	0	0%
PFNA	0.02	N/A	29,076	17	--	--	4,418	13	--	--
PFHxS	0.03	N/A	29,076	176	--	--	4,418	52	--	--
PFHpA	0.01	N/A	29,076	193	--	--	4,418	70	--	--
PFBS	0.09	N/A	29,076	8	--	--	4,418	5	--	--
17β-estradiol	0.0004	0.0009 / 0.09[2]	9,027	3	1 / 0[2]	0.01% / 0%[2]	961	1	1 / 0[2]	0.1% / 0%[2]
17α-ethynylestradiol	0.0009	0.035	9,028	3	0	0%	961	3	0	0%
Estriol	0.0008	0.35	9,027	1	0	0%	961	1	0	0%
Equilin	0.004	0.35	9,028	0	0	0%	961	0	0	0%
Estrone	0.002	0.35	9,028	0	0	0%	961	0	0	0%
Testosterone	0.0001	N/A	9,027	51	--	--	961	45	--	--
4-androstene-3,17-dione	0.0003	N/A	9,028	73	--	--	961	55	--	--

[1]Measured in µg/L (ppb)
[2]Where two reference concentrations are listed, the first number is associated with a 10^{-4} cancer risk; the second number a 10^{-6} cancer risk.
Where two results are presented the first number is associated with the first reference concentration; the second number is associated with the second reference concentration.

Table A-3: Draft CCL4 – Chemical Contaminant List

Compound	CASRN	Compound	CASRN
1,1,1,2-Tetrachloroethane	630-20-6	Captan	133-06-2
1,1-Dichloroethane	75-34-3	Chlorate	14866-68-3
1,2,3-Trichloropropane	96-18-4	Chloromethane	74-87-3
1,3-Butadiene	106-99-0	Clethodim	110429-62-4
1,4-Dioxane	123-91-1	Cobalt	7440-48-4
17 alpha-Estradiol	57-91-0	Cumene hydroperoxide	80-15-9
1-Butanol	71-36-3	Cyanotoxins	N/A
2-Methoxyethanol	109-86-4	Dicrotophos	141-66-2
2-Propen-1-ol	107-18-6	Dimethipin	55290-64-7
3-Hydroxycarbofuran	16655-82-6	Disulfoton	298-04-4
4,4-Methylenedianiline	107-77-9	Diuron	330-54-1
Acephate	30560-19-1	Equilenin	517-09-9
Acetaldehyde	75-07-0	Equilin	474-86-2
Acetamide	60-35-5	Erythromycin	114-07-8
Acetochlor	34256-82-1	Estradiol	50-28-2
ESA acid	187022-11-3	Estriol	50-27-1
Acetochlor OA acid	194992-44-4	Estrone	53-16-7
Acrolein	107-02-8	Ethinyl Estradiol	57-63-6
Alachlor ESA acid	142363-53-9	Ethoprop	13194-48-4
Alachlor OA acid	171262-17-2	Ethylene glycol	107-21-1
alpha-Hexachlorocyclohexane	319-84-6	Ethylene oxide	75-21-8
Aniline	62-53-3	Ethylene thiourea	96-45-7
Bensulide	741-58-2	Fenamiphos	22224-92-6
Benzyl chloride	100-44-7	Formaldehyde	50-00-0
Butylated hydroxyanisole	2501316-5	Germanium	7440-56-4

Table A-3: Draft CCL4 – Chemical Contaminant List (Cont.)

Compound	CASRN	Compound	CASRN
Halon 1011	74-97-5	n-Propylbenzene	103-65-1
HCFC-22	75-45-6	o-Toluidine	95-53-4
Hexane	110-54-3	Oxirane, methyl-	75-56-9
Hydrazine	302-01-2	Oxydemeton-methyl	301-12-2
Manganese	7439-96-5	Oxyfluorfen	42874-03-3
Mestranol	72-33-3	PFOS	1763-23-1
Methamidophos	10265-92-6	PFOA	335-67-1
Methanol	67-56-1	Permethrin	52645-53-1
Methyl bromide	74-83-9	Profenofos	41198-08-7
MTBE	1634-04-4	Quinoline	91-22-5
Metolachlor	51218-45-2	RDX	121-82-4
Metolachlor ESA acid	171118-09-5	sec-Butylbenzene	135-98-8
Metolachlor OA acid	152019-73-3	Tebuconazole	107534-96-3
Molinate	2212-67-1	Tebufenozide	112410-23-8
Molybdenum	7439-98-7	Tellurium	13494-80-9
Nitrobenzene	98-95-3	Thiodicarb	59669-26-0
Nitroglycerin	55-63-0	Thiophonate-methyl	23564-05-8
N-Methyl-2-pyroidone	872-50-4	Tolulene diisocyanate	26471-62-5
NDEA	55-18-5	Tribufos	78-48-8
NDMA	62-75-9	Triethylamine	121-44-8
NDPA	621-64-7	TPTH	76-87-9
N-Nitrosodimethylamine	86-30-6	Urethane	51-79-6
NPYR	930-55-2	Vanadium	7440-62-2
Nonylphenol	25154-52-3	Vinclozolin	50471-44-8
Norethindrone	68-22-4	Ziram	137-30-4

Source: Federal Register, Vol.80, No.23, Wed, February 4, 2015

APPENDIX B

Exhibit B-1: WRRF Operational Data

Exhibit B-2: Sample Naming Convention

Exhibit B-3: Laboratory Sampling and Packaging

Exhibit B-4: Sample Shipping Destinations

Exhibit B-5: Nanofiltration Membrane (DK) Manufacturer Data Sheet

Exhibit B-6: Reverse Osmosis Membrane (AG) Manufacturer Data Sheet

Exhibit B-7: MAST Lab Results – Test Membrane Properties

Exhibit B-8: Eurofins Eaton Analytical Certifications

Exhibit B-1: WRRF Operational Data

Parameter	COK						NTX						SOK					
	August MOR			September MOR			August MOR			September MOR			August MOR			September MOR		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Inf. Q (MGD)	11.73	14.41	13.14	11.61	13.87	12.97	15.7	28.4	20.98	9	20	17.4	8.83	10.55	9.39	8.2	10.69	9.12
Inf. BOD (mg/L)	176	251	209	185	256	219	116	257	178.4	89	230	146.3	22	390	209.76	119	444	222.32
Eff. BOD (mg/L)	2	16	3	2	7	3	2	5.1	2.85	2.1	3.5	2.5	3	6	3.83	3	6	4.2
Inf. Temp. (C)	24.7	32.5	29.3	23.5	26	24.9	25.2	27.5	26.5	23.6	27.4	25.9	*Data Not Available*					
Inf. COD (mg/L)	*Data Not Available*						319	776	567.3	198	590	380.7	230	464	331.33	362	474	428
Eff. COD (mg/L)	*Data Not Available*						60.5	90.7	74.5	50.6	90.8	63.5	29	31	30	37	375	153
Inf. VSS (mg/L)	*Data Not Available*						136	376	245.9	96	320	183	*Data Not Available*					
Inf. TSS (mg/L)	68	172	135	92	168	136	144	612	295.2	104	372	216.9	52	298	205	144	416	232
MLSS (mg/L)	3970	5726	4843	3866	6293	4995	1190	2680	1644	1480	2080	1759	1340	2160	1971	1400	2890	2020
SRT (Days)	10.5	11.1	10.7	9.2	14.4	10.9	6.5	34.7	11.8	5.77	55.5	13.7	1.74	4.5	3.35	2.14	4.51	3.34
Inf. TKN (mg/L)	*Data Not Available*						9.5	33.7	26.6	28	35.8	30.8	*Data Not Available*					
Inf. Total P)mg/L)	*Data Not Available*						*Data Not Available*						4.43	6.17	5.34	4.43	6.17	5.34

Exhibit B-2: Sample Naming Convention

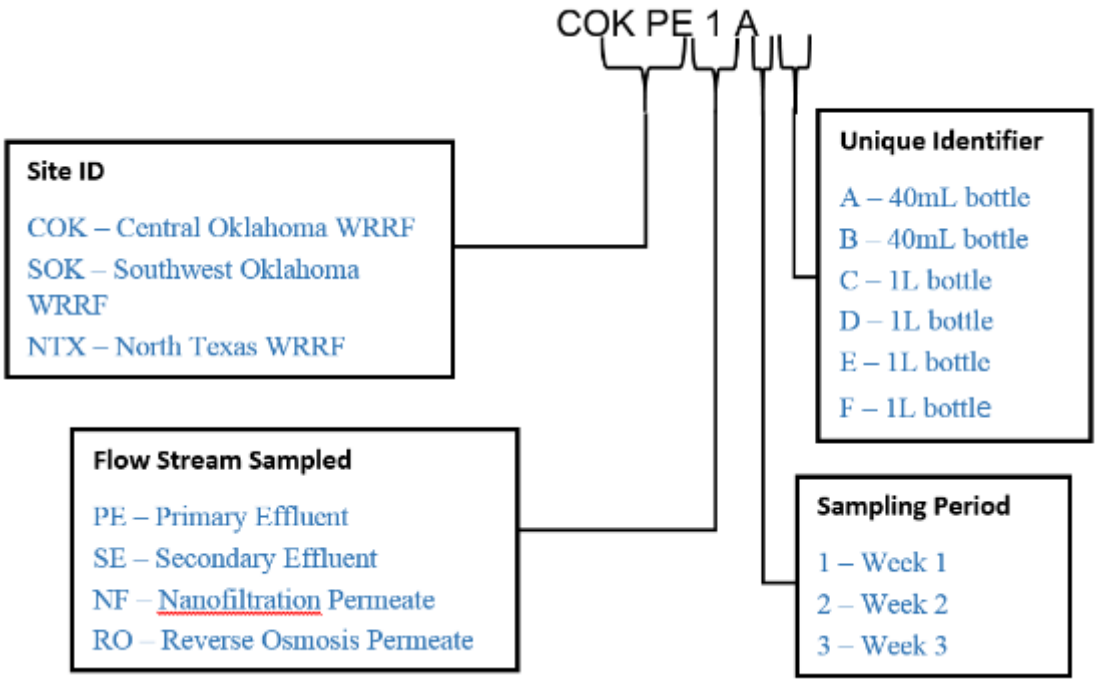


Exhibit B-3: Laboratory Sampling and Packaging Instructions

eurofins | Eaton Analytical	PPCP Sample Collection Protocols	Sampling Instruction No. 33 Revision Date: 10/22/13 Page 1 of 2

1. a) FREEZE GELPAKS UPON RECEIPT OF SAMPLE KIT AND ADD FROZEN GELPAKS TO THE COOLER ON THE DAY OF SAMPLING.
   b) WHEN SAMPLING, BRING OTHER AVAILABLE BAGGED WET ICE IN SEALED BAGS OR FROZEN GELPAKS TO CHILL SAMPLES DURING SAMPLE COLLECTION.

2. The sampler will receive a sample kit from our lab as follows:
   2 x 40 ml amber vials with preservative are provided for the small volume test, **or**
   2 x 500 ml or 1L amber glass bottles with preservative are provide for large volume tests

   Upon special request, our lab might include one or both additional kits below:
   Field Blank (FB) or Equipment blank (EB): 1 container filled with DI water and 1 container of FB/EB Sample Bottle

   Note: Sample bottle contains toxic preservatives to prevent biological degradation of PPCP. Be sure to NOT rinse out the container. Preservatives vary, depending upon the matrix being sampled and the target analyte(s).

3. We are measuring compounds at ng/L levels, so it is very prone to contamination. **Please take additional precautions below when sampling for PPCPs**
   a) Put on powderless nitrile gloves at all times, during sampling and processing. Change to clean gloves with each change in activity to avoid potential glove contamination.
   b) Avoid touching or even breathing into the samples and/or equipment.
   c) Avoid direct contact between yourself (including clothing) and the sample, sampling device, and processing equipment. Clothing is a source of detergents, fragrances, and fire retardants
   d) On the day of sampling activities, avoid contact with or consumption of the products listed below. Where contact with or consumption of these products is unavoidable, the collection of field blanks is strongly recommended.

   Wastewater and Personal Care or Pharmaceutical Product compounds:
   - Soaps and detergents, including antibacterial cleansers
   - DEET (active ingredient in most insect repellents)
   - Fragrances (cologne, aftershave, perfume)
   - Caffeine or Sweeteners (coffee, tea, colas)
   - Prescription drugs, medications, and hormonal substances
   - Over-the-counter medication
   - Human antibiotics
   - Veterinary antibiotics
   - Tobacco
   - Sunscreen
   - Antibiotics

4. If your kits include any additional blank samples, please follow the special instruction below:
   Field Blank (FB):
   - Transfer the DI water provided with your sample kit into the FB sample bottle.
   - Cap both containers and return them to the laboratory.

   Equipment Blank(EB):
   - Pour the DI water provided with your sample kit into the equipment (i.e. bailer or other non-tap sampling device) and transfer it into the EB sample bottle(s).
   - Cap all containers and return them to the laboratory.

5. Use indelible ink to clearly identify the sample bottles with the information listed below.
   - Client Name
   - Sample ID
   - Source of sample, if not already on label
   - Analysis required, if not already on label
   - Date and Time of collection
   - Preservative used, if not already on label

6. If sampling from a faucet,
   a) Remove the aerator, screen and/or hose attachments.
   b) Open the tap and let the water of the sample source run at fast flow for approximately 5 minutes.

Exhibit B-3: Laboratory Sampling and Packaging Instructions (Cont.)

c) Slow water flow to thickness of a pencil (to minimize splashing) and fill sample bottles.

7. Fill sample bottles to the base of the neck. Make sure the mouth of the bottle does not come in contact with anything other than the sample water. **DO NOT RINSE OUT PRESERVATIVE.**

8. Cap and invert the bottles at least 5 times to mix the sample and preservative.

9. Use indelible ink to clearly identify the sample bottles with the information listed below.
   - Client Name
   - Sample ID
   - Source of sample, if not already on label
   - Analysis required, if not already on label
   - Date and Time of collection
   - Preservative used, if not already on label

10. Store at 1-4˚C but above the freezing point of water for a minimum of 2 hours until transported to the lab. Note that some test suites do not require chilling. Check with your analytical service manager for details.

11. If sampling **NOT** from a faucet, please follow the following instruction to collect and process the sample(s):
    a) Select sampling and processing equipment made of fluorocarbon polymers, glass, aluminum, or stainless steel. **Avoid** equipment made of Tygon, polyethylene, or other plastics.
    b) Clean equipment thoroughly before use.
    c) Use non-antibacterial detergents.
    d) Take extra care to ensure that equipment is copiously rinsed with deionized (DI) water after the detergent wash. (Detergents are a source of interference in the analysis of pharmaceutical compounds and may include a target analyte (triclosan) of the method.)
    e) Follow the DI water rinse with a methanol rinse. Collect the used methanol solution into an appropriate container for disposal.
    f) **DO NOT** clean or field-rinse the sample bottles from the laboratory.
    g) And follow steps 7-10 above.

SAMPLE SHIPPING AND STORAGE

1. If shipping samples on the same day of sampling, chill samples until ≤6˚C by exchanging the ice used during sampling with available sealed bags of fresh frozen ice or frozen gelpaks.

2. **Pack chilled samples** in a cooler with **FROZEN** gelpaks or sealed bags of **WET ICE**.

3. Complete the Chain of Custody during sample collection. Place Kit Order and completed Chain of Custody in a ziplock bag in the cooler on top of packing material. The following information is required on the completed Chain of Custody.
   - Collector's name & signature
   - Client Name
   - Sample site
   - Date and time of collection
   - Comments about the sample, if applicable
   - Sample type

4. **Ship via overnight service such as FEDEX, UPS, or DHL, etc.** Maintain an environment at ≤6˚C but above the freezing point of water during transit. It is recommended that samples arrive within 48 hours of sampling, with no more than 40 hours for transit.

5. If samples are received on the same day as collection, temperature may be >10˚C with evidence of cooling.

6. Maximum **HOLDING TIME FOR SAMPLES** varies by test list, but it is generally **30 days** from time of collection.

7. Alternatively, cool the samples down by placing them **overnight** in a cooler with frozen refrigerant packs or water ice, or in a refrigerator (store chilled for at least 12 hours before packing for shipment). Maintain the cold samples until repacked in the cooler for shipment to the lab.

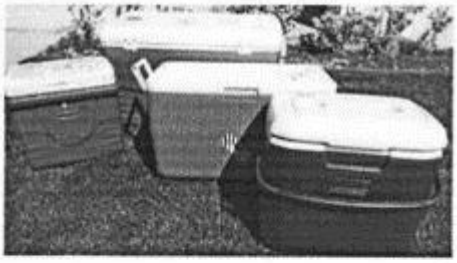
Exhibit B-3: Laboratory Sampling and Packaging Instructions (Cont.)

eurofins | Eaton Analytical	Wet Ice Packing Instructions	Sampling Instruction No. 34 Revision Date: 03/14/2014 Page 1 of 2

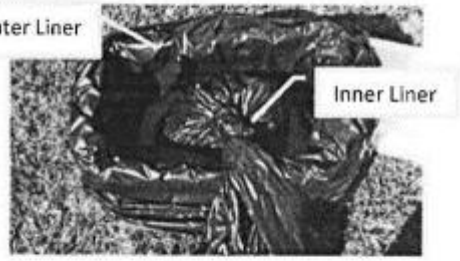
Wet Ice Packing Instructions

Courier delivery service (i.e. FEDEX or UPS) will NOT transport LEAKING Coolers. It is very important that the wet ice is all contained in sealed bags.

Packing Instructions for Larger Coolers (16 or 28 or 48 or 70 Quarts)



1) After sampling, insert sample containers back into original bubble wrap, Ziploc style bags, or other inserts.
2) Your kits should include 2 large heavy-weight plastic bags.
3) Place the first large bag in the interior of the cooler. This bag will be your "*outer liner*." No water or ice should be placed outside this bag.
4) Pour in some wet ice in a single layer to cover the bottom of the outer liner.
5) Add a second large bag to the cooler so that it fits inside the *outer liner*. The second bag will be your "*inner liner*."



6) Place bagged samples inside the inner liner.
7) Tie a knot at the top of the inner bag around the sample containers.
8) Pour ice onto and around the inner liner to fill up any empty spaces on the outside of the inner liner until the cooler is full. The ice should fill up about 30-50% of the content of cooler. Make sure that there are enough loose ends to tie the outer liner in a knot
9) Tie a knot at the top of the outer liner in a manner that ensures there will be no leakage.
10) Place completed Chain of Custody and Kit Order in a Ziploc bag and place them in the cooler on top of the outer liner.
11) Ensure contents will not move too much when cooler is closed.
12) Secure shut the cooler with packing tape before you ship it out.

Exhibit B-3: Laboratory Sampling and Packaging Instructions (Cont.)

eurofins | Eaton Analytical	Wet Ice Packing Instructions	Sampling Instruction No. 34 Revision Date: 03/14/2014 Page 2 of 2

Packing Instructions for Smaller Coolers (5 or 8 Quarts)

1) After sampling insert sample containers into original bubble wrap, Ziploc style bags or other inserts.
2) Your kits should include empty Ziploc style bags. Fill these bag(s) with fresh wet ice and seal the bag(s). The ice should take up 30-50% of the cooler.
3) Place sealed sample containers and ice bags in the cooler.
4) Place completed Chain of Custody and Kit Order in a Ziploc bag and place them in the cooler on top of the samples/ice.
5) Ensure contents will not move too much when cooler is closed.
6) Secure shut the cooler with packing tape before you ship it out.

Exhibit B-4: Sample Shipping Destinations

Osmonics Membrane Test Samples:

GE Osmonics Water & Process Technologies

5951 Clearwater Drive

Minnetonka, MN 55343

Eurofins Laboratory Analysis Samples Destination:

Eurofins Eaton Analytical, Inc.

750 Royal Oaks Drive,

Monrovia, CA 91016

Exhibit B-5: Nanofiltration (NF) Membrane (DK) Manufacturer Data Sheet

GE Power & Water
Water & Process Technologies

Fact Sheet

DK Series

Industrial High Rejection Nanofiltration Elements

The D-Series family of proprietary thin-film nanofiltration membrane elements is characterized by an approximate molecular weight cut-off of 150-300 Dalton for uncharged organic molecules. Divalent and multivalent anions are preferentially rejected by the membrane while monovalent ion rejection is dependent upon feed concentration and composition. Since monovalent ions pass through the membrane, they do not contribute to the osmotic pressure, thus enabling D-Series nanofiltration membrane systems to operate at feed pressures below those of RO systems.

Among other applications DK High Rejection NF Elements are used for dye removal/concentration, sodium chloride diafiltration and metals recovery.

Model	Spacer mil (mm)	Active area ft² (m²)	Outer wrap	Part number
DK2540C30	30 (0.76)	28 (2.6)	Cage	1206918
DK2540C50	50 (1.27)	18 (1.6)	Cage	1206919
DK2540F30	30 (0.76)	28 (2.6)	Fiberglass	1206925
DK2540F50	50 (1.27)	18 (1.6)	Fiberglass	1206926
DK4040C30	30 (0.76)	98 (9.1)	Cage	1206947
DK4040C50	50 (1.27)	65 (6.0)	Cage	1206946
DK4040F30	30 (0.76)	98 (9.1)	Fiberglass	3050075
DK4040F50	50 (1.27)	65 (6.0)	Fiberglass	3050073
DK8040C30	30 (0.76)	347 (32.1)	Cage	1206978
DK8040C50	50 (1.27)	270 (25.1)	Cage	1206979
DK8040F30	30 (0.76)	390 (36.2)	Fiberglass	1206993
DK8040F50	50 (1.27)	272 (25.3)	Fiberglass	1206994

Table 1: Element Specification

Membrane	D-Series, Thin-film membrane (TFM*)

Model	Average permeate flow gpd (m3/day)[1,2]	Minimum $MgSO_4$ rejection [1,2]
DK2540C30	560 (2.1)	98%
DK2540C50	350 (2.3)	98%
DK2540F30	540 (2.0)	98%
DK2540F50	340 (1.3)	98%
DK4040C30	2,000 (7.6)	98%
DK4040C50	1,300 (4.9)	98%
DK4040F30	2,000 (7.6)	98%
DK4040F50	1,300 (4.9)	98%
DK8040C30	6,900 (21.1)	98%
DK8040C50	5,400 (20.4)	98%
DK8040F30	7,800 (30.0)	98%
DK8040F50	5,400 (20.4)	98%

[1] Average salt rejection after 24 hours operation.
Individual flow rate may vary ±25%
[2] Testing conditions: 2,000ppm $MgSO_4$ solution at 110psi (760kPa) operating pressure, 77 °F (25°C), 15 % recovery.

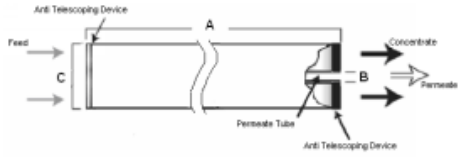


Figure 1: Element Dimensions Diagram – Female

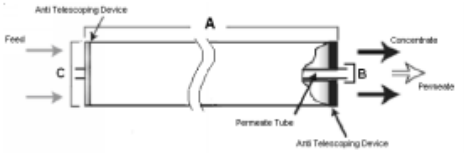


Figure 2: Element Dimensions Diagram – Male

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Exhibit B-5: Nanofiltration (NF) Membrane (DK) Manufacturer Data Sheet (Cont.)

Table 2: Dimensions and Weight

Model[1]	Dimensions, inches (cm)			Boxed
	A	B[2]	C[3]	Weight lbs (kg)
DK2540C30	40.0 (101.6)	0.75 (1.90) OD	2.4 (6.1)	4 (1.8)
DK2540C50	40.0 (101.6)	0.75 (1.90) OD	2.4 (6.1)	4 (1.8)
DK2540F30	40.0 (101.6)	0.75 (1.90) OD	2.4 (6.1)	4 (1.8)
DK2540F50	40.0 (101.6)	0.75 (1.90) OD	2.4 (6.1)	4 (1.8)
DK4040C30	40.0 (101.6)	0.625 (1.59)	3.9 (9.9)	9 (4.1)
DK4040C50	40.0 (101.6)	0.625 (1.59)	3.9 (9.9)	9 (4.1)
DK4040F30	40.0 (101.6)	0.75 (1.90) OD	3.9 (9.9)	9 (4.1)
DK4040F30	40.0 (101.6)	0.75 (1.90) OD	3.9 (9.9)	9 (4.1)
DK8040C30	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	29 (13.2)
DK8040C50	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	29 (13.2)
DK8040F30	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	29 (13.2)
DK8040F50	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	29 (13.2)

[1]These elements are dried then bagged before shipping.
[2]Internal diameter unless specified OD (outside diameter).
[3]The element diameter (dimension C) is designed for optimum performance in GE pressure vessels. Other pressure vessel dimension and tolerance may result in excessive bypass and loss of capacity.

Table 3: Operating and CIP parameters

Typical Operating Flux	5 - 20 GFD (8 - 34 LMH)
Maximum Operating Pressure	600psi (4,137kPa) if T<95°F (35°C) 435psi (3,000kPa) if T>95°F (35°C)
Maximum Temperature	Continuous operation: 122°F (50°C) Clean-In-Place (CIP): 122°F (50°C)
pH Range	Continuous operation: 3-9 Clean-In-Place (CIP): 2-10.5
Maximum Pressure Drop	Over an element: 15psi (103kPa) Per housing: 60psi (414kPa)
Chlorine Tolerance	500 ppm hours, dechlorination recommended

Exhibit B-6: Reverse Osmosis (RO) Membrane (AG) Manufacturer Data Sheet

GE Power & Water
Water & Process Technologies

Fact Sheet

AG HR Series

High Rejection Brackish Water RO Elements

The A-Series family of proprietary thin-film reverse osmosis membrane is characterized by high flux and high sodium chloride rejection. AG HR brackish water elements are selected when high rejection and operating pressures as low as 200 psi (1,379 kPa) are desired. These elements are recommended for brackish water with salt concentration (TDS) levels between 1,000 and 10,000mg/l or when very high salt rejection of monovalent ions is required.

Table 1: Element Specification

Membrane	Thin-film membrane (TFM*)

Model	Average permeate flow gpd (m3/day)[1,2]	Average NaCl rejection[1,2]	Minimum NaCl rejection[1,2]
AG-90	2200 (8.3)	99.8%	99.3%
AG-365	9600 (36.3)	99.8%	99.3%
AG-400	10500 (39.7)	99.8%	99.3%
AG-400, 34	10500 (39.7)	99.8%	99.3%
AG-440	11500 (43.5)	99.8%	99.3%
AG-1600	42000 (159.0)	99.8%	99.3%

[1]Average salt rejection after 24 hours operation. Individual flow rate may vary +25%/-15%.
[2] Testing conditions: 2,000ppm NaCl solution at 225psi (1,550kPa) operating pressure, 77°F (25°C), pH7 and 15% recovery.

Model	Active area ft² (m²)	Outer wrap	Part number
AG-90	90 (8.4)	Fiberglass	3056665
AG-365	365 (33.9)	Fiberglass	3056666
AG-400	400 (37.2)	Fiberglass	3056667
AG-400, 34	400 (37.2)	Fiberglass	3056668
AG-440	440 (40.9)	Fiberglass	3056669
AG-1600	1600 (148.6)	Fiberglass	3056670

Table 2: Operating and CIP parameters

Typical Operating Pressure	200 psi (1,380 kPa)
Typical Operating Flux	10-20GFD (15-35LMH)
Maximum Operating Pressure	600 psi (4,137 kPa)
Maximum Temperature	Continuous operation: 122°F (50°C) Clean-In-Place (CIP): 122°F (50°C)
pH range	Optimum rejection: 7.0-7.5, Continuous operation 4.0-11.0, Clean-In-Place (CIP): 2.0-11.5
Maximum Pressure Drop	Over an element: 12 psi (83 kPa) Per housing: 50 psi (345 kPa)
Chlorine Tolerance	1,000+ ppm-hours, dechlorination recommended
Feedwater[3]	NTU < 1 SDI < 5

[3]SDI is measured on a non-linear scale using a 0.45 micron filter paper. Additionally, finer colloids, particulates and microorganisms that pass through the filter paper and not measured in the SDI test, will potentially foul the RO element. For performance consistency and project warranty, please use Winflows projection software and consult your Filters with Membranes representative.

Figure 1a: Element Dimensions Diagram – Male

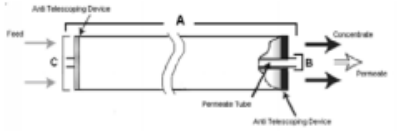
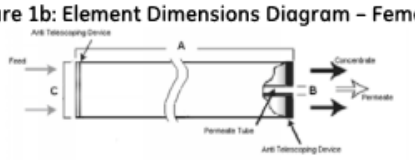


Figure 1b: Element Dimensions Diagram – Female



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FSpwAGHRSeries_EN Feb-11

Exhibit B-6: Reverse Osmosis (RO) Membrane (AG) Manufacturer Data Sheet (Cont.)

Table 3: Dimensions and Weights

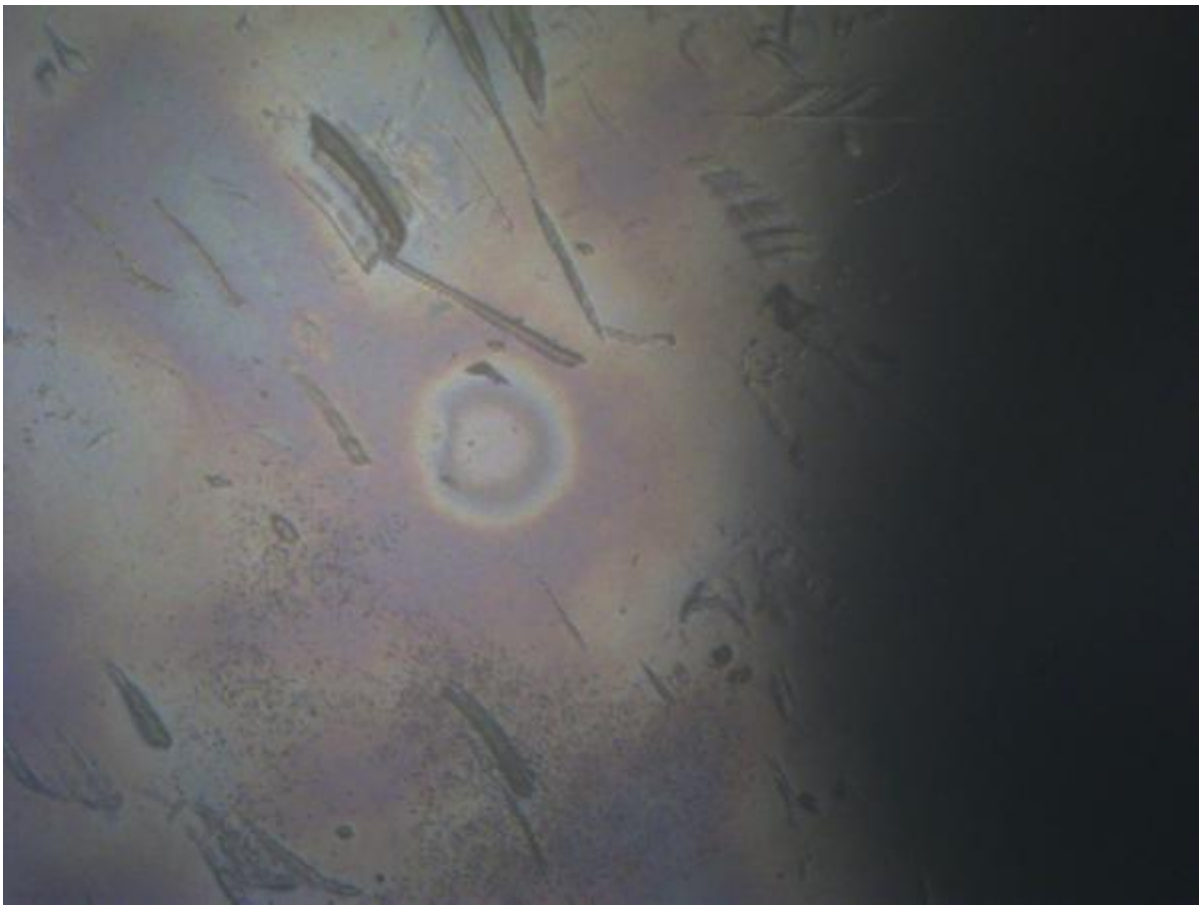
Model[1]	Type	Dimensions, inches (cm)			Boxed
		A	B[2]	C	Weight lbs (kg)
AG-90	Male	40.0 (101.6)	0.75 (1.90)	3.9 (9.9)	9 (4)
AG-365	Female	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	35 (16)
AG-400	Female	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	35 (16)
AG-400, 34	Female	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	35 (16)
AG-440	Female	40.0 (101.6)	1.125 (2.86)	7.9 (20.1)	35 (16)
AG-1600	Female	40.0 (101.6)	3.000 (7.620)	16.0 (40.6)	120 (54)

Exhibit B-7: UA MAST Lab Results – Test Membrane Properties

1. DK (NF)	a) AFM
	b) Contact Angle
	c) Surface Zeta Potential
2. AG (RO)	a) AFM
	b) Contact Angle
	c) Surface Zeta Potential

1) DK – Nanofiltration Membrane

a) Atomic Force Microscopy (AFM)



Area	Size of measurement	Roughness, R_q (nm)
Normal (gray)	2 μm	4.1
	1 μm	5.03
	500 nm	3.81
Purple	2 μm	12.1
	1 μm	10.5
	500 nm	7.12

Exhibit B-7: UA MAST Lab Results – Test Membrane Properties (Cont.)

Normal Area

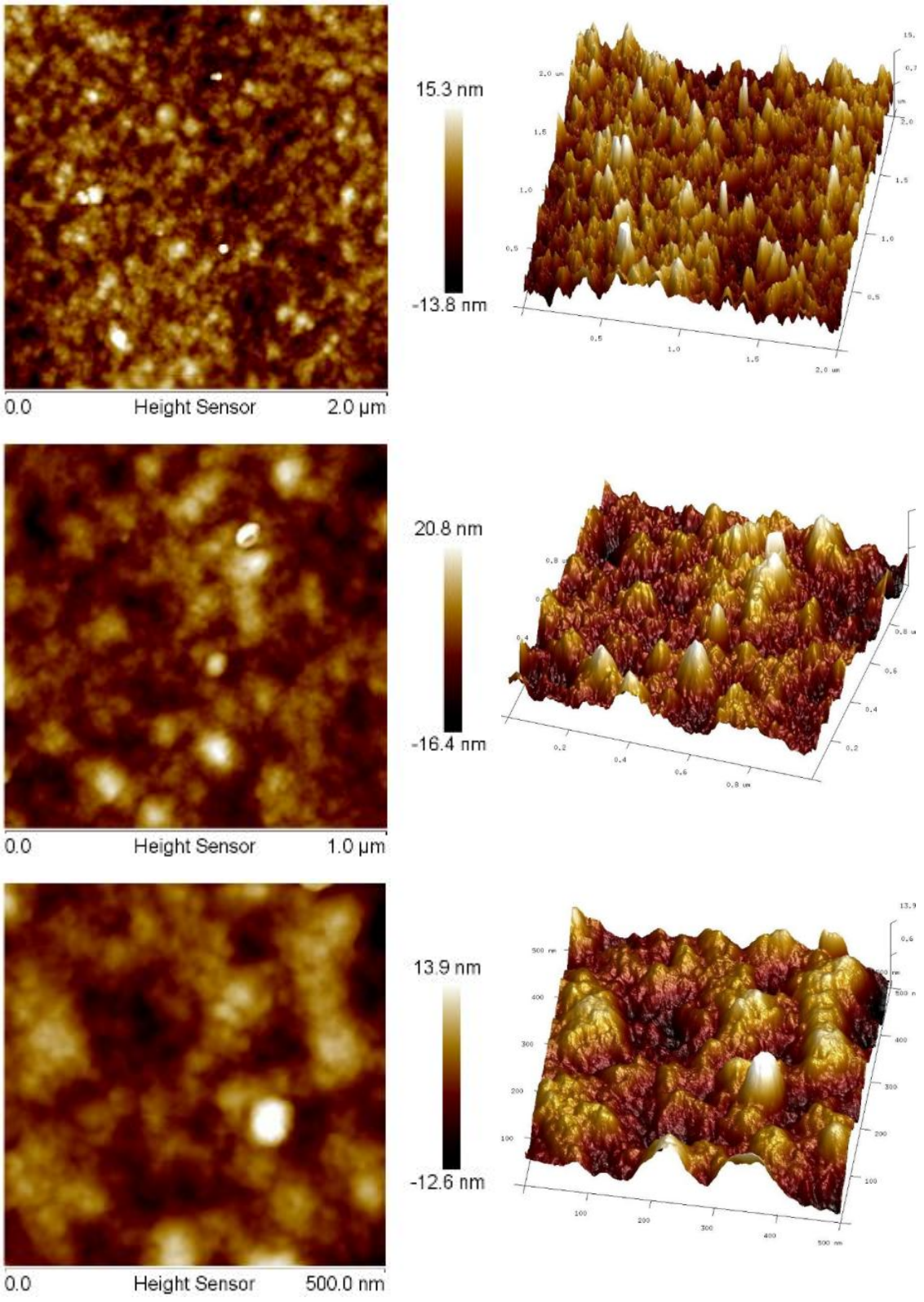
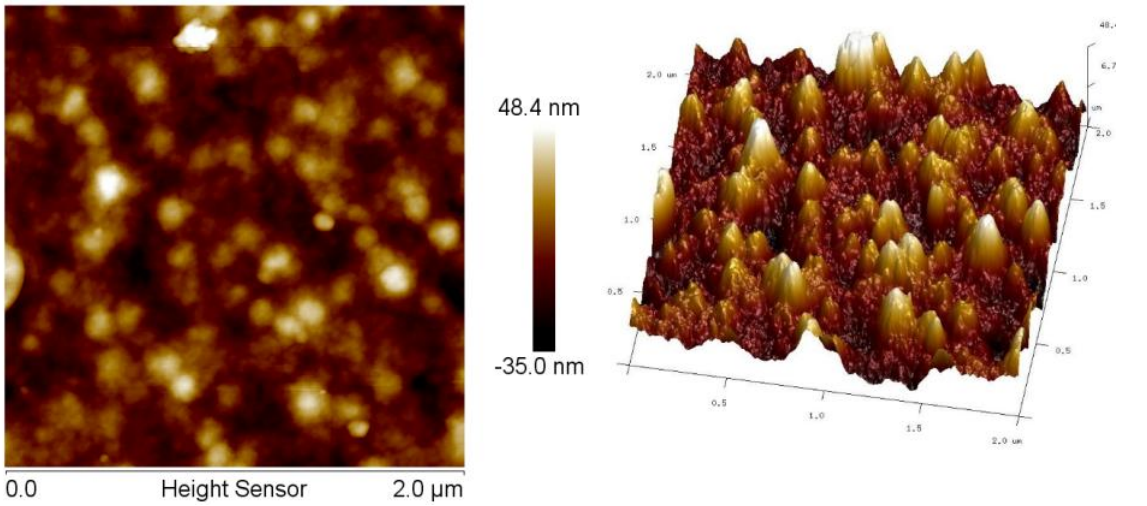
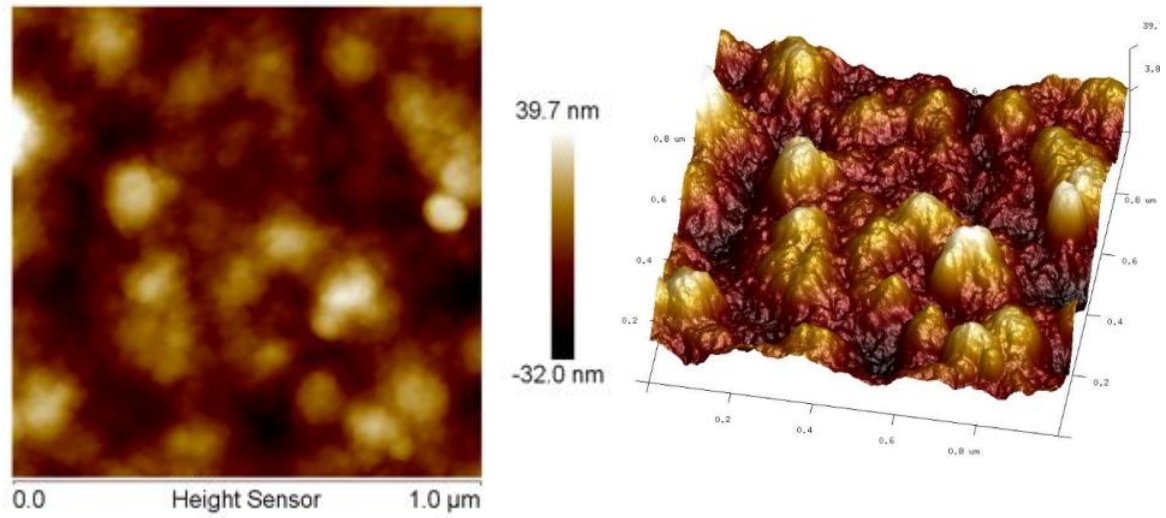


Exhibit B-7: UA MAST Lab Results – Test Membrane Properties (Cont.)

Purple Area





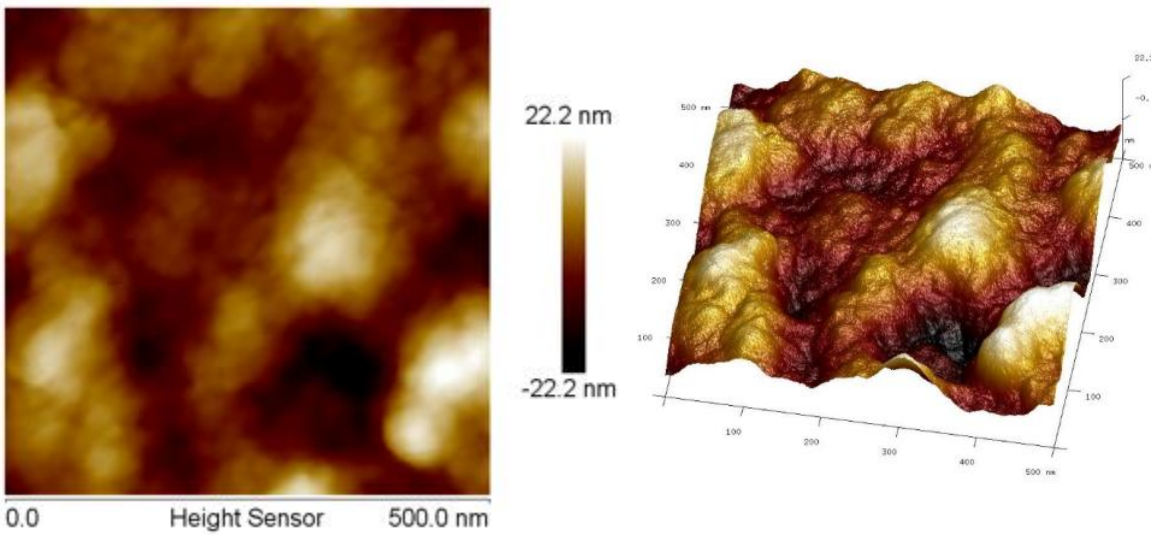
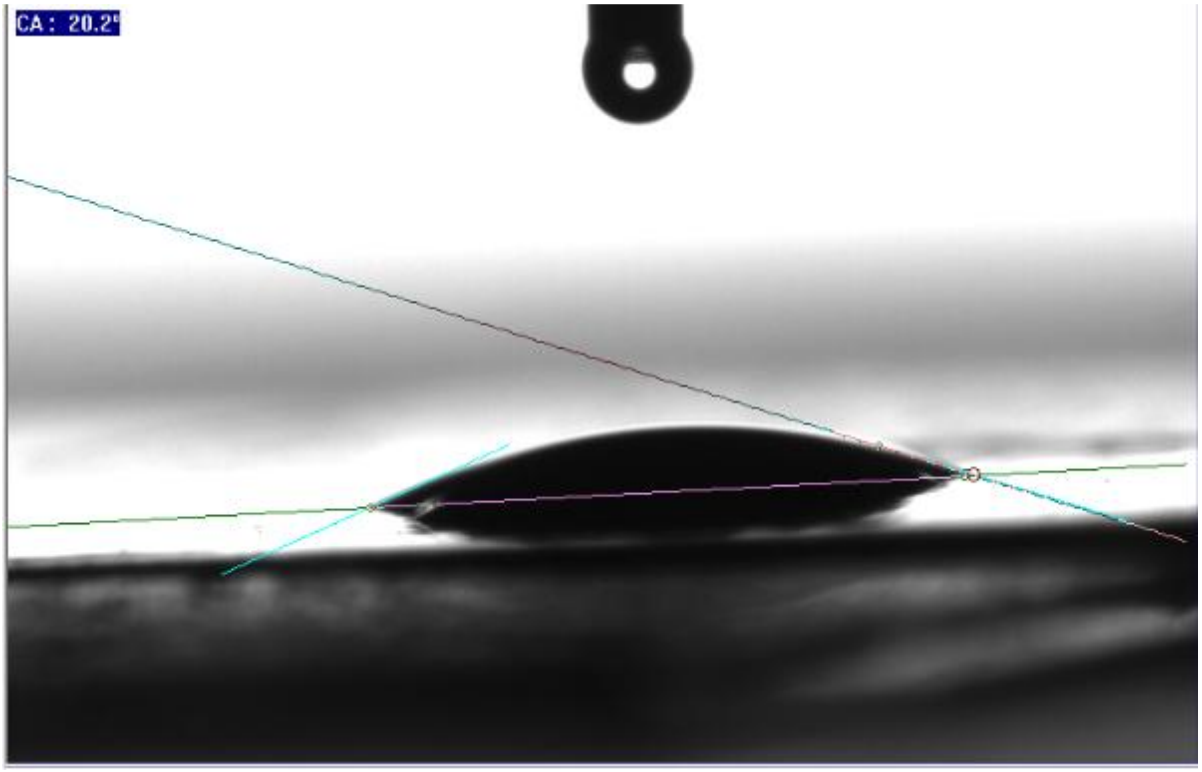


Exhibit B-7: UA MAST Lab Results – Test Membrane Properties (Cont.)

b) Contact Angle (~20-25°)



c) Surface Zeta Potential

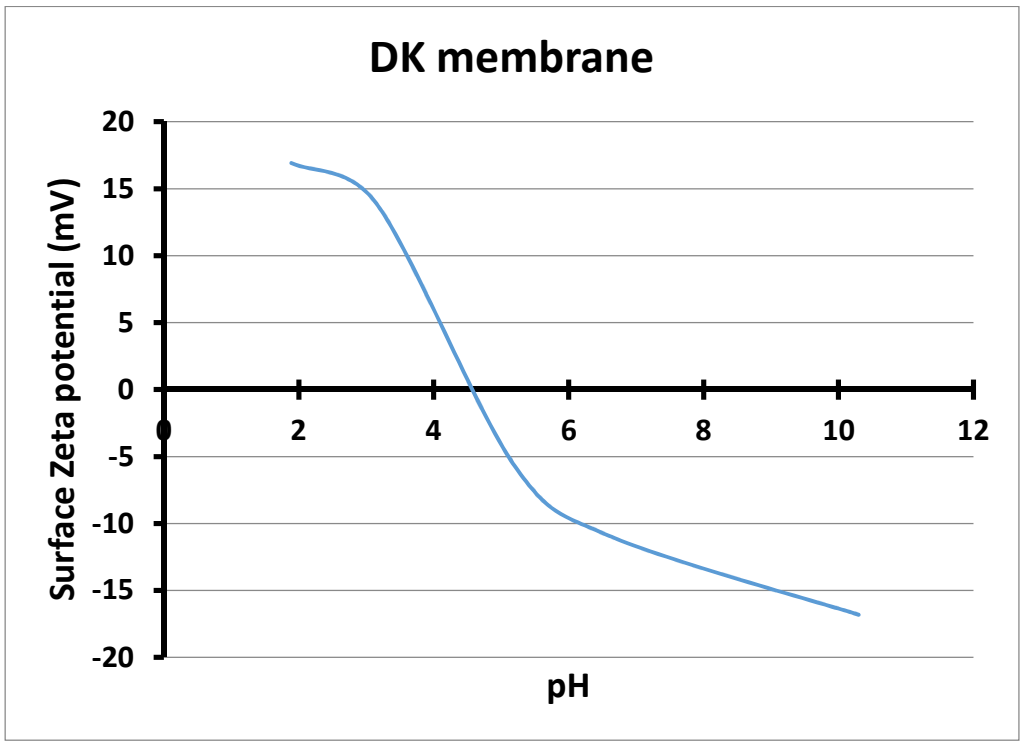
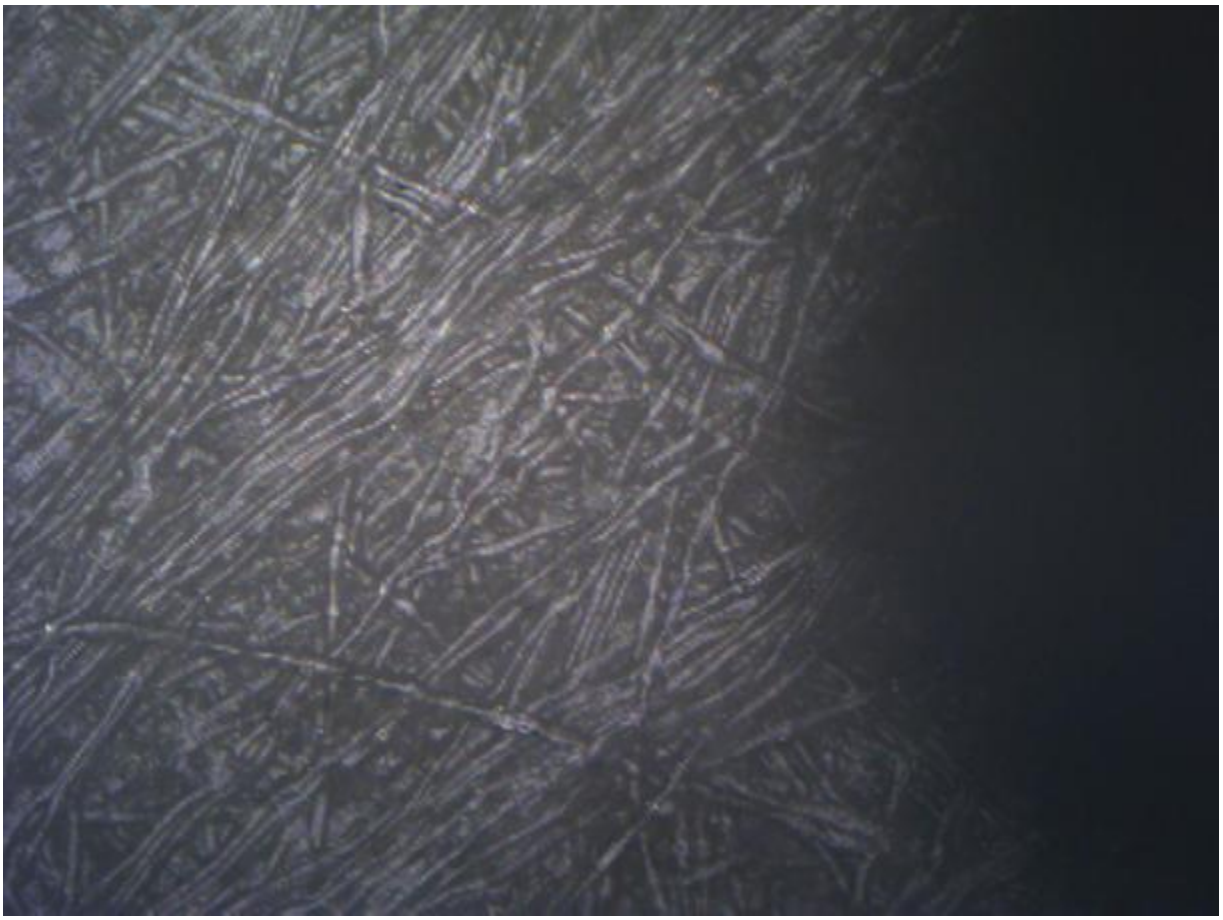


Exhibit B-7: UA MAST Lab Results – Test Membrane Properties (Cont.)

2) AG – Reverse Osmosis Membrane

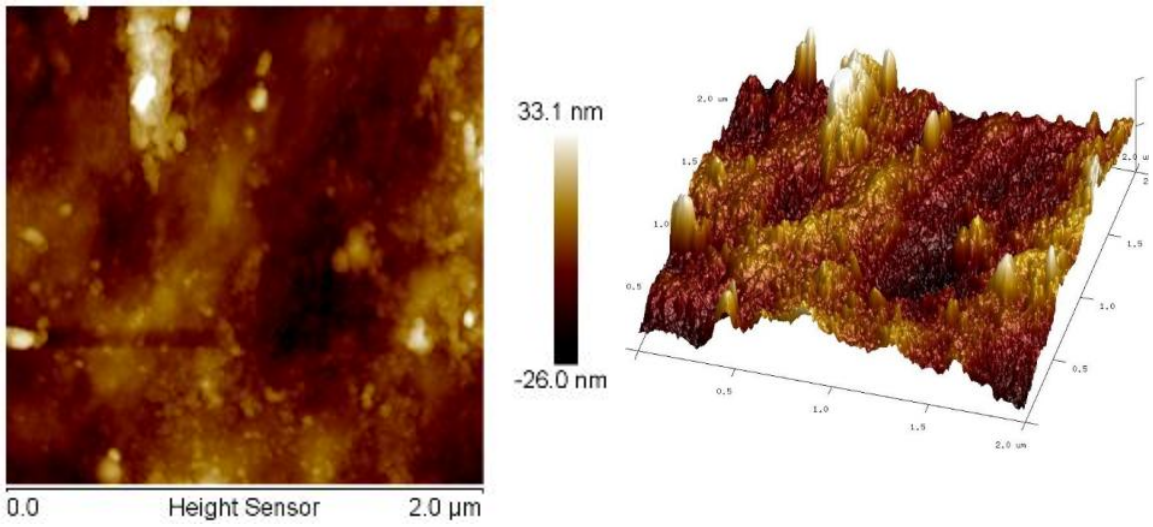
a) Atomic Force Microscopy (AFM)

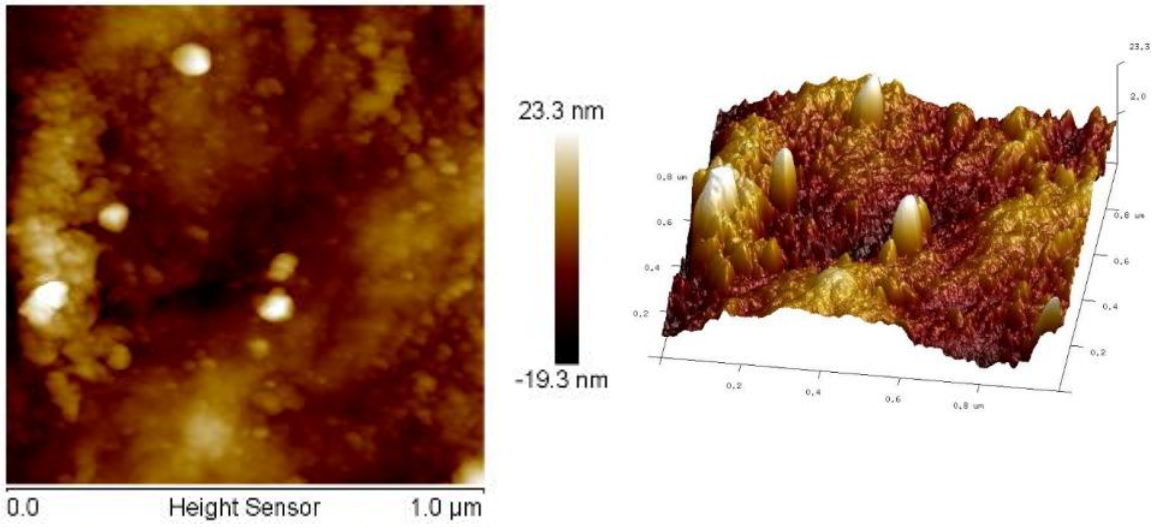


Area	Size of measurement	Roughness, R_q (nm)
Flat (gray)	2 μm	7.66
	1 μm	5.69
	500 nm	3.31
Stripe	2 μm	28.3
	1 μm	9.81
	500 nm	6.03

Exhibit B-7: UA MAST Lab Results – Test Membrane Properties (Cont.)

Flat area (gray)





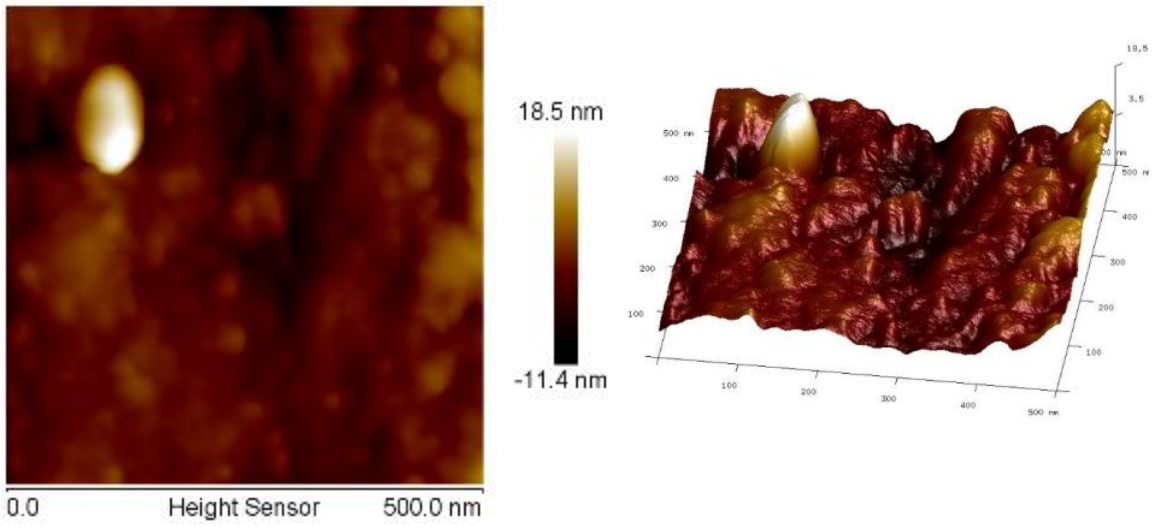
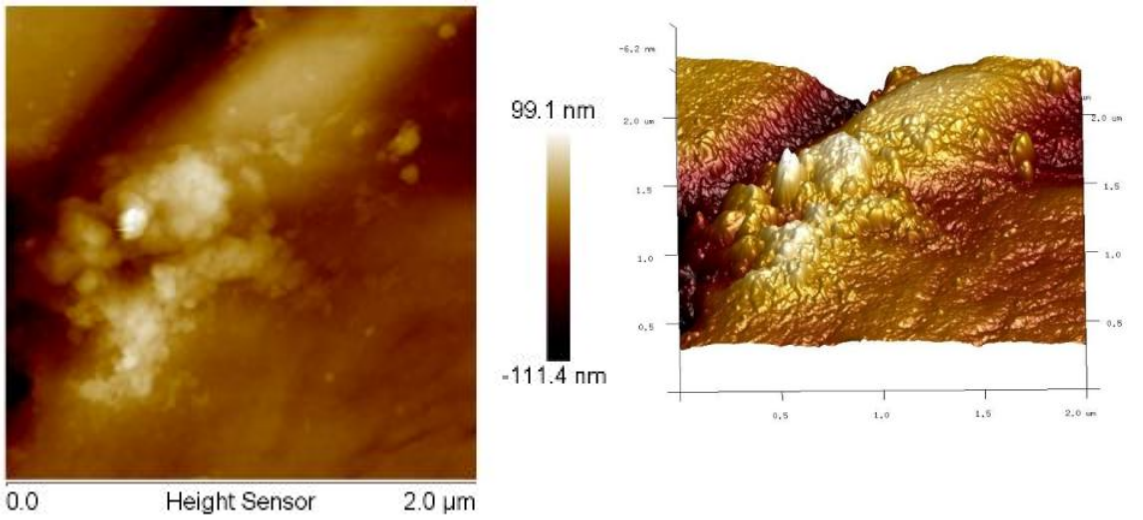
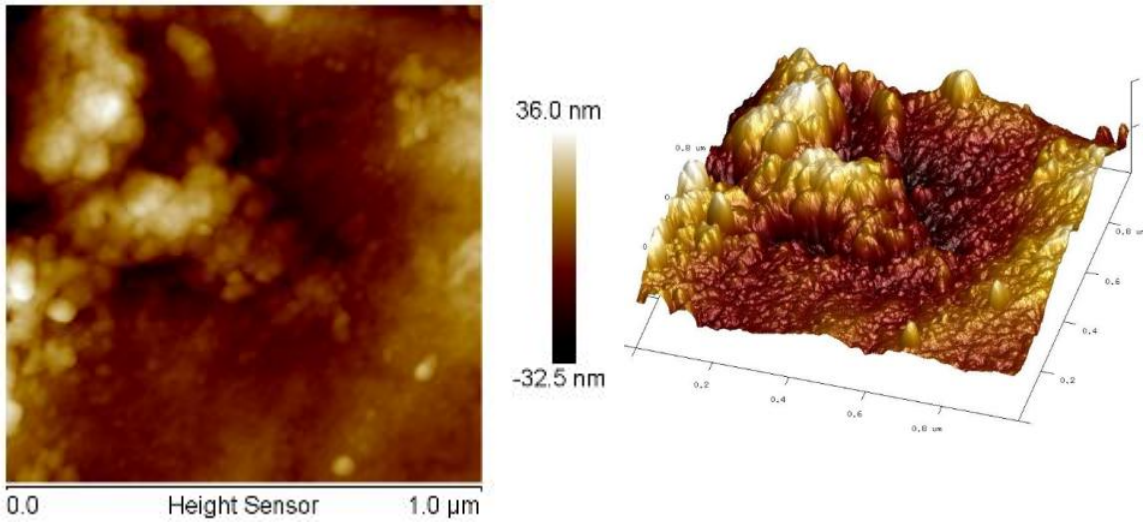


Exhibit B-7: UA MAST Lab Results – Test Membrane Properties (Cont.)

Stripe area





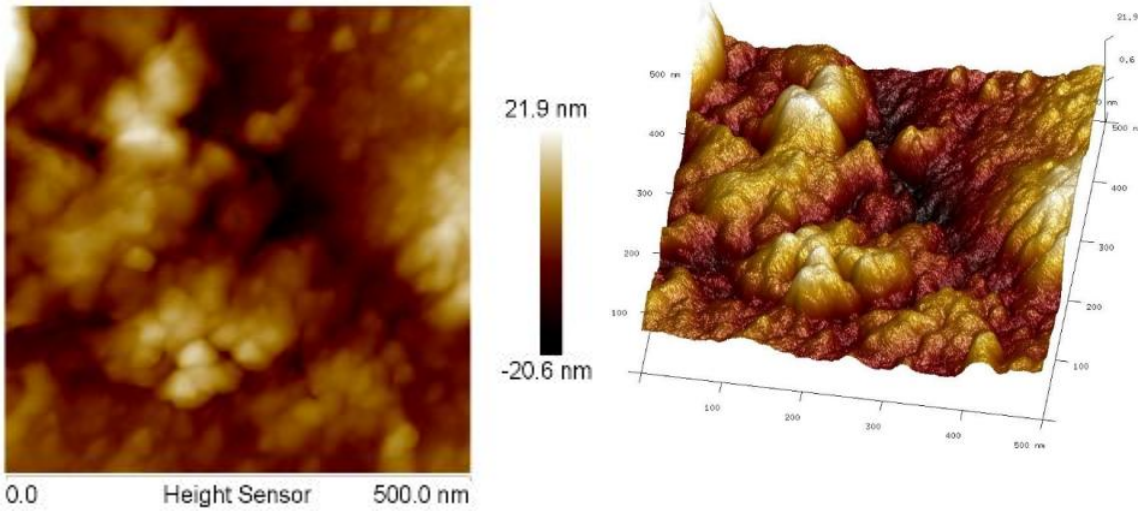
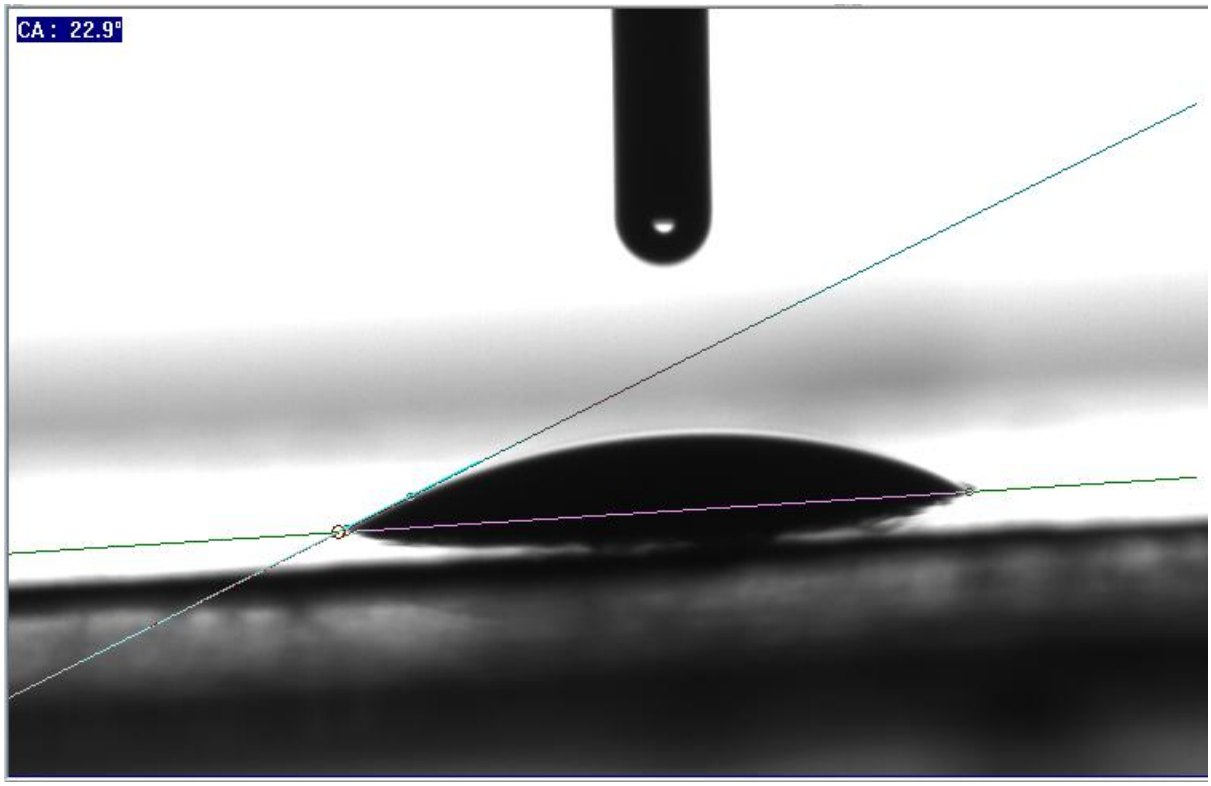


Exhibit B-7: UA MAST Lab Results – Test Membrane Properties (Cont.)

b) Contact Angle (~23-30°)



c) Surface Zeta Potential

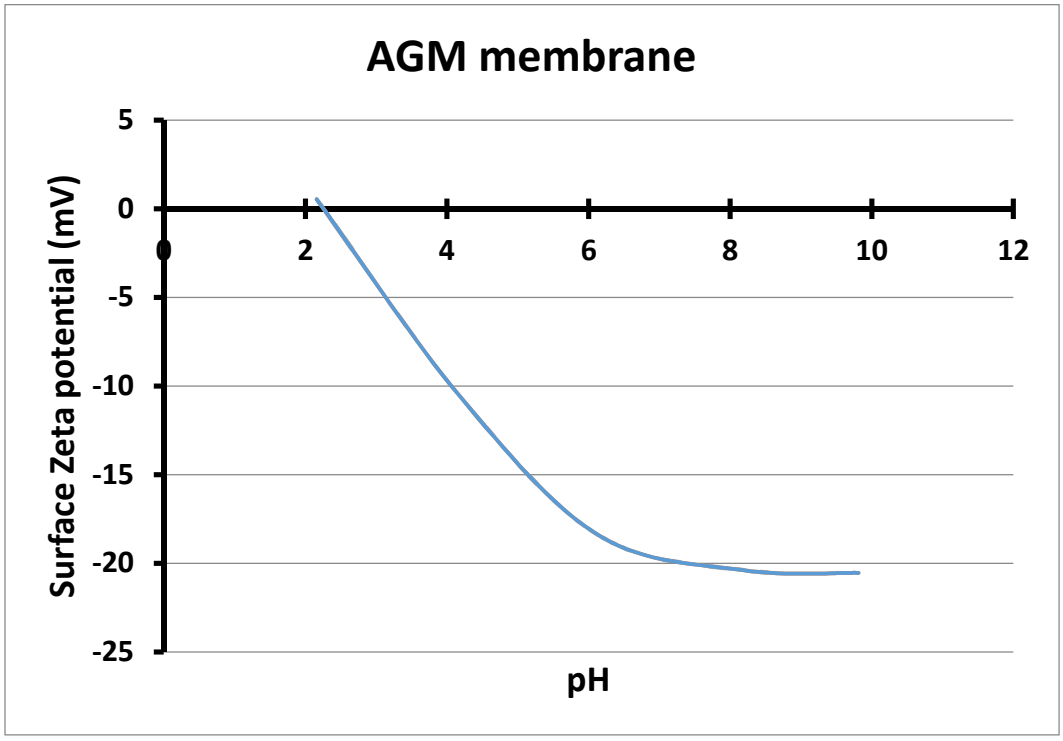


Exhibit B-8: Eurofins Eaton Analytical Certifications

About Eurofins Eaton Analytical

Eurofins Eaton Analytical is the largest potable water focused commercial laboratory in the United States, serving more than 500 clients across the U.S. and more than 100 foreign countries. We are a full-service environmental testing operation certified in 50 states and territories under the Safe Drinking Water Act and/or the National Environmental Laboratory Accreditation Program (TNI). We routinely analyze more than 200 individual water quality parameters for water and analyses according to 40 CFR 141 and 40 CFR 136 and other acceptable water quality test methodologies.

We have been in the commercial laboratory business for nearly 50 years, providing our clients with a reliable contract laboratory and regulatory information resource.

Highlights include:

- EPA contractor for the National Pesticide Survey (1987-88).
- Information Collection Rule accredited laboratory (1997-99).
- EPA contractor for UCMR1 Methods Validation (2000) and Small Systems (2001-05)
- EPA contractor for UCMR2 Small Systems (2008-10)
- EPA contractor for UCMR3 Methods Validation (2012) and Small Systems (2013-15)
- EPA 314 method Co-Author for Perchlorate
- WaterRF 4167 (Methods for PPCP analysis) Co-Principal Investigator
- Contract laboratory for the USGS, USBR and all branches of the Armed Forces
- Contract laboratory for the states of Arkansas, Arizona, Delaware, Minnesota, Mississippi, New Jersey, Nevada, South Carolina and Utah.
- Contract laboratory for U.S. Territories in American Samoa, Guam and the CNMI
- California CEC Blue Ribbon Panel participant
- California DPH ELTAC Advisory Board participant
- Standard Methods Joint Editorial Board chair/member
- Active member/officer for ACWA, AWWA, GRA and WateReuse

Exhibit B-8: Eurofins Eaton Analytical Certifications (Cont.)

Certifications

Every assignment you entrust to us will be performed to the highest possible standards. Eaton Analytical meets the stringent certification requirements in 50 states and territories, and is accredited by the NELAC Institute (TNI) and ISO/IEC17025.

Each year our laboratories are audited by many organizations including the states in which we are certified, as well as the American National Standards Institute, US Air Force, US Army Public Health Command, and the United States Environmental Protection Agency.

For a copy of our current certification in a particular state, please look at the list of states and territories. Click on a link in the list to download the information in Adobe Acrobat (PDF) format.

Monrovia, CA	South Bend, IN
• Alabama.pdf • Arizona.pdf • Arkansas.pdf • California.pdf • Colorado.pdf • Connecticut.pdf • Delaware.pdf • Florida.pdf • Georgia.pdf • Hawaii LT2.pdf • Hawaii.pdf	• Alabama.pdf • Alaska.pdf • Arizona.pdf • Arkansas.pdf • California.pdf • Colorado Radiochemistry.pdf • Colorado.pdf • Connecticut.pdf • Delaware.pdf • Florida.pdf • Georgia.pdf

- Idaho.pdf
- Illinois.pdf
- Indiana.pdf
- Kansas.pdf
- Kentucky.pdf
- Louisiana.pdf
- Maine.pdf
- Maryland.pdf
- Massachusetts.pdf
- Michigan.pdf
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- Montana.pdf
- Nebraska.pdf
- Nevada.pdf
- New Hampshire.pdf
- New Jersey.pdf
- New Mexico.pdf
- New York.pdf
- North Carolina.pdf
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- Oregon.pdf
- Pennsylvania.pdf
- Puerto Rico.pdf
- Rhode Island.pdf
- South Carolina.pdf
- South Dakota.pdf
- Tennessee.pdf
- Texas.pdf
- Utah.pdf
- Vermont.pdf
- Virginia.pdf
- Washington.pdf
- Wisconsin.pdf
- Wyoming.pdf

- Hawaii.pdf
- Idaho.pdf
- Illinois Micro.pdf
- Illinois.pdf
- Indiana Micro.PDF
- Indiana.pdf
- Iowa.pdf
- Kansas.pdf
- Kentucky.pdf
- Louisiana.pdf
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- Michigan.pdf
- Minnesota.pdf
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- Montana.pdf
- Nebraska.pdf
- Nevada.pdf
- New Hampshire.pdf
- New Jersey.pdf
- New Mexico.pdf
- New York.pdf
- North Carolina.pdf
- North Dakota.pdf
- Ohio.pdf
- Oklahoma.pdf
- Oregon.pdf
- Pennsylvania.pdf
- Puerto Rico.pdf
- Rhode Island.pdf
- South Carolina.pdf
- South Dakota.pdf

- ALL EPA ICR Approval.pdf
- UCMR Aeromonas Approval.pdf
- Legionella Certificate.pdf
- UCMR CLO4.pdf
- UCMR2 Approval.pdf
- ISO certificate of Accreditation.pdf
- UCMR3 Approval.pdf
- Soil Certificate.pdf

- Fresno Service Center.pdf
- Inland Empire Service Center.pdf
- Sacramento Service Center.pdf

- Monrovia ELAP.pdf
- Monrovia NELAP.pdf

- Tennessee.pdf
- Texas.pdf
- Utah.pdf
- Vermont.pdf
- Virginia.pdf
- Washington.pdf
- West Virginia.pdf
- Wisconsin.pdf
- Wyoming.pdf

- UCMR3 - Approval.pdf
- NELAP Approval.pdf

Exhibit B-8b: EEA Sample Certifications – US EPA UCMR3, California, Texas

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268
Office of Ground Water and Drinking Water
Technical Support Center
August 1, 2012

Eurofins Eaton Analytical Inc, formerly known as MWH Labs
750 Royal Oaks Drive
Monrovia, CA 91016

Dear Nilda Cox,

Based on your application and successful participation in a Unregulated Contaminant Monitoring Rule 3 (UCMR 3) Proficiency Testing (PT) Study for each of the listed methods, EPA has given the status of "approved" to your laboratory for the method(s) listed below. This letter is being issued to reflect the name change for your laboratory. The application and PT criteria are listed in the "UCMR 3 Laboratory Approval Requirements and Information Document, Version 2.0." Your laboratory continues to be "approved" to conduct UCMR 3 analyses using the following method(s):

LabID: CA00006

Method Name		**Approval Date**
Hormones by LC/MS/MS	EPA 539	5/2/2012
Perfluorinated compounds by LC/MS/MS	EPA 537	5/2/2012
VOCs by GC/MS	EPA 524.3	5/2/2012
1,4-Dioxane by GC/MS	EPA 522	5/2/2012
Inorganic anions by IC (Chlorate)	EPA 300.1	5/2/2012
Hexavalent chromium by IC	EPA 218.7	5/2/2012
Trace Element Metals by ICP/MS	EPA 200.8	5/2/2012

End of Method List

The information will be forwarded to the UCMR 3 Webmaster for inclusion in the list of UCMR 3 approved laboratories. Your approval status will be maintained during UCMR 3 by continuing to meet the criteria given in the "UCMR 3 Laboratory Approval Requirements and Information Document, Version 2.0," and any revisions to the aforementioned document. Please be aware that you are only permitted to conduct UCMR 3 analyses using those methods for which you have EPA approval. Should you wish to comment on any of these determinations, please write to:

UCMR 3 Laboratory Approval Coordinator
USEPA, Technical Support Center
26 W. Martin Luther King Drive (MS 140)
Cincinnati, OH 45268
UCMR_Sampling_Coordinator@epa.gov

Michella S. Karapondo
UCMR Laboratory Approval Coordinator

Internet Address (URL) • http://www.epa.gov
Recycled/Recyclable • Printed with Vegetable Oil Based Inks on 100% Postconsumer, Process Chlorine Free Recycled Paper

Exhibit B-8b: EEA Sample Certifications – US EPA UCMR3, California, Texas (Cont.)

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

CALIFORNIA STATE

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM

CERTIFICATE OF ENVIRONMENTAL ACCREDITATION

Is hereby granted to

Eurofins Eaton Analytical, Inc. - Monrovia

750 Royal Oaks Drive, Suite 100

Monrovia, CA 91016

Scope of the certificate is limited to the
"Fields of Testing"
which accompany this Certificate.

Continued accredited status depends on successful completion of on-site inspection, proficiency testing studies, and payment of applicable fees.

This Certificate is granted in accordance with provisions of Section 100825, et seq. of the Health and Safety Code.

Certificate No.: **2813**

Expiration Date: **1/31/2017**

Effective Date: **2/1/2015**

Sacramento, California
subject to forfeiture or revocation

Christine Sotelo, Chief
Environmental Laboratory Accreditation Program

Exhibit B-8b: EEA Sample Certifications – US EPA UCMR3, California, Texas (Cont.)

Texas Commission on Environmental Quality

NELAP-Recognized Laboratory Accreditation is hereby awarded to

Eurofins Eaton Analytical, Inc. - Monrovia, CA

750 Royal Oaks Drive, Suite 100

Monrovia, CA 91016

in accordance with Texas Water Code Chapter 5, Subchapter R, Title 30 Texas Administrative Code Chapter 25, and the National Environmental Laboratory Accreditation Program.

The laboratory's scope of accreditation includes the fields of accreditation that accompany this certificate. Continued accreditation depends upon successful ongoing participation in the program. The Texas Commission on Environmental Quality urges customers to verify the laboratory's current location(s) and accreditation status for particular methods and analyses (www.tceq.texas.gov/goto/lab). Accreditation does not imply that a product, process, system or person is approved by the Texas Commission on Environmental Quality.

[redacted]

Executive Director Texas Commission on Environmental Quality

Certificate Number: T104704230-15-9
Effective Date: 10/1/2015
Expiration Date: 9/30/2016

APPENDIX C

Exhibit C-1: COK CEC Analytical Results

Exhibit C-2: SOK CEC Analytical Results

Exhibit C-3: NTX CEC Analytical Results

Exhibit C-4: Modeled Rejection Coefficients by CEC Analyte

Exhibit C-1: COK CEC Analytical Results

DPR Treatability Study
University of Arkansas / Garver
SMJ PhD Research
2014
Sample Site: COK

	Sampled 8/12/2014 Week 1				Sampled 8/20/2014 Week 2				Sampled 8/26/14 Week 3					
Analyte	PE	SE	NF	RO	PE	SE	NF	RO	PE	SE	NF	RO	Units	MRL
1,7-Dimethylxanthine	430				6,200	41			4,600				ng/L	10
Acetaminophen	64,000	1,199			69,000	480			6,800	940			ng/L	500
Albuterol	22	18			28	23			32	26			ng/L	5
Amoxicillin (semi-quantitative)	8,900	6,357			14,000	8,000			1,400	3,000			ng/L	200
Androstenedione					700				580				ng/L	5
Atenolol	3,200				1,400				960	41			ng/L	50
Atrazine	16												ng/L	5
Azithromycin	3,500	1,558	130		2,300	570			1,900	1,300			ng/L	20
Bezafibrate													ng/L	5
Bromacil					24	22							ng/L	5
Caffeine	59,000	83			55,000	93			58,000	66			ng/L	500
Carbadox													ng/L	5
Carbamazepine	320	376	12		190	220	6		210	250	14		ng/L	5
Carisoprodol	100				80	60							ng/L	5
Chloridazon													ng/L	5
Chlorotoluron	8												ng/L	5
Cimetidine	1,700	1,264			890	520			1,100	960	20		ng/L	50
Cotinine	3,500	32			3,400	41			3,600	23			ng/L	100
Cyanazine													ng/L	5
DACT						10				6			ng/L	5
DEA	11				520	10							ng/L	5
DEET	8,300	80			8,000	160			10,000	13			ng/L	1,000
Dehydronifedipine													ng/L	5
DIA	8	35	28		22	66	18		22	120	21		ng/L	5
Diazepam						8							ng/L	5
Dilantin	150	82			1,300	640			830	520			ng/L	20
Diltiazem	190	108			150	85			120	68			ng/L	5
Diuron						84					7		ng/L	5
Erythromycin	14												ng/L	10
Flumeqine													ng/L	10
Fluoxetine	330	301	110		27	30			41	32	12		ng/L	10
Isoproturon													ng/L	100
Ketoprofen	97				100								ng/L	5
Ketorolac	20				36								ng/L	5
Lidocaine	280	136			630	300			440	220			ng/L	5
Lincomycin					82								ng/L	10
Linuron					36	11			10				ng/L	5
Lopressor	860	434			1,100	600			1,000	460			ng/L	200
Meclofenamic Acid													ng/L	5
Meprobamate	230	152			1,500	1,300	6		1,500	680	9		ng/L	5
Metazachlor													ng/L	5
Metolachlor													ng/L	5
Nifedipine					150								ng/L	20
Norethisterone									170				ng/L	5
Oxolinic acid													ng/L	10
Pentoxifylline	6												ng/L	5
Phenazone													ng/L	5
Primidone	180	144			160	140			140	100			ng/L	5
Progesterone					1,900				280				ng/L	5
Propazine													ng/L	5
Quinoline	140		16	14									ng/L	5
Simazine	150	200	31		150	210	29		150	190	23		ng/L	5
Sulfachloropyridazine													ng/L	5
Sulfadiazine					610	150							ng/L	5
Sulfadimethoxine													ng/L	5
Sulfamerazine													ng/L	5
Sulfamethazine													ng/L	5
Sulfamethizole													ng/L	5
Sulfamethoxazole	3,200	1,194	100		4,000	1,400	81		2,700	1,100	110		ng/L	50
Sulfathiazole					370	140					5		ng/L	5
TCEP	210	102	64		710	280	46		460	290	140	14	ng/L	10
TCPP	1,400	2,873			400	980			560	990			ng/L	1,000
TDCPP	550	733			550	620			350	580			ng/L	100
Testosterone					250								ng/L	5
Theobromine	760				24,000				24,000				ng/L	10
Theophylline	10,000				11,000	82			14,000				ng/L	20
Trimethoprim	810	431			1,200	590			1,000	580			ng/L	5
2,4-D	52	7			70	90	12		840	37			ng/L	5
4-nonylphenol - semi quantitative								760	630	410		230	ng/L	100
4-tert-Octylphenol									410	250			ng/L	50
Acesulfame-K	15,000		96		18,000	300	270			740			ng/L	20
Bendroflumethiazide													ng/L	5
BPA	130				63		39	15			11		ng/L	10
Butalbital						6			28	14			ng/L	5
Butylparaben					7				47				ng/L	5
Chloramphenicol									730				ng/L	10
Clofibric Acid					18				23				ng/L	5
Diclofenac	69	59			86	35			120	140			ng/L	5
Estradiol	39												ng/L	5
Estrone	10				10					14			ng/L	5
Ethinyl Estradiol - 17 alpha													ng/L	5
Ethylparaben					88		45		3,300				ng/L	20
Gemfibrozil	1,100	36			1,000	34			2,600	84			ng/L	5
Ibuprofen	3,200				4,800								ng/L	10
Iohexal	11,000				10,000	1,000	12		28,000				ng/L	10
Iopromide					11				96				ng/L	5
Isobutylparaben					9				47				ng/L	5
Methylparaben					53				1,900				ng/L	20
Naproxen	3,200	16			4,100	12			190	10			ng/L	10
Propylparaben	100		5		380				910				ng/L	5
Sucralose	24,000	23,351	160	180	23,000	21,000			14,000	15,000			ng/L	100
Triclocarban	170		29	5	180	16		6		11			ng/L	5
Triclosan	490	29	35		580	30	32			29			ng/L	10
Warfarin									12	7			ng/L	5

PE = primary effluent; SE = secondary effluent; NF = nanofiltration permeate; RO = reverse osmosis permeate; MRL = minimum reporting limit

Exhibit C-2: SOK CEC Analytical Results

DPR Treatability Study
University of Arkansas / Garver
SMJ PhD Research
2014
Sample Site: SOK

	Sampled 8/12/2014 Week 2				Sampled 8/20/2014 Week 3				Sampled 9/9/2014 Week 4					
Analyte	PE	SE	NF	RO	PE	SE	NF	RO	PE	SE	NF	RO	Units	MRL
1,7-Dimethylxanthine	240				7,100								ng/L	10
Acetaminophen	33,000				46,000				380	45			ng/L	500
Albuterol	38	35			34	25			20	21			ng/L	5
Amoxicillin (semi-quantitative)	3,800	1,200			13,000	910			3,200	1,300			ng/L	20
Androstenedione					180				46				ng/L	5
Atenolol	930	300			680	140			230	70	7		ng/L	50
Atrazine	85	120	15				24		30	41	15		ng/L	5
Azithromycin	1,200	3,200			1,400	1,200				770			ng/L	20
Bezafibrate													ng/L	5
Bromacil													ng/L	5
Caffeine	32,000	73			39,000	45			18,000	26			ng/L	500
Carbadox													ng/L	5
Carbamazepine	140	160	5		210	260	19		90	78	12		ng/L	5
Carisoprodol	230	710					7			26			ng/L	5
Chloridazon													ng/L	5
Chlorotoluron	8												ng/L	5
Cimetidine	310	70			180	340							ng/L	5
Cotinine	3,200	78			3,700	42			1,300	24			ng/L	100
Cyanazine									6	7			ng/L	5
DACT									6				ng/L	5
DEA	66	77					35		160	31	27		ng/L	5
DEET	9,300	26			9,200				3,000	22			ng/L	1000
Dehydronifedipine		12											ng/L	5
DIA		20				12					9		ng/L	5
Diazepam													ng/L	5
Dilantin	54	76			540	920			24	41			ng/L	20
Diltiazem	57	33			68	37			12	7			ng/L	5
Diuron											18		ng/L	5
Erythromycin													ng/L	10
Flumeqine													ng/L	10
Fluoxetine	71	81			17				28	19			ng/L	10
Isoproturon													ng/L	100
Ketoprofen	73								55				ng/L	5
Ketorolac	19												ng/L	5
Lidocaine	320	160			420	230			120	100			ng/L	5
Lincomycin	20												ng/L	10
Linuron													ng/L	5
Lopressor	960	640			1,100	370			360	340			ng/L	20
Meclofenamic Acid													ng/L	5
Meprobamate	170	210			540	850	9		71	130			ng/L	5
Metazachlor													ng/L	5
Metolachlor					5	8							ng/L	5
Nifedipine	36								120	37			ng/L	20
Norethisterone													ng/L	5
Oxolinic acid													ng/L	10
Pentoxifylline	12												ng/L	5
Phenazone													ng/L	5
Primidone	110	110			95	97			43	47			ng/L	5
Progesterone					110								ng/L	5
Propazine													ng/L	5
Quinoline	280	18					7		82	22			ng/L	5
Simazine						7				5			ng/L	5
Sulfachloropyridazine													ng/L	5
Sulfadiazine													ng/L	5
Sulfadimethoxine	19	32								ND			ng/L	5
Sulfamerazine													ng/L	5
Sulfamethazine													ng/L	5
Sulfamethizole													ng/L	5
Sulfamethoxazole	2,300	1,800	42		2,000	1,600	96		690	770	130		ng/L	50
Sulfathiazole													ng/L	5
TCEP	410	240	35		520	290	130		150	130	120		ng/L	10
TCPP	1,400	1,400			1,100	520			630	680			ng/L	1000
TDCPP	620	760			500	460			680	440			ng/L	100
Testosterone													ng/L	5
Theobromine	540	150			7,800	45			2,300	49			ng/L	10
Theophylline	6,400	34			7,000				700				ng/L	20
Trimethoprim	430	63			480	30							ng/L	5
2,4-D	460	280			490	95	34		500	160			ng/L	5
4-nonylphenol - semi quantitative							1,200	950	260		130		ng/L	100
4-tert-Octylphenol									910	420			ng/L	50
Acesulfame-K	11,000	950			12,000	1,200	1,100		36,090	10,000	76		ng/L	20
Bendroflumethiazide													ng/L	5
BPA	49					13	13						ng/L	10
Butalbital	5	7			7				150	72			ng/L	5
Butylparaben													ng/L	5
Chloramphenicol					11								ng/L	10
Clofibric Acid	6								41				ng/L	5
Diclofenac	66	81			77	49			680	110			ng/L	5
Estradiol													ng/L	5
Estrone	16	8			17	13							ng/L	5
Ethinyl Estradiol - 17 alpha													ng/L	5
Ethylparaben					52								ng/L	20
Gemfibrozil	1,000	46			1,200	36			2,300	86			ng/L	5
Ibuprofen	1,700				2,500								ng/L	10
Iohexal	13,000	580			15,000	480			31,000	620			ng/L	10
Iopromide	1,200	7			1,900	92			9,900	170			ng/L	5
Isobutylparaben													ng/L	5
Methylparaben					22				1,500				ng/L	20
Naproxen	2,600	110			2,700	92	14		44	49			ng/L	10
Propylparaben	75				170				530				ng/L	5
Sucralose	18,000	18,000			25,000	14,000			27,000	33,000			ng/L	100
Triclocarban	470	110			760	100							ng/L	5
Triclosan	550	54			820	28				100			ng/L	10
Warfarin									29				ng/L	5

PE = primary effluent; SE = secondary effluent; NF = nanofiltration permeate; RO = reverse osmosis permeate; MRL = minimum reporting limit

Exhibit C-3: NTX CEC Analytical Results

DPR Treatability Study
University of Arkansas / Garver
SMJ PhD Research
2014
Sample Site: NTX

	Sampled 8/12/2014 Week 1				Sampled 8/21/2014 Week 2				Sampled 8/27/2014 Week 3					
Analyte	PE	SE	NF	RO	PE	SE	NF	RO	PE	SE	NF	RO	Units	MRL
1,7-Dimethylxanthine	1,000				5,800				4,100				ng/L	10
Acetaminophen		250			70,000	570			50,000				ng/L	500
Albuterol	21	30			31	36							ng/L	5
Amoxicillin (semi-quantitative)	11,000	8,200			15,000	15,000			7,500				ng/L	20
Androstenedione									110				ng/L	5
Atenolol	2,100	500			840	450	9		930	610	27		ng/L	50
Atrazine	150	140	16			22	20		96	110	13		ng/L	5
Azithromycin	2,100	3,500	120	20	1,800	1,800			4,000	2,800			ng/L	20
Bezafibrate	53												ng/L	5
Bromacil													ng/L	5
Caffeine	31,000	45			44,000	61			31,000	37	11		ng/L	500
Carbadox													ng/L	5
Carbamazepine	200	210	8		160	170	12		180	160	16		ng/L	5
Carisoprodol	60	98											ng/L	5
Chloridazon													ng/L	5
Chlorotoluron													ng/L	5
Cimetidine	1,200	470			2,400	960	10		920	98	22		ng/L	5
Cotinine	2,200	130			2,000	95							ng/L	100
Cyanazine											15		ng/L	5
DACT	15	28	23				5		27	29			ng/L	5
DEA	180	180			170	230	68			710	43		ng/L	5
DEET	16,000	110	18		18,000	160	21		15,000	68			ng/L	1,000
Dehydronifedipine		9											ng/L	5
DIA	12		41		79	81	14		18	52	34		ng/L	5
Diazepam													ng/L	5
Dilantin	64	69			320	450			65	55			ng/L	20
Diltiazem	120	82			94	82			300	90			ng/L	5
Diuron											15		ng/L	5
Erythromycin									52	19			ng/L	10
Flumeqine													ng/L	10
Fluoxetine	160	120	100	68	20	14			170	210	10		ng/L	10
Isoproturon													ng/L	100
Ketoprofen	85	36							170	50			ng/L	5
Ketorolac	45	18			38								ng/L	5
Lidocaine	610	480			620	430			740	240			ng/L	5
Lincomycin	62	28			750	320							ng/L	10
Linuron													ng/L	5
Lopressor	1,000	480			1,300	410			3,800	210			ng/L	20
Meclofenamic Acid													ng/L	5
Meprobamate	140	200			450	500	6		160	62	7		ng/L	5
Metazachlor													ng/L	5
Metolachlor													ng/L	5
Nifedipine	29								120	22			ng/L	20
Norethisterone													ng/L	5
Oxolinic acid													ng/L	10
Pentoxifylline	36	11							88				ng/L	5
Phenazone													ng/L	5
Primidone	110	120			100	110			110	110			ng/L	5
Progesterone													ng/L	5
Propazine			5										ng/L	5
Quinoline	210	32	14	14					120	25			ng/L	5
Simazine	36	28	6		39	34	8		27	15			ng/L	5
Sulfachloropyridazine													ng/L	5
Sulfadiazine					440	140							ng/L	5
Sulfadimethoxine													ng/L	5
Sulfamerazine													ng/L	5
Sulfamethazine													ng/L	5
Sulfamethizole													ng/L	5
Sulfamethoxazole	2,100	1,600	140	10	2,500	1,500	220		1,000	720	85		ng/L	50
Sulfathiazole													ng/L	5
TCEP	310	300			430	350	130		280	210	160		ng/L	10
TCPP	2,800	2,400	58		800	980			2,200	2,500			ng/L	1,000
TDCPP	1,100	870			680	640			1,300	850			ng/L	100
Testosterone													ng/L	5
Theobromine	6,200	120			14,000	160			9,900				ng/L	10
Theophylline	10,000	85			8,900				7,800				ng/L	20
Trimethoprim	630	460			740	580			430	260	16		ng/L	5
2,4-D	38	18			130	60	9		320	19			ng/L	5
4-nonylphenol - semi quantitative							1,600	540	190	1,400		320	ng/L	100
4-tert-Octylphenol									420	640			ng/L	50
Acesulfame-K	14,000	1,200	420		13,000	1,700	1,500		44,000	4,100	86		ng/L	20
Bendroflumethiazide													ng/L	5
BPA	22	200			94	31	35				16		ng/L	10
Butalbital	8	9							80	18			ng/L	5
Butylparaben					12								ng/L	5
Chloramphenicol													ng/L	10
Clofibric Acid													ng/L	5
Diclofenac	85	69			72	61				150			ng/L	5
Estradiol													ng/L	5
Estrone	9				13	9				8			ng/L	5
Ethinyl Estradiol - 17 alpha													ng/L	5
Ethylparaben					150								ng/L	20
Gemfibrozil	490	150			550	150			1,200	180			ng/L	5
Ibuprofen	1,600				2,000				12,000				ng/L	10
Iohexal	11,000	4,300			8,200	6,200		32	24,000	12,000			ng/L	10
Iopromide									11				ng/L	5
Isobutylparaben					15								ng/L	5
Methylparaben					280								ng/L	20
Naproxen	2,600	33			3,300	61			31	71			ng/L	10
Propylparaben	280				800								ng/L	5
Sucralose	22,000	22,000	120		18,000	20,000			43,000	57,000			ng/L	100
Triclocarban	500	35	7	5	330	35			650	76			ng/L	5
Triclosan	1,200	13	14		960	91				120			ng/L	10
Warfarin										11			ng/L	5

PE = primary effluent; SE = secondary effluent; NF = nanofiltration permeate; RO = reverse osmosis permeate; MRL = minimum reporting limit

Exhibit C-4: Modeled Rejection Coefficients by CEC Analyte

Note: If a sample was not detected ("ND") in SE, it was not modeled and therefore not shown below. Each analyte's name is associated with an "n.#" where # indicates the data sample actual size.

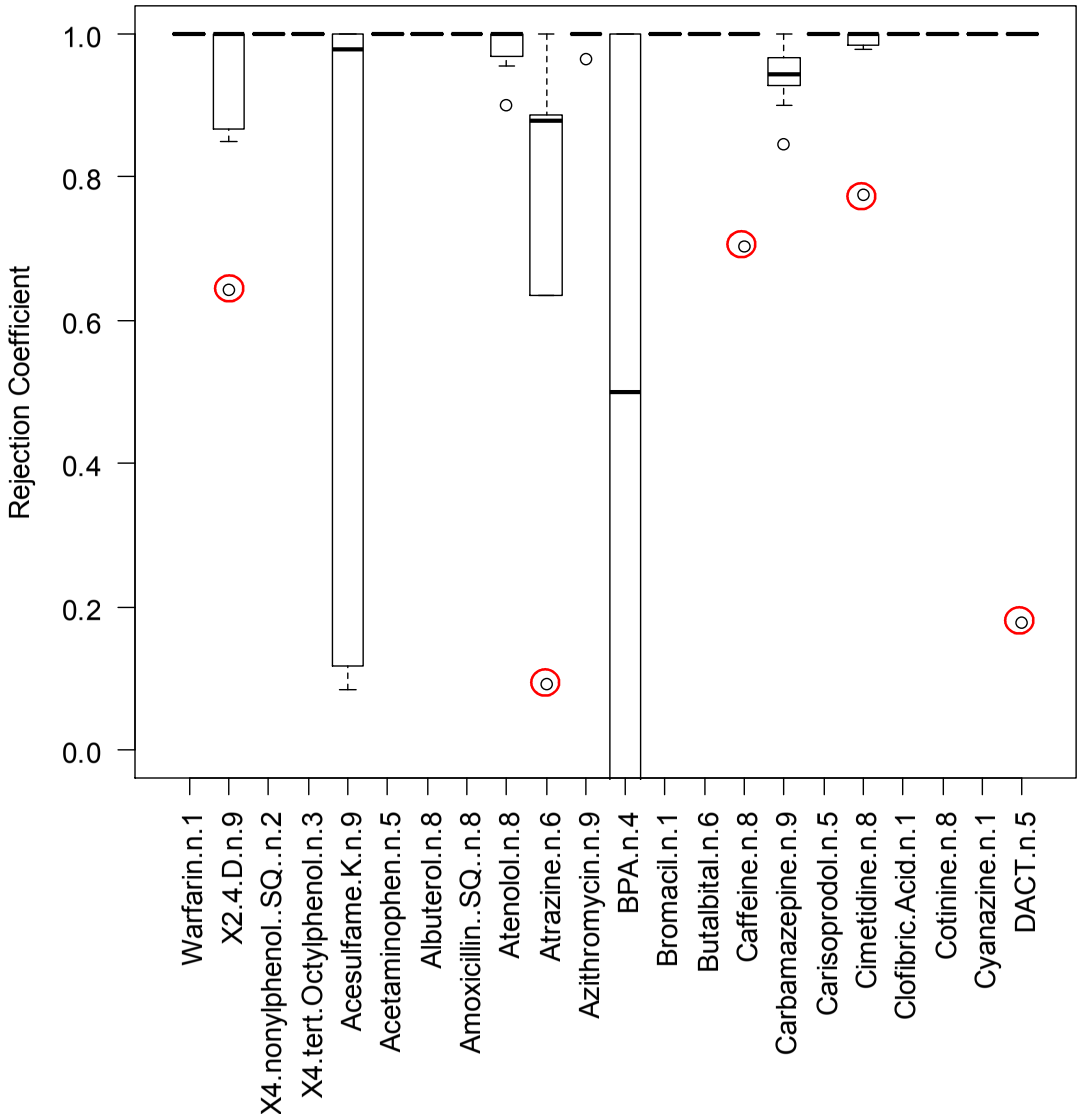

Exhibit C-4: Modeled Rejection Coefficients by CEC Analyte (Cont.)

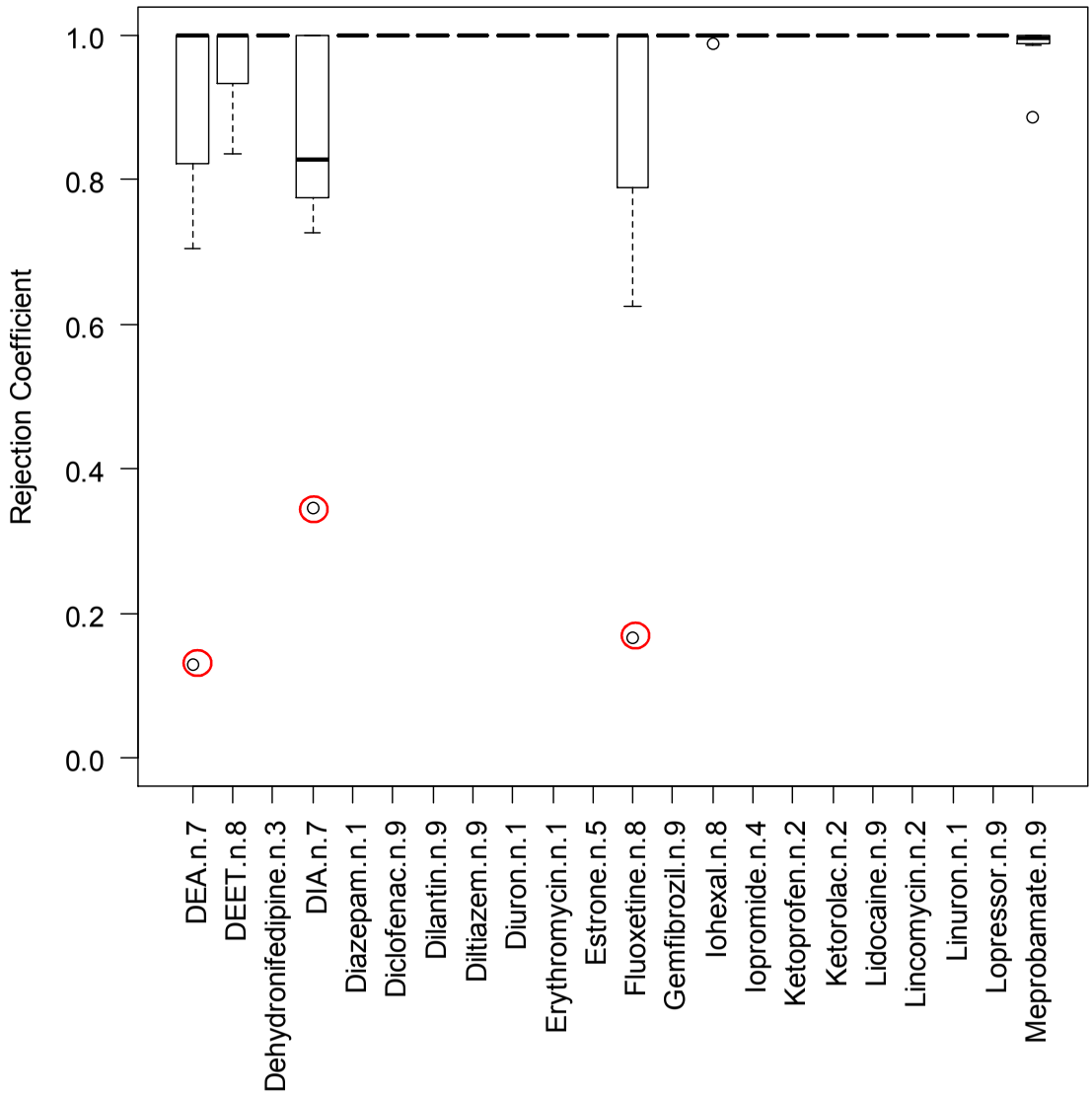

Exhibit C-4: Modeled Rejection Coefficients by CEC Analyte (Cont.)