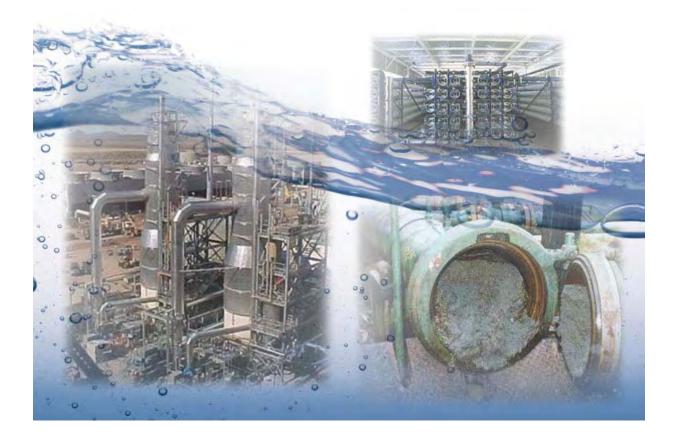


Secondary/Emerging Constituents Report

Southern California Regional Brine-Concentrate Management Study – Phase I Lower Colorado Region





U.S. Department of the Interior Bureau of Reclamation

Contents

Abbreviations and Acronymsvii			
1	Intr	oduction and Study Objectives	1
	1.1 I	Introduction	1
	1.2 \$	Study Objectives	3
	1.3 \$	Study Components	3
	1.4 I	Report Objectives	4
2	Con	pounds of Emerging Concern	7
	2.1 I	Background Information on CECs	7
	2.2 0	Categories and Description of CECs	11
	2.2.1	Synthetically and Naturally Occurring Hormones	11
	2.2.2		
	2.2.3	B Personal Care Products	14
	2.2.4		
	2.2.5		
	2.2.6	5 Disinfection By-products	20
	2.2.7		
3	Trea	atment Technologies	23
	3.1 I	Introduction	23
	3.2 I	Physical-Chemical Treatment Processes	25
	3.2.1	5	
	3.2.2		
	3.2.3	•	
	3.2.4	4 Ozone and Ozone/Hydrogen Peroxide	32
	3.2.5		
		Oxidation	35
	3.2.6	5 Membranes	37
	3.2.7	7 Magnetic Ion Exchange	41
	3.2.8		
	3.3 I	Biological Treatment Processes	
	3.3.1	•	
	3.3.2		
	3.3.3	Biological Aerated Filters and Biologically Active Carbon	49
	3.4 I	Natural Treatment Systems	
	3.4.1		
	3.4.2		
4	Reg	ulatory Status and Treatment Requirement for CECs	57
	-	Regulatory Status for CECs	
		Freatment Requirements for CECs	
5		hnology Selection and Cost Estimate	
		Fechnology Overview	
		Fechnologies with Moderate Removal Efficiency	
	5.2.1	•	
	5.2.2	-	

Summa	ary, Conclusions and Recommendations	
5.3.4	UV/AOP	
5.3.3	Reverse Osmosis	
5.3.2	Ozonation	71
5.3.1	Membrane Bioreactor	71
5.3 Tec	hnologies with High-Level Removal Efficiency	71
5.2.3	Conventional Activated Sludge	
	5.3 Tec 5.3.1 5.3.2 5.3.3 5.3.4	 5.2.3 Conventional Activated Sludge

Tables

Table 1.1	List of BEMT Members	1
Table 2.1	Chemicals With CDPH Notification Levels	10
Table 2.2	Endocrine-Disrupting and Other Chemicals	10
Table 2.3	Categorization of Hormones	12
Table 2.4	Commonly Detected PHACS	13
Table 2.5	Common Personal Care Products	
Table 2.6	USEPA List of Types of Pesticides	16
Table 2.7	Commonly Detected Pesticides	17
Table 2.8	Classification of EDCS Found in Industrial and Household	
	Products	18
Table 2.9	Common Disinfection By-Products	20
Table 3.1	Oxidants and Oxidation (Redox) Potentials	30
Table 4.1	Recommended emerging contaminants For GRRP Monitoring	58
Table 5.1	Treatment Technologies That Exhibit Moderate or High-level	
	Efficiency for Removal of CECs	62
Table 5.2	Brackish and Reuse RO Concentrate Water Quality	68

Figures

Figure 1.1	Map of Southern California Study Area	2
Figure 2.1	Compounds of Emerging Concern and Suspected Endocrine	
	Disrupters	8
Figure 3.1	GAC and PAC Material	. 27
Figure 3.2	GAC Towers Used in the Water Treatment industry	. 28
Figure 3.3	Chlorine Contact Basin Used in Wastewater Disinfection	. 31
Figure 3.4	Cross-Section of an Ozone Dielectric Plate	. 32
Figure 3.5	Ozone Contactors in Clark County, Nevada	. 33
Figure 3.6	Closed-Vessel UV Reactors	. 35
Figure 3.7	Submerged MF System (Left), Pressurized MF System (Right)	. 37
Figure 3.8	EMWD Perris Desalination Facility RO membranes	. 39
Figure 3.9	Schematic of RO Rejection Model (Continued on Next Page)	. 40
Figure 3.10	MIEX Process Flow Diagram	. 42
Figure 3.11	Package EDR Unit	. 43
Figure 3.12	Process Flow Schematic of a CAS system	. 46
Figure 3.13	Process Flow Schematic of an MBR System	. 49
Figure 3.14	BAF System at a WWTP	. 50
Figure 3.15	Process Schematic of an RBF system	. 52

Attachments

Attachment A Physical-Chemical Properties Attachment B CEC Removal Efficiencies

Abbreviations and Acronyms

°C	degrees Celsius
μg/L	micrograms per liter
АМО	ammonia monooxygenase
AOP	advanced oxidation process
APEO	alkylphenolic ethoxylate
AWWA	American Water Works Association
AWWARF	American Water Works Association Research Federation
BAA	biologically active anthracite
BAC	biologically active carbon
BAF	biological aerated filters
BAS	biologically active sand
BAT	best available technology
BEMT	Brine Executive Management Team
BHA	Butylatedhydroxinaisole
BHT	Butylatedhydroxytoluene
BNR	biological nutrient removal
BOD	biochemical oxygen demand
С	carbon
CAS	conventional activated sludge
CCL	Contaminant Candidate List
CCR	California Code of Regulation
CDCP	Center for Disease Control and Prevention
CDPH	California Department of Public Health
CEC	compound of emerging concern
COD	chemical oxygen demand
CW	constructed wetland

DA	Daltons
DBP	disinfection by-product
DDT	dichlorodiphenyltrichloroethane
DEET	N,N-Diethyl-meta-toluamide
DNA	deoxyribonucleic acid
DO	dissolved oxygen
DOC	dissolved organic carbon
E1	estrone
E2	estradiol
E3	estriol
EBPR	enhanced biological phosphorus system
EDC	endocrine-disrupting compound (chemical)
EDR	electro dialysis reversal
EDSTAC	Endocrine Disruptor Screening and Testing Advisory Committee
EDSTP	Endocrine Disruptors Screening and Testing Program
EDTA	ethylenediamine tetra acetic acid
EE2	ethinylestradiol
EMWD	Eastern Municipal Water District
GAC	granular-activated carbon
gal/d-sq-ft	gallons per day per square foot
gfd	gallons per square foot of membrane per day
gpm/sq-ft	gallon per minute per square foot
GRRP	groundwater recharge and reuse projects
GWRS	Groundwater Replenishment System
H_2O_2	hydrogen peroxide
HAA	haloacetic acid
HAH	halogenated aromatic hydrocarbon
HO*	hydroxyl free radical
HOC^1	hypochlorous acid

HRT	hydraulic retention time
IOC	inorganic contaminant
Κ	sorption capacity
Kow	octanol water partition coefficient
kV	kilovolts
L	liter
Lbs/d-sq.ft	pounds per day per square feet
LPHO	low-pressure high-output
MBR	membrane bioreactor
MCL	maximum contamination level
MF	microfiltration
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mgd	million gallons per day
MIEX	magnetic ion exchange
mJ/cm ²	milliJoules per square centimeter
mL	milliliter
MLSS	mixed-liquor suspended solids
MTBE	methyl tert-butyl ether
MW	molecular weight
MWCO	molecular weight cut-off
NDBA	N-nitrosodi-n-butylamine
NDEA	N-nitrosodiethyamine
NDMA	N-nitrosodimehylamine
NDPA	N-nitrosodi-n-propylamine
NF	nanofiltration
ng	nanogram
ng/L	nanogram per liter
NH ₃ -N	ammonia-nitrogen
NHANES III	National Health and Nutrition Examination Survey

NL	notification level
nm	nanometer
NMEA	N-nitrosomethylethylamine
NOM	natural organic matter
NPDES	National Pollutant Discharge Elimination System
NPEO1	Nonylphenol monoethoxylate
NPEO2	Nonylphenol diethoxylate
NPIP	N-nitrosopiperidine
NYPR	N-nitrospyrrolidine
O&M	operation and maintenance
O ₂	diatomic oxygen
O ₃	triatomic oxygen
OC1-	hypochlorite ion
OPEO1	Octylphenol monoethoxylate
OPEO2	Octylphenol diethoxylate
PAC	powder-activated carbon
PADEP	Pennsylvania Department of Environmental Protection
РАН	polycyclic aromatic hydrocarbon
РСВ	polychlorinated biphenyl
p-chem	physical-chemical
PCP	personal care product
PhAC	pharmaceutically active compound
рКа	acid solubility coefficient
ppb	parts per billion
PPCP	pharmaceuticals and personal care product
ppt	parts per trillion
psi	pounds per square inch
PSRO	precipitative softening reverse osmosis
RAS	return activated sludge
Reclamation	U.S. Department of the Interior Bureau of Reclamation

RF	riverbank filtration
RNA	ribonucleic acid
RO	reverse osmosis
RWQCB	Regional Water Quality Control Board
SDWA	Safe Drinking Water Act
SOC	synthetic organic compound
SRT	solids retention time
TCA	trichloroacetic acid
TCE	trichloroethylene
TCEP	tri(2-chloroethyl)phosphate
TDS	total dissolved solids
THM	trihalomethane
TOC	total organic carbon
TSS	total suspended solid
U.S.	United States
UF	ultrafiltration
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UV	ultraviolet
WERF	Water Environment Research Foundation
WHO	World Health Organization
WWTP	wastewater treatment plant

1 Introduction and Study Objectives

This section of the report has the following subsections:

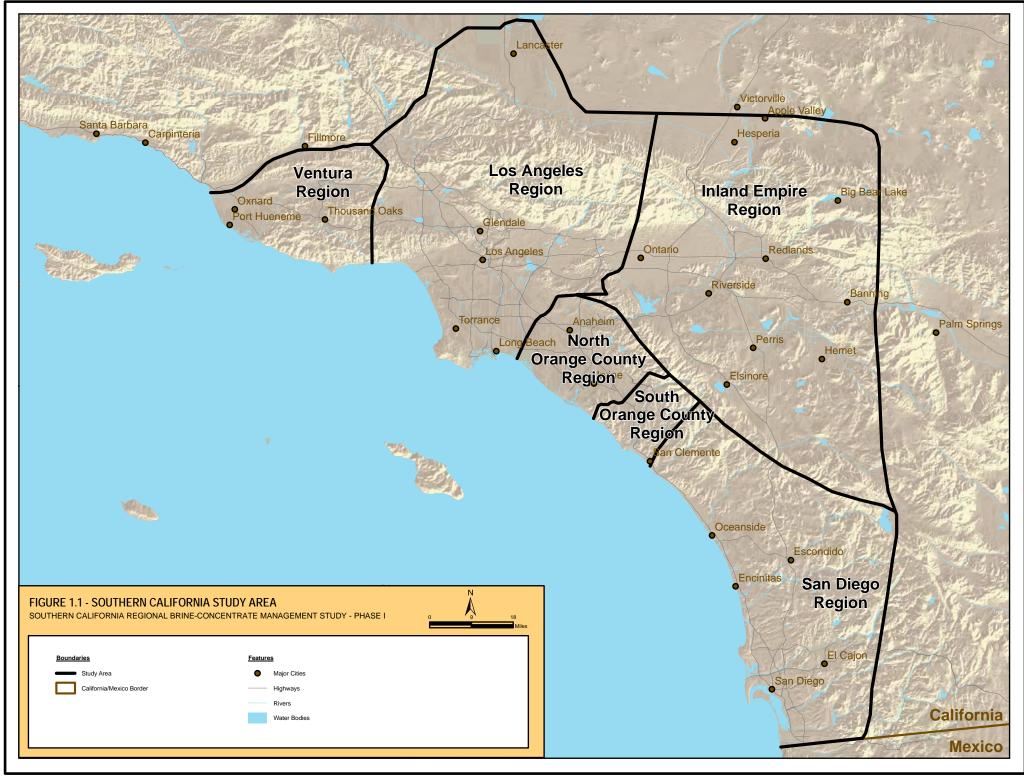
- Introduction
- Study Objectives
- Study Components
- Report Objectives

1.1 Introduction

The Southern California Regional Brine-Concentrate Management Study is a collaboration between the United States (U.S.) Department of the Interior Bureau of Reclamation (Reclamation) and 14 local and state agency partners. Table 1.1 provides a list of the agencies represented on the Brine Executive Management Team (BEMT). The project is funded on a 50/50 cost-sharing basis between Reclamation and the cost-sharing partners, who together form the BEMT. The purpose of the BEMT is to formulate, guide, and manage technical activities of the study. Figure 1.1 shows a map of the study area.

TABLE 1.1 LIST OF BEMT MEMBERS			
List of BEMT Members			
City of San Bernardino	Orange County Sanitation District		
California Department of Water Resources	Otay Water District		
City of San Diego	Rancho California Water District		
Inland Empire Utilities Agency	San Diego County Water Authority		
Sanitation Districts of Los Angeles County	Santa Ana Watershed Project Authority		
Los Angeles Department of Water and Power	U.S. Department of the Interior Bureau of Reclamation		
Metropolitan Water District of Southern California	Western Municipal Water District		
National Water Resources Institute/ Southern California Salinity Coalition			

1



1.2 Study Objectives

The objectives of this study are twofold:

- To assess the brine-concentrate landscape in southern California including brineconcentrate management technologies, regulatory environment, existing infrastructure, and future needs
- To make recommendations for Phase 2 pilot/demonstration projects

To accomplish these objectives, the study will develop six reports that ultimately will be incorporated into a final study report.

1.3 Study Components

The Southern California Regional Brine-Concentrate Management Study has six major components. Each component is focused on providing a piece of the southern California brine-concentrate management landscape. Each component will be summarized in a draft report that will be incorporated into the Final Study Report. The six components of the study are:

- Survey Report A regional survey to collect data from local agencies about the brine-concentrate landscape in southern California
- Regulatory Issue and Trends Report A summary of regulatory issues and trends associated with implementing a brine-concentrate project in southern California
- CECs Report A summary of constituents of emerging concern (CECs) and how regulation of CECs might affect brine-concentrate management in southern California
- Institutional Issues Report A summary of organizational structures that can be used to foster collaborative relationships between agencies implementing brine-concentrate management projects
- Brine-Concentrate Management Treatment and Disposal Options Report A summary of brine-concentrate technologies and identification of potential local and regional solutions
- Pilot/Demonstration Project Recommendations Report A list of recommended pilot/demonstration projects that could be implemented in the inland and coastal areas southern California

These six reports will be incorporated as appendices in the Final Study Report. The Final Report will provide highlights and conclusions of the six component reports in an executive summary format.

1.4 Report Objectives

Endocrine-disrupting compounds (EDCs), pharmaceutically active compounds (PhACs), and personal care products (PCPs) are important classes of emerging contaminants that occur ubiquitously in municipal wastewater effluent and have been found in drinking water. PhACs and PCPs have been grouped with other emerging contaminants (such as nitrosamines, disinfection by-products [DBPs], and metals) and are referred to as CECs. Although CECs have been known to occur in U.S. waters for over 30 years, it is only in the past decade that health and environmental concerns have been linked to these chemicals and have been brought to the forefront of the regulatory, scientific, and environmental communities. These compounds are receiving attention because a number of them have been reported to interfere with animal and human hormone systems at subnanogram (ng) levels of exposure. Because these chemicals have been detected in wastewater effluent and drinking water sources, reverse osmosis (RO) concentrate streams are expected to contain these chemicals.

The objective of this report is to:

- Identify and categorize CECs
- Define and characterize RO concentrate water quality from wastewater treatment plant (WWTP) effluent and brackish groundwater sources
- Identify treatment technologies that are applicable for reducing CECs and highlight the capabilities, treatment efficiencies, and implementation issues associated with each treatment process. Because no study has been done to understand fate and removal efficiencies of CECs in RO concentrate streams, the treatment technologies and CEC removal efficiencies are largely based on drinking and wastewater treatment studies cited in the literature.
- Identify the most suitable treatment options for removing CECs in RO concentrate originating from WWTP and brackish groundwater.

A number of key terms are used throughout this report. The definitions of these key terms are provided as a precursor for the report to provide clarity for the reader.

Pharmaceutically Active Compounds (PhACs): Pharmaceutically active compounds are a family of compounds that include prescription drugs such as analgesics, beta blockers, cancer medications, antibiotics, over-the-counter medications, drugs used in hospitals, and veterinary drugs.

Personal Care Products (PCPs): Personal care products are used by individuals for personal health or cosmetic purposes. A number of chemical substances are included in fragrances, lotions, and cosmetics.

Endocrine-Disrupting Chemicals (EDCs): Endocrine-disrupting chemicals or compounds are exogenous agents that interfere with the "synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body which are responsible for the maintenance of homeostasis, reproduction, development, and/or

behavior" (USEPA, 1996). The three major classes of EDCs are estrogenic (compounds that mimic or block natural estrogen), androgenic (compounds that mimic or block natural testosterone), and thyroidal (compounds with direct or indirect impacts on the thyroid glands). EDCs include a broad range of compounds such as hormones, pesticides, certain PhACs, PCPs, and DBPs.

Disinfection By-Products (DBPs): Disinfection by-products are generated when chlorine or other disinfection agents such as chlorine dioxide, chloramines, and ozone react with organic compounds in water. The most common forms of DBPs include trihalomethanes (THMs), haloacetic acids (HAAs), N-nitrosodimethylamine (NDMA), and aldehydes. DBPs are a concern because certain DBPs formed during water and wastewater treatment could behave like EDCs.

Compounds of Emerging Concern (CECs): Compounds of emerging concern are naturally and synthetically occurring hormones, PhACs, PCPs, DBPs, industrial and household chemicals, and metals. The term *CEC* has been used since 2007 when the Water Environment Research Federal (WERF) lumped several group of compounds, which were suspected endocrine disrupters, together under the term CECs.

2 Compounds of Emerging Concern

This section of the report contains the following subsections:

- Background information on CECs
- Categories and descriptions of CECs

2.1 Background Information on CECs

For over 70 years, researchers have reported that certain synthetic compounds, such as detergents and pesticides, and natural compounds, such as sex hormones, can affect the balance of normal hormonal function in animals. These substances are collectively known as endocrine-disrupting compounds and have been linked to a variety of adverse effects in humans and wildlife (Snyder et al., 2007). For example, fish feminizations have been linked to the presence of EDCs in outfalls from Los Angeles County, Orange County, and San Diego County in California, as well as in the Thames River in the United Kingdom.

The feminization of fish is generally characterized by increased hormone levels, development of the intersex conditions (organisms with biological characteristics of both male and female sexes), or skewed sex ratios. In some amphibian populations, supernumerary (extra) limbs and missing limbs have been attributed to certain pesticides and anthropogenic compounds (Sparling, 2000). The United States Environmental Protection Agency (USEPA) has defined environmental EDCs as exogenous agents that interfere with the "synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body which are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior" (USEPA, 1996). The three major classes of EDCs are estrogenic (compounds that mimic or block natural estrogen), androgenic (compounds that mimic or block natural testosterone), and thyroidal (compounds with direct or indirect impacts to the thyroid glands) (Snyder et al., 2007).

More recently, PhACs and PCPs have been discovered in various surface and groundwaters, some of which have been linked to ecological impacts at trace concentrations (at 1 nanogram per liter [ng/L], for example). These PhACs and PCPs were eventually grouped with other emerging contaminants (that is, with nitrosamines, DBPs, and metals) and referred to as CECs (Drewes, 2006; WERF, 2007), shown in Figure 2.1.

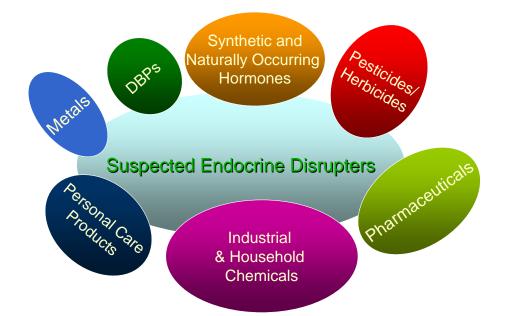


FIGURE 2.1 COMPOUNDS OF EMERGING CONCERN AND SUSPECTED ENDOCRINE DISRUPTERS

Sources of CECs in the environment are varied and widespread. Occurrence surveys suggest these substances are entering public water supplies in trace quantities through natural processes and nonpoint source pollution (such as agricultural runoff and wastewater discharges). Some of these compounds have been suspected in developmental and reproductive changes in fish and amphibians, and evidence indicates that mammals might be sensitive to extremely low concentrations of hormones, PhACs, and PCPs. For this reason, USEPA is studying CECs for possible health effects (AWWARF, 2005).

To date, no firm evidence for association between low-dose exposure to CECs and adverse human health effects has been found. Therefore, the health effects on humans at low-dose exposures are unknown for many CECs. Most endocrine disruptors currently are considered "suspect" rather than "known" because "current understanding of the effects posed by EDCs to wildlife and humans is incomplete" (WHO, 2002). One key reason for this lack of understanding is that, until recently, few analytical methods have been capable of detecting these compounds at the low concentrations that might be expected to occur in the environment. Modern analytical techniques have increased the accuracy and sensitivity, allowing ultratrace levels of a wide variety of compounds to be identified and quantified. As a result, about 87,000 compounds are listed as suspect compounds (AWWARF, 2005). Although many compounds are referred to as EDCs, no definitive list of EDCs exists, and assays for determination of whether a particular chemical, or mixture of chemicals, results in adverse impacts to the endocrine system have not been compiled (Snyder et al., 2007). So far, the following compounds have been identified as EDCs:

- Dichlorodiphenyltrichloroethane (DDT)
- Polychlorinated biphenyls (PCB)

- Phenols
- Organochlorines phthalates
- Alkylphenolic ethoxylates (APEOs)
- Phthalates
- Polycyclic aromatic hydrocarbons (PAHs)
- Halogenated aromatic hydrocarbons (HAH)
- Natural and synthetic estrogenic hormones

APEOs and estrogenic hormones (17b-estradiol and estrone, for example) have received the greatest attention from environmental scientists due to their presence in wastewater effluent and a demonstrated impact on wildlife. A U.S. Geological Survey (USGS) surveillance study looked at 15 biogenic and synthetic hormones and sterols, as well as 35 household and industrial wastewater products in 30 United States streams (Buxton, 2002). The most commonly detected compounds (that is, compounds found in more than 40 percent of samples) included ethanol-2-butoxy-phosphate, triclosan, tri(2-chloroethyl)phosphate (TCEP), para-nonylphenol, and bisphenol A.

Not all PCPs and PhACs are EDCs, and vice versa. Clearly, certain compounds (such as certain oral contraceptive medications and estrogen replacement pharmaceuticals) can fit both categories. Despite sparse data on health risks from human exposure to trace concentrations of emerging contaminants through drinking water and water recycling projects, it appears that public perception will be a key factor for the implementation of more advanced treatment technologies to further reduce emerging compounds in water and wastewaters and to explore human health relevance (Snyder et al., 2007).

California Department of Public Health (CDPH) recommended monitoring of additional constituents including pharmaceuticals, EDCs, PCPs, and other indicators of municipal wastewater contaminants at groundwater recharge projects (CDPH, 2007). Although these chemicals are not currently under CDPH regulation, a majority of these compounds have been detected at least once in drinking water supplies. CDPH has set notification level (NL) for some chemicals and recommended monitoring parameters for groundwater recharge and reuse projects (GRRP). The most updated Groundwater Recharge Reuse Draft Regulation (August 2008) does not specifically identify monitoring parameters for GRRP but recommends that GRRP investigate chemicals (presented in Tables 2.1 and 2.2), or use surrogates that could represent one or more constituents in each category. This revision was made considering limitations of the analytical methods for identification and detection of emerging contaminants. In either case, the information is useful for providing insight on the frequency of detection of emerging compounds.

Chemicals with CDPH Notification Levels ^a			
Formaldehyde	1,2,4-trimethylbenzene		
n-Butylbenzene	1,3,5-trimethylbenzene		
sec-Butylbenzene	Nitrosamines		
tert-Butylbenzene	N-nitrosodiethyamine (NDEA)		
Carbon disulfide	N-nitrosodimethylamine		
Chlorate	N-nitrosodi-n-propylamine (NDPA)		
2-Chlorotoluene	N-nitrosodi-n-butylamine (NDBA)		
1,4-Dioxane	N-nitrosomethylethylamine (NMEA)		
Isopropylbenzene	N-nitrosopiperidine (NPIP)		
N-propylbenzene	N-nitrospyrrolidine (NYPR)		

TABLE 2.1 CHEMICALS WITH CDPH NOTIFICATION LEVELS

Note:

^a Contaminants listed are from the January 2007 Title 22 California Code of Regulations, Groundwater Recharge Reuse Draft Regulations. The updated August 2008 version of the draft does not recommend any specific chemicals

Source: CDPH, 2007 and 2008

TABLE 2.2

ENDOCRINE-DISRUPTING AND OTHER CHEMICALS

Endocrine-Disrupting and Other Chemicals ^a			
Ethinyl estradiol (Hormone)	Caffeine (Other Indicators)		
17 $β$ -Estradiol (Hormone)	Carbamazepine (Pharmaceutical)		
Estrone (Hormone)	Ciprofloxacin (Pharmaceutical)		
Bisphenol A (Industrial EDC)	Ethylenediamine Tetra Acetic Acid (EDTA)		
Nonylphenol (Industrial EDC)	Gemfibrozil (Pharmaceutical)		
Nonylphenol polyethoxylate (Industrial EDC)	Ibuprofen (Pharmaceutical)		
Octylphenol (Industrial EDC)	Iodinated Contrast Media (Other Indicators)		
Octylphenol polyethoxylate (Industrial EDC)	Lipitor (Pharmaceutical)		
Polybrominated diphenyl ethers (Industrial EDC)	Methadone (Pharmaceutical)		
Acetaminophen (Pharmaceutical)	Morphine (Pharmaceutical)		
Amoxicillin (Pharmaceutical)	Salicylic Acid (Pharmaceutical)		
Azithromycin (Pharmaceutical)	Triclosan (PCP)		

Note:

^aContaminants listed are from the January 2007 Title 22 California Code of Regulations, Groundwater Recharge Reuse Draft Regulations. The updated August 2008 version of the draft does not recommend any specific chemicals

Source: CDPH, 2007 and 2008

Studies of CECs are also taking place in other states, such as in Pennsylvania where a USGS committee is developing a list of potential drinking water contaminants not currently regulated by the Pennsylvania Department of Environmental Protection (PADEP) (MacGillivray, 2007). The committee is reviewing databases and considering the treatability of potential contaminants. Results from this study were used as part of a data set for a nationwide reconnaissance of emerging contaminants in streams (Loper et al., 2007). The performance of such studies, together with monitoring of emerging contaminants recommended by agencies similar to CDPH, might result in the development of a regulatory framework through which some of the contaminants listed in Tables 2.1 and 2.2 could be regulated in the near future.

2.2 Categories and Description of CECs

CECs fit into different categories based on their impacts to humans or the environment. As presented in Figure 2.1, CECs can be categorized into the following groups:

- Synthetically and naturally occurring hormones
- PhACs
- PCPs
- Pesticides, herbicides, and insecticides
- Industrial and household chemicals
- DBPs
- Metals

Although nutrients and microorganisms have been included in the list of emerging compounds by some researchers, a majority of these compounds are either regulated (for example, nitrogen and coliform) or the impact of these compounds on aquatic life and human health has been well documented. Therefore, these compounds were excluded from analysis in this report because they are not constituents of emerging concern. The following subsections of this report will provide a description of the above-listed CECs, including the reasoning that makes each a concern, and a description of potential treatment mechanisms.

2.2.1 Synthetically and Naturally Occurring Hormones

The estrogenic hormones include the natural hormones estrone (E1), 17β -estradiol (E2), 17α -estradiol, and estriol (E3), as well as the synthetic hormone 17α -ethinylestradiol (EE2) found in birth control pills. Estrogenic hormones are discharged to the environment mainly through wastewater effluent and agricultural runoff. These hormones are potent endocrine disruptors capable of causing feminization of male fish at concentrations as low as 1 ng/L (Lange and Dietrich, 2002; Routledge et al., 1998; Thorpe et al., 2001). Concentrations of hormones above 1 ng/L have been observed both in municipal wastewater effluent and effluent-dominated receiving waters (Desbrow et al., 1998; Kolodziej and Sedlak, 2003). These hormones have received the greatest attention from environmental scientists due to their presence in wastewater effluent and demonstrated impacts on

wildlife. 17β -estradiol is considered the most potent estrogenic hormone; therefore, estrogenic activity in water samples is often reported in estradiol equivalents because all possible estrogenic compounds have not been identified (Snyder et al., 2001). Synthetic hormones, such as 17α -ethinylestradiol and equilin, are generally more stable in water than naturally occurring hormones (Drewes, 2005). The USGS categorization of hormones is presented in Table 2.3.

CATEGORIZATION OF HORMONES	
Name	Category
Naturally Occurring Hormones	
Estrone	Female Hormone
17 α-Estradiol	Female Hormone
17 β -Estradiol	Female Hormone
Estriol	Biogenic
Testosterone	Male Hormone
Progesterone	Biogenic
Cis-Androsterone	Biogenic
Synthetic Hormones	
17 α-Ethynylestradiol	Ovulation Inhibitor
Mestranol	Ovulation Inhibitor
19-Norethisterone	Ovulation Inhibitor
Equilenin	Hormone Replacement Therapy
Equilin	Hormone Replacement Therapy
Cholesterol	Fecal Indicator
3 β -Coprostanol	Carnivore Fecal Indicator
Stigmastanol	Plant Sterol

TABLE 2.3 CATEGORIZATION OF HORMON

A majority of hormones, especially naturally occurring hormones, can be effectively removed during secondary, tertiary, and advanced water treatment processes. An octanol water partition coefficient (Kow) is the ratio of concentration of a compound in two phases of a mixture of two immiscible solvents (in other words, octanol and water) at equilibrium. A relatively high octanol water partition coefficient of log Kow greater than 2 indicates that those compounds can accumulate in sediments and biota. A high octanol water partition coefficient also indicates that these compounds can be effectively removed using an adsorption process such as granular-activated carbon (GAC).

2.2.2 Pharmaceutically Active Compounds

Pharmaceutically active compounds are a family of compounds that include prescription drugs (such as analgesics, beta blockers, cancer medications, and

antibiotics) over-the-counter medications, drugs used in hospitals, and veterinary drugs. A variety of PhACs were reported in wastewater effluent, surface water, and groundwater in Europe as early as 1990 (AWWARF, 2005). Although no known human health effects have been associated with exposure of drinking water that contain trace concentrations of PhACs, the scientific community, regulators, and consumers have expressed concerns about exposure to PhACs. Analysis of most commonly used PhACs in the United States indicates that they are ubiquitous in wastewater effluent.

In 2005, the AWWARF collaborated with the pharmaceutical industry to identify the most commonly used prescription drugs in the United States and determine the estimated concentrations of these drugs in wastewater influent. AWWARF estimated concentrations of commonly used prescription drugs in wastewater influent by dividing the mass of drug excreted by patients by the volume of wastewater discharged to municipal wastewater treatment plants. Estimated concentrations of drugs in wastewater treatment plants. Estimated concentrations of drugs in wastewater treatment influent ranged from less than 1 ng/L to approximately 130,000 ng/L, but the majority of concentrations were between 100 ng/L and 1,000 ng/L. Table 2.4 shows 40 PhACs whose concentrations exceeded 1,000 ng/L (AWWARF, 2005).

PhACs have diverse physical-chemical (for example, solubility, Kow, and acid solubility coefficient [pKa]) and structural properties. For this reason, no single treatment technology is suitable for the treatment of more than 10,000 PhACs.

Name	Classification
Acetaminophen	Analgesic
Ibuprofen	Analgesic, anti-inflammatory
Amoxicillin	Antibiotic
Metformin	Antidiabetic
Cephalexin	Antibiotic
Nabumetone	Analgesic, anti-inflammatory
Azithromycin	Antibiotics
Oxaprozin	Analgesic, anti-inflammatory
Sodium valproate	Anticonvulsant
Gabapentin	Anticonvulsant
Carisoprodol	Skeletal muscle relaxant
Penicillin	Antibiotic
Sulfamethoxazole	Antibiotic
Gemfibrozil	Cholesterol lowering
Metoprolol	Beta blocker

TABLE 2.4 COMMONLY DETECTED PHACS

Name	Classification
Ciprofloxacin	Antibiotic
Ranitidine	H ₂ -receptor antagonist
Mupirocin	Antibiotic
Clarithromycin	Antibiotic
Phenytoin	Anticonvulsant
Diltiazem	Calcium channel blocker
Naproxen	Analgesic, anti-inflammatory
Verapamil	Calcium channel blocker
Ipratropium	Bronchlodialator
Trimethoprim	Antibiotic
Tramadol	Analgesic
Cimetidine	H ₂ -receptor antagonist
Clavulanic acid	Antibiotic
Propoxyphene	Opioid analgesic
Bupropion	Antidepressant
Hydrochlorothiazide	Diuretic
Troglitazone	Antidiabetic
Cefprozil	Antibiotic
Pseudoephedrine	Decongestant
Erythromycin	Antibiotic
Atenolol	Beta blocker
Sertraline	Antidepressant
Triamterene	Diuretic
Nefazodone	Antidepressant
Tetracycline	Antibiotic
Allopurinol	Antigout

TABLE 2.4 COMMONLY DETECTED PHACS

Source: Sedlak and Pinkston, 2001; AWWARF, 2005

2.2.3 Personal Care Products

Personal care products are products used by individuals for personal health or cosmetic purposes, including a number of chemical substances such as fragrances, lotions, and cosmetics. The major source of PCPs found in the environment is a result of human activities such as bathing, shaving, and swimming. PCPs in the

environment are frequently found in aquatic environments because PCPs dissolve easily and do not evaporate at ambient temperatures and pressures.

Triclosan, a potent wide-spectrum antibacterial and antifungal agent, is one of the most commonly detected PCPs and is used primarily in soaps, toothpastes, and detergents. Triclosan reacts with free chlorine in tap water to form chloroform gas, which is classified as a probable human carcinogen by USEPA, and produces smaller amounts of other compounds such as 2,4-dichlorophenol (Rule et al., 2005). The compounds created during intermediate reactions, convert into dioxins upon exposure to light. Some dioxins are extremely toxic and are potent endocrine disruptors. Table 2.5 provides a list of the most commonly referenced PCPs and their sources.

Due to diverse physical-chemical, molecular, and structural properties, no single treatment exists to effectively remove all PCPs. For this reason, treatment methods need to be assessed on a compound-by-compound basis.

Compound	Source
Benzophenone	Sunscreen
Oxybenzone	Sunscreen
Triclosan	Anti-microbial
Alkylphenol ethoxylates	Surfactant
Nonlyphenol ethoxylates	Surfactant
3-Phenylpropionate	Fragrance
Acetophenone	Fragrance
Diethyl 3-phenylpropionate	Fragrance
Galaxolide	Fragrance
Musk Ketone	Fragrance
1,4 Dioxane	Shampoo

TABLE 2.5

COMMON PERSONAL CARE PRODUCTS

2.2.4 Pesticides, Herbicides, and Insecticides

Pesticides, herbicides, and insecticides consist of substances or mixtures of substances intended for preventing, destroying, repelling, or mitigating pests (that is, any insects, mice or other animals, unwanted plants or weeds, fungi, or microorganisms like bacteria and viruses).

Certain pesticides in environmentally relevant concentrations can affect the reproductive systems of animals. In addition, supernumerary and missing limbs have been attributed to pesticides in some amphibian populations (for example, trace quantities of the herbicide atrazine in the endocrine disruption of frogs in the Midwestern U.S.). The source of these pesticides is generally from agricultural runoff. DDT is a well-publicized EDC that is responsible for eggshell thinning and

altered gonadal development in birds of prey. A recent DDT spill was also blamed for the decline of alligator populations and the decrease of reproductive capability among panthers at Lake Apopka in Florida (van Vuuren, 2008).

Most pesticides are removed from effluent via biodegradation and adsorption during wastewater treatment processes; however, some pesticides with more hydrophilic (water-loving) characteristics might be capable of escaping conventional treatment processes. Advanced water treatment processes such as nanofiltration (NF), RO, ozone, and ultraviolet (UV)/advanced oxidation processes (AOP) could remove the remaining pesticides effectively. Also, ozone is generally effective at removing pesticides, herbicides, and insecticides but it is not effective on herbicides such as atrazine, and pesticides such as DDT and N,*N*-Diethyl-meta-toluamide (DEET). In fact, DEET has a high frequency (100 percent) of occurrence in source waters as well as in finished waters (over 90 percent), thereby showing that DEET is difficult to remove from water using conventional treatment processes (Snyder et al., 2007). However, DEET can be removed effectively using UV/AOP, ozone/AOP, and RO. A comprehensive list of the pesticides is provided in Table 2.6.

Type of Pesticide	Use of Pesticide
Algaecides	Control algae in lakes, canals, swimming pools, water tanks, and other sites
Antifouling agents	Kill or repel organisms that attach to underwater surfaces, such as boat bottoms
Antimicrobials	Kill microorganisms (such as bacteria and viruses)
Attractants	Attract pests (for example, to lure an insect or rodent to a trap. However, food is not considered a pesticide when used as an attractant)
Biocides	Kill microorganisms
Disinfectants and sanitizers	Kill or inactivate disease-producing microorganisms on inanimate objects
Fungicides	Kill fungi (including blights, mildews, molds, and rusts)
Fumigants	Produce gas or vapor intended to destroy pests in buildings or soil
Herbicides	Kill weeds and other plants that grow where they are not wanted
Insecticides	Kill insects and other arthropods
Miticides (also called acaricides)	Kill mites that feed on plants and animals
Microbial pesticides	Microorganisms that kill, inhibit, or out compete pests, including insects or other microorganisms
Molluscicides	Kill snails and slugs
Nematicides	Kill nematodes (microscopic, worm-like organisms that feed on plant roots)

TABLE 2.6 USEPA LIST OF TYPES OF PESTICIDES

Type of Pesticide	Use of Pesticide
Ovicides	Kill eggs of insects and mites
Pheromones	Biochemicals used to disrupt the mating behavior of insects
Repellents	Repel pests, including insects (such as mosquitoes) and birds
Rodenticides	Control mice and other rodents
Defoliants	Cause leaves or other foliage to drop from a plant, usually to facilitate harvest
Desiccants	Promote drying of living tissues, such as unwanted plant tops
Insect growth regulators	Disrupt the molting, maturity from pupal stage to adult, or other life processes of insects
Plant growth regulators	Substances (excluding fertilizers or other plant nutrients) that alter the expected growth, flowering, or reproduction rate of plants

TABLE 2.6 USEPA LIST OF TYPES OF PESTICIDES

Source: USEPA, 2009

Extensive research has been performed on a number of pesticides resulting in many of them being regulated by USEPA as primary maximum contamination level (MCLs). The compounds alachlor (MCL of 2 micrograms per liter [μ g/L]), atrazine (MCL of 3 μ g/L), chlordane (MCL of 2 μ g/L), and lindane (MCL of 0.2 μ g/L) are regulated by USEPA as primary MCLs. These MCLs have been effective since the early 1990s. Although regulated compounds are no longer emerging compounds, these four compounds were included in this report because they have been frequently detected in groundwater, drinking water, and wastewater effluent; research studies performed to understand the fate of CECs through treatment processes have included these compounds. Table 2.7 is a list of commonly detected pesticides.

TABLE 2.7

COMMONLY DETECTED PESTICIDES

Chemical	Category	Concern
Lindane ^a	Insecticide/Pesticide	EDC
Dichloro-diphenyl- trichloroethane	Synthetic Pesticide	EDC
Atrazine ^a	Herbicide	EDC/Carcinogen
Metolachlor	Herbicide	EDC
Carbaryl	Insecticide	Carcinogen
cis-Chloridane ¹	Pesticide	EDC/Carcinogen
Dieldrin	Insecticide	EDC/Carcinogen
Alachlor ^a	Herbicide	EDC/Carcinogen
Mirex	Synthetic Insecticide	EDC/Carcinogen
DEET	Insect Repellent	EDC/Seizures

Chemical Category	Concern
Diazinon Insecticide	EDC
Chlorpyrifos Insecticide/Pesticide	EDC
Methyl parathion Insecticide/Acaricide	EDC/Carcinogen

TABLE 2.7 COMMONLY DETECTED PESTICIDES

Notes:

^a Currently regulated by USEPA MCL.

2.2.5 Industrial and Household Products

Industrial and household products include PAHs, antioxidants, solvents, plastilizer, wood preservatives, fire retardants, and detergent metabolites. Some of the EDCs commonly used in industrial and household products are provided in Table 2.8. Extensive research has been performed on a number of compounds resulting in many of them being regulated by USEPA as primary MCLs since the 1990s. Compounds such as benzo(a)pyrene (MCL of $0.2 \ \mu g/L$), tetrachloroethylene (MCL of $5 \ \mu g/L$), 1,4-dichlorobenzene (MCL of $75 \ \mu g/L$), bis(2-ethylhexyl)adipate (MCL of $400 \ \mu g/L$), bis(2-ethylhexyl)phthalate (MCL of $6 \ \mu g/L$) are already regulated by federal and state regulations. The regulations for these compounds came into effect between 1989 and 1994 and required that these chemicals be monitored and reported continuously. Although there is a lot of information and data about these compounds, they were included in the list of CEC because they are EDCs.

Name	Classification
Naphthalene	Polycyclic Aromatic Hydrocarbons (Fossil Fuel)
Phenanthrene	Polycyclic Aromatic Hydrocarbons (Fossil Fuel)
Anthracene	Polycyclic Aromatic Hydrocarbons (Fossil Fuel)
Fluoranthene	Polycyclic Aromatic Hydrocarbons (Fossil Fuel)
Pyrene	Polycyclic Aromatic Hydrocarbons (Fossil Fuel)
Benzo(a)pyrene ¹	Polycyclic Aromatic Hydrocarbons (Fossil Fuel)
2,6-di-tert-Butylphenol	Antioxidants
5-Methyl-1H-benzotriazole	Antioxidants
Butylatedhydroxinaisole (BHA)	Antioxidants
Butylatedhydroxytoluene (BHT)	Antioxidants
2,6-di-tert-Butyl-p-benzoquinone	Antioxidants
Tetrachloroethylene*	Solvent
1,4-Dichlorobenzene*	Fumigant
p-Cresol	Wood Preservative

TABLE 2.8

CLASSIFICATION OF EDCS FOUND IN INDUS	
Name	Classification
Phthalic anhydride	Used in plastics
Bisphenol A	Plasticizer
Bis(2-Ethylhexyl)adipate*	Plasticizer
Ethanol-2-butoxy-phosphate	Plasticizer
Bis(2-Ethylhexyl)phthalate*	Plasticizer
Diethylphthalate	Plasticizer
Triphenyl phosphate	Plasticizer
p-Nonylphenol	Detergent metabolite
Nonylphenol monoethoxylate (NPEO1)	Detergent metabolite
Nonylphenol diethoxylate (NPEO2)	Detergent metabolite
Octylphenol monoethoxylate (OPEO1)	Detergent metabolite
Octylphenol diethoxylate (OPEO2)	Detergent metabolite
Tri(2-Chloroethyl)phosphate	Fire retardant
Tri(dichloropropyl)phosphate	Fire retardant

TABLE 2.8

CLASSIFICATION OF EDCS FOUND IN INDUSTRIAL AND HOUSEHOLD PRODUCTS

Notes:

*Currently regulated by USEPA MCL.

Plasticizers, such as bisphenol A, are extensively used in the production of polycarbonate and epoxy resins. It commonly can be found in adhesives, reinforced pipes, coatings, flooring, electronic goods, paints, and some resistant plastic foods and drinks containers (van Vuuren, 2008). Bisphenol A has been known to mimic estrogen when given in large amounts to animals and has the ability at much lower doses to affect hormonal processes involved in development when an animal is exposed as a fetus or during infancy. Bisphenol A leaches in small amounts from plastic items such as polycarbonate baby bottles and is present in infant formula coming from epoxy-lined cans. Studies by the National Health and Nutrition Examination Survey (NHANES III) conducted by the Centers for Disease Control and Prevention (CDCP) found detectable levels of bisphenol A in 93 percent of 2,517 urine samples from people 6 years of age and older (U.S. Department of Health and Human Services, 2008).

Phthalates are another category of compound that is commonly found in many industrial and household products. Phthalates are used to add flexibility to a range of plastic goods and are found in some paints, inks, adhesives, and cosmetic products. The fact that specific phthalates can adversely affect reproduction has been known for more than 25 years. Also, phthalates affect animals more the younger they are (in other words, fetuses are more susceptible than newborns, and newborns are more susceptible than adults). In humans, studies have linked a mother's exposure to specific phthalates to adverse impacts in their children including decreased testosterone levels in boys (U.S. Department of Health and Human Services, 2008).

Another EDC with industrial uses is TCEP, a flame retardant used in the production of liquid polyester resins and in textile back-coating formulations. TCEP has been detected in rivers, seawater, drinking water, sediment, fish and shellfish, and even a few food items (WHO, 2009). TCEP is of particular importance and concern due to its extreme resilience to conventional oxidation, biodegradation, and advanced oxidation processes. TCEP, as well as the impact it has on the environment, remains for extended periods.

Diverse physical-chemical, molecular, and structural properties make the removal of industrial and household products via a single treatment process difficult. For this reason, treatment methods need to be assessed on a compound-by-compound basis.

2.2.6 Disinfection By-products

In the early 1970s, the use of oxidants, such as chlorine and ozone, in water treatment plants for disinfection or for taste and odor and color removal was discovered to result in production of undesirable DBPs (USEPA, 2008). Formation of DBPs is of great concern because of the potential impact to public health including cancer and birth defects. Chloroform is a well-known carcinogen, and many of the constituent haloforms are thought to be carcinogenic as well. THMs and HAAs are the DBPs occurring most frequently and with highest concentration. Both THMs and HAAs are tightly regulated under Federal Drinking Water Regulations. Table 2.9 provides a list of DBPs.

Chlorination-Based DBPs	Group
Chloroform ^a	Trihalomethane
Bromodichloromethane ^a	Trihalomethane
Dibromochloromethane ¹	Trihalomethane
Bromoform ^a	Trihalomethane
Monochloroacetic acid ^a	HAAS
Dichloroacetic acid ^a	HAAS
Trichloroacetic acid ^a	HAAS
Bromoacetic acid ^a	HAAS
Dibromoacetic acid ^a	HAAS
Bromochloroacetonitrile	Haloacetonitrile
Dibromoacetonitrile	Haloacetonitrile
Dichloroacetonitrile	Haloacetonitrile
Trichloroacetonitrile	Haloacetonitrile
Dichloroacetic aldehyde	Haloaldehyde

TABLE 2.9 COMMON DISINFECTION BY-PRODUCTS

Chlorination-Based DBPs	Group
Trichloroacetic aldehyde	Haloaldehyde
1,1-dichloropropanon	Haloketone
1,1,1-trichloropropanon	Haloketone
1,1-dichloro-2-butanon	Haloketone
1,1,1-trichloro-2-butanon	Haloketone
2-chlorophenol	Chlorophenol
2,4-dichlorophenol	Chlorophenol
2,4,6-trichlorophenol	Chlorophenol
Chloropicrin	Others
Cyanogen chloride	Others
MX	Other
Chlorite ^b	Others
Bromate ^b	Others
Ozonation-Based DBPs	Group
Formaldehyde	Ozonated aldehyde
Glyoxal	Ozonated aldehyde
Acetaldehyde	Ozonated aldehyde
Others	Group
NDEA	Nitrosamine
NDMA	Nitrosamine
NDPA	Nitrosamine
NDBA	Nitrosamine
NMEA	Nitrosamine
NPIP	Nitrosamine
NYPR	Nitrosamine

TABLE 2.9 COMMON DISINFECTION BY-PRODUCTS

Notes:

^a Regulated by USEPA Primary MCL for total THMs. Sum of all four THMs should be equal or less than 80 parts per billion (ppb).

^b Regulated by USEPA Primary MCL. Sum of all five HAAs should be equal or less than 80 ppb.

Source: Nawrocki, Undated.

Another DBP that recently has been discovered in disinfected treated wastewater effluent is NDMA, which is a member of a class of compounds known as nitrosamines. Nitrosamines are among the most powerful carcinogens known (Tchobanoglous et al, 2003). California drinking water regulation has established a notification level of 0.01 μ g/L or parts per billion (ppb) for NDMA. Data from studies have demonstrated that NDMA is associated with the use of chloramines and, to a lesser extent, free chlorine.

The Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) has recommended that DBPs be evaluated for potential endocrine disruptive effects because it has been suggested that certain DBPs formed during wastewater disinfection can behave as EDCs. Chlorination performed on waters containing natural organic matter (NOM) increases the estrogenicity of the water (Scruggs et al., 2004). It should be noted, however, that although chlorination might increase the estrogenic effect of NOM, chlorination also decomposes many individual compounds, resulting in an overall decrease in the estrogenic effect. Hence, the attempted control of EDCs and PCPs by chlorination might, in fact, prove to be counterproductive because of the DBPs produced. (Scruggs et al., 2004).

Certain DBPs (that is, NDMA, THMs, and 2-chloro-phenol) are very difficult to remove via conventional and advanced treatment processes (for example, RO can remove only up to 50 percent of the NDMA). Although UV/AOP can effectively remove NDMA and other DBPs, the best approach is to eliminate the production of DBPs by using alternative disinfection technologies (such as UV or paracetic acid).

2.2.7 Metals

Metals either occur naturally in the environment or enter the WWTPs via industrial discharge and stormwater runoff. Metals can form complexes with colloidal and particulate matter during coagulation-flocculation, which are then removed through clarification and filtration. In biological treatment, metals undergo adsorption onto biomass and subsequently are removed during the solids separation processes (that is, settling, and filtration).

The metals contained in water, which result in health concerns, include cadmium, lead, and mercury. Through National Pollutant Discharge Elimination System (NPDES) permits, the USEPA and the Regional Water Quality Control Boards (RWQCBs) establish discharge limitations for concentrations of a number of metals including arsenic, copper, lead, mercury, cadmium, chromium, nickel, selenium, silver, and zinc. These limitations are based on requirements to protect identified beneficial uses of water.

The USEPA has established primary and secondary drinking water regulations for metals. In addition, CDPH has established primary and secondary MCLs for metals (Title 17 and Title 22 California Code of Regulations [CCR], 2009). Because most metals are now federally regulated with a primary or secondary MCL, they do not fit the description of emerging contaminants of concern and will not be discussed in this report.

3 Treatment Technologies

This section of the report contains the following subsections:

- Introduction
- Physical-Chemical Treatment Processes
- Biological Treatment Processes
- Natural Treatment Systems

3.1 Introduction

Some CECs exhibit adverse ecological effects that have caused concern among the regulatory and utility communities and the public regarding the fate of these compounds during water and wastewater treatment. Determining the fate and removal efficiencies of these compounds during treatment processes is a fairly complex task.

Many CECs occur at trace levels (in parts per trillion [ppt], for example) and some of the CECs are more polar (more charge density) than currently regulated aromatic compounds (Snyder et al., 2007). Despite the improvements in analytical techniques, detection, and assessment of the fate and removal performance of CECs in drinking, tertiary, and advanced water treatment processes, these CECs are still a unique challenge. High total dissolved solids (TDS) (specifically, more chloride and sulfate in concentrate) can interfere with analytical results, thereby making identification and quantification of CECs in concentrate difficult.

CECs are a broad range of compounds with very diverse structures and physicalchemical (p-chem) characteristics (that is, molecular weight, water solubility, Kow and pKa, and charge density). The removal efficiencies of CECs in water and wastewater treatment are closely related to the p-chem characteristics of CECs. Considering the diverse nature of CECs, a single treatment process cannot remove all CECs. The p-chem properties of some CECs are summarized in Attachment A.

Wastewater treatment facilities are not designed to remove specific compounds (i.e., individual CECs) but are designed to meet effluent quality parameters (such as total suspended solids [TSS], biochemical oxygen demand [BOD], and chemical oxygen demand [COD]). Removal efficiencies of CECs cannot be determined using effluent quality contamination surrogates (such as BOD and COD), and NPDES permits do not require WWTPs to monitor for CECs. In fact, very little attempt has been made to identify and quantify these compounds in wastewater influent and effluent. As a result, limited information is available for treatment efficiencies of CECs through the treatment processes, and a majority of the research and information is based on drinking-water treatment processes.

Conventional drinking water treatment facilities primarily use adsorptive, precipitative, and oxidative processes to remove and/or transform organic material. Studies have shown that most conventional treatment processes used in drinking water applications have a limited success for removal of CECs. Advanced water treatment processes are effective in removing CECs, but they generally require high capital and operation and maintenance (O&M) costs. Also, some advanced water treatment processes (RO, for example) generate waste streams (concentrate) that have to be dealt with. Disposing of waste streams is often challenging from a time, economic, and environmental point of view.

Because CECs are not regulated, treatment requirements for CECs are unknown. CDPH requires a double-barrier process (that is, RO and advanced oxidation) at groundwater recharge projects to protect groundwater against emerging contaminants. CDPH also requires additional removal for 1,4 dioxane (0.5-log) and NDMA (1.2-log). These requirements result in the removal of a number of CECs because they are easier to remove than NDMA.

RO concentrate has a relatively high TDS, typically ranging between 5,000 and 25,000 milligrams per liter (mg/L) depending upon treated water characteristics via RO (that is, wastewater RO or brackish water RO) and recovery of the RO. In addition, RO concentrate might contain a high concentration of organic material (TOC), nitrogen (that is, ammonia, nitrate, and organic nitrogen), metals, and potential inhibitory substances. These constituents could have profound impacts on process performance, process selection, and pretreatment requirements. For example, a high TDS concentration (ionic strength) could adversely affect the efficiency of settling and adsorption-type processes. Reduced compounds (such as ammonia) could exert demand and increase the dose of the oxidation agents (such as chlorine, chloramine, and ozone) in oxidative treatment. Certain metals might be inhibitory to the biological treatment microbial community even at trace levels. Because no study has been done to demonstrate the fate and removal efficiencies of emerging contaminants in RO concentrate streams, the CEC treatment technologies and projected treatment efficiencies in this report are largely based on findings of drinking and wastewater research projects cited in the literature.

To date, researchers have focused on understanding the fate of approximately 80 CECs primarily during potable water treatment. These compounds were selected because the analytical techniques were available to detect them at threshold concentrations as low as 1 ng/L. The compounds reflect a broad spectrum with similar and dissimilar functional groups and p-chem properties. Also, the impacts to aquatic life have been well documented for these compounds. In this report, the CEC species and their removal efficiencies are limited to compounds that have been studied and documented. Currently, AWWARF, WERF, and research institutions are collaborating to develop a structure-based model to estimate removal efficiencies of CECs, using current data and information as a foundation. Once this work is completed, the removal efficiencies of more CECs will be predicted and available for use.

CECs can be removed using different process types including adsorption, oxidation, photolysis, hydrolysis, biodegradation, biotransformation, biosorption, volatilization, size exclusion and steric hindrance, and electrostatic repulsion. Treatment processes for CEC removal can be categorized into three groups:

- P-chem processes
- Biological treatment processes
- Natural treatment systems

Each treatment process has subcategories as presented in Sections 3.2 through 3.4. These subsections will describe treatment technologies for CECs and discuss capabilities of treatment processes along with implementation issues. The treatment requirements and process selection for treating CECs in concentrate streams are discussed in Section 5.

3.2 Physical-Chemical Treatment Processes

P-chem treatment processes use physical, chemical, and/or a combination of physical and chemical processes to remove contaminants from water. P-chem processes have been investigated for CEC removal through treatment of drinking water (AWWARF, 2005). Translation of the results for CEC removal in RO concentrate could result in different outcomes; therefore, this information is provided for informational purposes only.

3.2.1 Coagulation, Flocculation, and Softening

Coagulation uses metal salts (typically, iron or aluminum) to precipitate metal hydroxides. Chemical softening removes calcium and magnesium using lime and soda ash to precipitate calcium carbonate at a pH greater than 9.0 and magnesium hydroxide at a pH greater than 11. Coagulation and softening removes suspended solids and colloidal material. Organic compounds absorb onto the suspended particles and calcium carbonate/metal hydroxide precipitates and coprecipitate with the solids.

Studies indicate that compounds with high octanol water partition coefficient (log Kow over more than 5) generally exhibit some degree of removal, primarily due to particle bindings and subsequent removal through settling or filtration (AWWARF, 2005). However, Kow is not the only important factor; other factors such as concentration of the suspended solids and availability of surface site for absorption could hinder CEC removal through coagulation and softening. With the exception of benzo(a)pyrene and DDT, the removal efficiencies of tested CECs via coagulation and softening have been poor (that is, less than 20 percent removal), thereby indicating that coagulation and softening are generally ineffective for CEC removal (AWWRF, 2005).

Implementation Issues

Removal of organic compounds in concentrate using coagulation, flocculation, and settling has never been demonstrated. The water quality of concentrate (in other

words, high TDS) alters the water chemistry that might reduce or diminish process performance, as well as require application of higher chemical doses. Also, settling of the sludge could be a challenge because of the high TDS which alters both chemistry and buoyancy of the water. Sludge disposal could be costly if the wet toxicity testing results in classification of the sludge as a hazardous waste.

3.2.2 Activated Carbon Adsorption

Adsorption is the accumulation of a substance at the interface between two phases, such as liquid and solid. The molecule that accumulates or adsorbs at the interface is called an adsorbate, and the solid on which adsorption occurs is the adsorbent (AWWARF, 2005). Activated carbon removes NOM and synthetic organic compounds (SOCs) from water through hydrophobic interactions between organics and the activated carbon surface. Pore structure has a large influence on adsorption capacity and kinetics.

The efficiency of activated carbon adsorption is generally estimated by Freundlich isotherm parameters (that is, sorption capacity, K). Freundlich "K" values are available for numerous compounds regulated under the Safe Drinking Water Act (SDWA) and correlated with physical properties of the organic compounds. The Freundlich equation is used to determine the adsorption coefficients. The Freundlich equation is expressed as:

$$Q_e = K * C_e^n$$

Where:

 Q_e : Equilibrium capacity of the carbon for the target compound C_e : Equilibrium liquid phase concentration of the target compound K and n: Freundlich coefficients

Typically, when K values are greater than 200, activated carbon adsorption is considered technically and economically feasible (AWWARF, 2005). K values are not currently available for CECs; however, they can be estimated using lab-scale experiments or using quantitative structure activity relationship models.

Both powder-activated carbon (PAC) and GAC have been used for many decades in drinking water treatment, predominantly in control of the taste and odor. PAC is generally applied to raw water in a slurry form prior to the filtration treatment stage. Key factors in the design of PAC treatment are:

- Good mixing of PAC
- Sufficient contact time for the adsorption of contaminants
- Minimum interference by other treatment chemicals
- No degradation of water quality

The ability of PAC to remove organic compounds depends on PAC dose and contact time and the p-chem properties of the target compounds. Figure 3.1 shows the GAC (photograph on left) and PAC (photograph on right) materials that are commonly used in the water treatment industry.

FIGURE 3.1 GAC AND PAC MATERIAL



Source: Siemens Water Technologies

GAC is used in the water treatment industry by moving water through the system using gravity or pressure and providing contact time with the GAC media, which is in fixed beds. Several factors are involved in the design of GAC including:

- Type of GAC
- Surface loading rate
- Empty bed contact time
- Contaminant type and concentration
- Contaminant competition
- Carbon depth and usage

The molecular size of the absorbate is an important factor because many compounds are too large to diffuse into the pore structure of the activated carbon (Faust and Aly, 1998). Figure 3.2 shows a photograph of the GAC adsorbers at a water treatment facility.



FIGURE 3.2 GAC TOWERS USED IN THE WATER TREATMENT INDUSTRY

The ability of GAC to remove a broad spectrum of organic compounds (that is, pesticides, DBPs, and PAHs) from water is well documented. As part of SDWA Amendments in 1986, the use of GAC adsorption and filtration was recommended as the best available technology for the removal of diverse organic compounds from drinking water.

More recently, the efficiency in removal of CECs using activated carbon has been evaluated through bench- and full-scale studies. In a bench-scale study, 20 mg/L of PAC with a 1-hour contact time reduced concentration of lindane, a moderately hydrophobic pesticide with a log Kow of 3.72, from 10 to 0.1 ppb (Kouras et al., 1998). Another study determined that 17_b-estradiol was quickly adsorbed by GAC, and equilibrium was reached after 50 to 180 minutes (Fuerhacker et al., 2001). The equilibrium removals were 49 and 81 percent for initial E2 concentrations of 1 and 100 ng/L. Pilot and full-scale studies also have shown that activated carbon is effective for the removal of EDCs and pharmaceuticals and personal care products (PPCPs) (AWWARF, 2005). However, removal efficiencies vary significantly depending upon p-chem characteristics (such as molecular size, hydrophobicity, and charge) of the target compounds, as well as concentration and type of other compounds that are competing with target compounds for surface adsorption sites (AWWARF, 2005). In addition, the studies found that NOM competes for binding sites and can block the pores within the activated carbon structure and reduce efficacy of the activated carbon treatment process for CEC removal. CEC removal efficiencies for tested compounds through a pilot PAC and a full-scale GAC facility are presented in Attachment B.

As can be seen in Attachment B, PAC is highly effective for the removal of the tested compounds. PAC dose and contact time are the two critical parameters to achieve effective CEC removal. An advantage of PAC is that it is introduced as a new product, and not recycled through the treatment process, thereby keeping relatively fresh carbon in the system.

GAC is also effective for the removal of tested compounds but removal efficiency varied, depending on the constituent removed. GAC with modified surface characteristics had a significantly higher capacity for EDC and PPCP removal compared to conventional GAC (AWWARF, 2005). At full-scale treatment facilities that routinely regenerate or replace activated carbon, removal efficiencies of organic contaminants were excellent, while those with GAC that had been in operation for longer periods without the regeneration or replacement of activated carbon had poor removal rates for organic compounds (AWWARF, 2005). Therefore, regeneration or replacement of GAC is essential to assure good CEC removal.

Also, Kow of neutral compounds were well correlated with the percentage of EDC and PPCP removed (AWWARF, 2005). Generally, compounds with log Kow of greater than 2 can be effectively removed using PAC or GAC because adsorption of neutral compounds on activated carbon is dominated by hydrophobic interactions for which Kow is a good indicator. The relationship between log Kow and removal efficiency has been well-illustrated for bisphenol A, estradiol, and ethynyl estradiol (Snyder et al., 2006). Although high Kow is typically correlated with good removal of CECs, some researchers have found low removal efficiencies with high Kow, which indicates that removal mechanisms in activated carbon systems are complex.

The acid solubility constant (pKa) determines if a compound contains a charge (that is, protonated or unprotonated) at a given pH. Therefore, the removal of charged species is pH dependent. Also, very large molecules tend to have a low rate of removal by GAC or PAC due to steric hindrance. For example, large steroids and hormones (that is, estradiol, estriol, and estrone) have low removal rates when GAC or PAC is used. These factors also contribute to the complexity of determining the effectiveness of adsorption.

Implementation Issues

Removal of organic compounds in RO concentrate streams using GAC or PAC has not been demonstrated or documented; therefore, performance, cost estimates, and O&M data are not available. Treating concentrate streams by using GAC or PAC might be difficult because of high TDS and organic content. Implementation includes the following issues.

- NOM competes for binding sites and can block the pores within the activated carbon structure and reduce the efficacy of activated carbon.
- Concentrate could contain highly diverse organic compounds. Compounds with very high water solubility can break through the GAC column relatively quickly and reduce the time between GAC regeneration or replacement. Also, the high ionic strength of the solution can interfere with GAC performance because certain ions can be precipitated and block the activated carbon pores.
- Pretreatment for NOM or total organic carbon (TOC) is the key factor to improving process efficiency and to reducing the size and O&M costs of the facilities.

- Routine regeneration or replacement of activated carbon is important for the efficiency of activated carbon.
- Spent activated carbon might contain hazardous substances that require special handling and have costly disposal fees.
- Permitting air emission permits) could be complex for thermal regeneration of activated carbon due to the constituents in the exhausted GAC material.

3.2.3 Chlorination/Chloramination

Chlorine is a commonly used chemical to disinfect water and wastewater. Free residual chlorination is the application of chlorine in either a gaseous or concentrated hypochlorite solution to form hypochlorous acid and/or hypochlorite ion (OCl-) and hypochlorous acid (HOCl) in water. The speciation of chlorine is pH dependent. At a pH of less than 7.5, HOCl dominates and is a stronger oxidizing agent (that is, compared to an OCl-); therefore, the oxidative power of chlorine strongly depends on the pH of the solution. Although an increased chlorine dose and contact time are generally well correlated with the efficiency of oxidation, chlorine is not particularly strong oxidant compared to other commonly used oxidants. Table 3.1 provides a list of common oxidants and their respective oxidation (redox) potential; higher redox potentials indicate stronger oxidants.

Oxidant	Redox Potential (electron volt)
Hydroxyl Radical	2.80
Ozone	2.07
Hydrogen Peroxide	1.78
Permanganate	1.69
Chlorine Dioxide	1.56
Chlorine	1.36
Oxygen	1.23

TABLE 3.1 OXIDANTS AND OXIDATION (REDOX) POTENTIALS

Notes:

Chloramine oxidation potential is less than chlorine.

Free chlorine preferentially reacts with electron-rich bonds of organic compounds (that is, carbon [C]=C bonds. In other words, the more reactive compounds are generally composed of aromatic rings with hydroxyl, amine, or methoxy groups that react rapidly and selectively with chlorine. In contrast, the least reactive compounds (no aromatic rings) have electron- accepting functional groups (carboxyl groups), which react poorly with chlorine (AWWARF, 2005). The removal mechanism for chlorination includes direct oxidation, substitutions reaction, and/or addition reaction.

One of the major drawbacks of free chlorine is that it can form DBPs, such as THMs and HAAs. In addition, some reaction products (compounds with chlorinated ring structure) could pose taste and odor problems and potential health risks. Figure 3.3 presents a photograph of a chlorine contact basin used for wastewater disinfection.



FIGURE 3.3 CHLORINE CONTACT BASIN USED IN WASTEWATER DISINFECTION

Chlorine reacts with ammonia to form chloramines. Chloramines are not as strong a disinfectant/oxidant as chlorine but are more stable, and thus provide a longer lasting residual disinfectant. Due to its relatively low oxidation potential, chloramination the formation of DBPs and other oxidation by-products is reduced. However, chloramines are less effective than free chlorine for reducing organic compounds. Recent studies have shown that chloramines produce more nitrosoamines, such as NDMA, a potent carcinogen, than free chlorine.

The efficiency of free chlorine and chloramines for oxidation of CECs depend upon chlorine and chloramine dose, contact time, pH, water temperature and chlorine demand of the water.

AWWARF has tested the efficacy of chlorination and chloramination on selected CECs and compiled the findings in a report (AWWARF, 2005). These studies were based on a chlorine and chloramine dose of 3-5 mg/L with a contact time of 2-5 minutes. Temperature and pH were not reported in these studies. The report indicates that compounds with the phenol functional group including phenolic hormones (for example, 17 b-estradiol, estrone, and ethynyl estradiol), oxybenzone, and triclosan can be efficiently oxidized (greater than 95 percent removal) by free chlorine. Similarly, compounds with a primary amine attached to a conjugated ring structure, such as trimethoprin and sulfamethoxazole, exhibit more than 90 percent removal using free chlorine. PAHs with electron-donating substituents (such as

benzo(a)pyrene, diclofenac, and oxybenzone) exhibit high reactivity with free chlorine. Hormones with ketone functional groups (for example, testosterone and progesterone) and compounds with amide structures (iopromide and meprobamate, for example) are only partially removed by free chlorine (a removal rate of less than 20 percent). The efficiency of the removal of target CECs by using free chlorine at drinking water doses are provided in Attachment B. The AWWARF study showed that chloramination is much less effective than free chlorine. The study also showed that although increased doses and contact time could improve organic removal efficiencies, it can result in the creation of more DBPs.

Implementation Issues

Organic and inorganic constituents (that is, reduced forms of iron and manganese and suspended solids containing other reduced compounds) in concentrate might exert a significant chlorine demand, greatly increasing DBP formation for a given removal of target CECs. Due to DBP concerns and the lack of efficiency in the removal of a majority of organic contaminants, the use of chlorination and chloramination is not a suitable process for the removal of CECs in RO concentrate streams.

3.2.4 Ozone and Ozone/Hydrogen Peroxide

Ozone is a pale blue gas that forms when diatomic oxygen (O_2) is excited to a higher energy state with a triatomic form (O_3) . This transformation occurs as oxygen is exposed to a source of high energy. Ozone can be generated on site by passing a high-voltage alternating current (6-20 kilovolt [kV]) across a dielectric discharge gap through which oxygen or oxygen-laden air passes, resulting in the formation of ozone. An example dielectric cross-section is provided in Figure 3.4

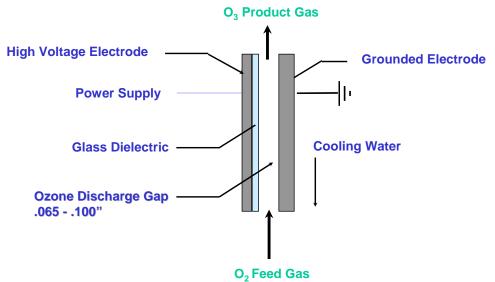


FIGURE 3.4 CROSS-SECTION OF AN OZONE DIELECTRIC PLATE

Source: PCI-WEDECO Environmental Technologies

Ozone is used in treatment plants for a variety of reasons, including primary disinfection, oxidation of taste and odor compounds, oxidation of iron and

manganese, and (indirectly) control of chlorinated DBPs. The most common application of ozone is for primary disinfection. Ozone is a strong oxidant and disinfectant. Unlike free chlorine or chloramine, however, ozone decays very rapidly in aqueous solutions, and it does not maintain a residual concentration. Oxidation reactions are not selective; therefore, ozone reacts in water with a wide variety of materials (that is, both organic and inorganic materials). These reactions create an ozone demand that is characteristic to the specific water quality. Figure 3.5 shows an ozone contactor in the Clark County Water Reclamation District in Nevada.



FIGURE 3.5 OZONE CONTACTORS IN CLARK COUNTY, NEVADA

Correct determination of ozone demand and decay is the key parameter used to design the system. Ozone reacts with organic contaminants through the direct reaction with molecular ozone or through the formation of free radicals such as the hydroxyl free radical (HO* radical) (AWWARF, 2005). The formation of HO* radical occurs through a series of stepwise reactions, which involve initiators such as hydrogen peroxide (H₂O₂), UV radiation, NOM, or the hydroxide ion. Both molecular ozone and hydroxyl radical pathways can lead to the transformation of organic compounds including CECs (AWWARF, 2005). In most treatment applications, the concentration of hydroxyl radicals is extremely low and does not result in significant transformation of target organic compounds. To increase HO* radical concentrations, an AOP, (such as ozone [O₃] and H₂O₂, followed by UV with H₂O₂) is applied. An explanation of how this process works will be covered in the next subsection of this report, which is focused on AOP.

Ozone reacts directly with many EDC and PPCP compounds, which results in significant reductions in concentrations of CECs at a 5-mg/L dose typical of water disinfection. Also, ozone is effective for the removal of target organic compounds (AWWARF, 2005). Electron-donating groups (that is, phenolic compounds) can

enhance the reactivity of ozone, while electron-accepting groups (that is, ketone functional structures) inhibit its reactivity (AWWARF, 2005). For example, all target compounds with phenolic structures, such as acetaminophen, oxybenzone, and several estrogens, can be effectively removed using ozone. A number of compounds with electron donating capability including gemfibrozil, hydrocodone, naproxen, and sulfamethoxazole also were almost completely removed using ozone. On the other hand, ketone functional hormones, such as progesterone and testosterone, had lower removal efficiencies compared to the phenolic hormones. TCEP is the most challenging compound to oxidize (AWWARF, 2005). Oxidation efficiencies of the target compounds at an ozone dose of 5 mg/L are summarized in Attachment B.

With the exception of oxidation-resistant compounds (such as TCEP, atrazine, iopromide, and meprobamate), CECs are generally well-oxidized by ozone. A 2-minute contact time with disinfection doses of 2 to 5 mg/L for drinking water was highly efficient in removing more than 50 percent of the compounds tested. One major advantage of ozone is that it forms fewer regulated DBPs than free chlorine and chloramine.

Implementation Issues

To date, no study has been done to evaluate the use of ozone for the removal of organic compounds in concentrate. Major implementation issues for the use of ozone are similar in nature to the issues with the use of chlorination and chloramination. These issues include the following.

- Organics, turbidity, and reduced forms of iron and manganese in concentrate exert an ozone demand that reduces efficiency and could substantially increase facility costs.
- Ozone creates certain DBPs (that is, bromate and aldehydes), but these DBPs are of lesser concern than those formed during chlorination and chloramination.
- Ozone decays rapidly; therefore, other chemicals are needed if residual chlorine is needed for secondary disinfection.
- Ozone breaks down organic material and makes it more bio-available for degradation, so an additional treatment step might be required to address the bio-available organics after ozone treatment.
- Unlike other chemicals, ozone requires onsite generation and will require a larger facility to provide for ozone generation and off-gas destruction facilities.
- Good mixing and solubility of ozone is important for process performance. High salinity in concentrate may reduce ozone solubility.
- The quality of concentrate water might complicate accurate determination of ozone decay and other design parameters through measurement interferences.
- Ozone is a highly toxic and flammable gas; therefore, generation and off-gas destruction impose health and safety concerns.

3.2.5 UV Irradiation and UV Hydrogen Peroxide Advanced Oxidation

Ultraviolet disinfection uses UV irradiation to damage genetic material (that is, deoxyribonucleic acid [DNA] and ribonucleic acid [RNA]) of microorganisms, which eliminates the ability of microorganisms to reproduce. UV light has been established as an effective primary disinfectant for *giardia* and *cryptosporidium* (Swaim et al., 2007). The effectiveness of a UV disinfection system depends on the following.

- Characteristics of the water, most importantly the UV transmittance
- Intensity of UV radiation
- Amount of time microorganisms are exposed to radiation

The energy carried by the UV irradiation (200-280 nanometer [nm]) is theoretically sufficient to break chemical bonds in organic compounds capable of absorbing those wavelengths. (This process is termed direct photolysis.) However, in reuse disinfection applications, typical UV doses are between 50 and 100 milliJoules per square centimeter (mJ/cm²), which is ineffective in removing most CECs (AWWARF, 2005).

Many utilities are now focusing attention on control of emerging contaminants and looking at the effectiveness of UV/AOP as part of a multiple-barrier treatment train for improving water quality. UV/AOP relies on the addition of hydrogen peroxide to absorb UV light and generate highly reactive HO* radicals, which react indiscriminately with most organic pollutants including recalcitrant contaminants such as 1,4 dioxane, trichloroethylene (TCE), and methyl tert-butyl ether (MTBE). Unlike the disinfection doses, UV/AOP requires much higher UV doses (that is, 500 mJ/cm² or higher). The efficiency of UV/AOP depends on water quality (that is, UV transmittance and the presence of free radical scavengers), type of compound (that is, recalcitrant versus readily able to be oxidized), and UV dose. Figure 3.6 shows a closed-vessel UV system that can be used in UV/AOP (photograph on left) and UV disinfection (photograph on right) applications.

FIGURE 3.6 CLOSED-VESSEL UV REACTORS



The efficiency for removal of selected CECs by using UV and UV/AOP was investigated through bench- and full-scale studies by AWWARF in 2007. The studies indicated that UV at typical UV disinfection doses (that is, 40 mJ/cm²) was ineffective for the removal of most target compounds. Compounds, such as diclofenac, triclosan, and sulfamethoxazole, which have the ability to absorb UV light, had high rates of removal. A majority of compounds were not capable of absorbing UV light at 254 nm, resulting in poor rates of removal, as shown in Attachment B. However, this study used a low-pressure high-output UV system, which emits UV light monochromatically, and emissions were produced at a wavelength of 254 nm. Medium-pressure lamps emit UV light polychromatically and produce emissions at a broader wavelength. Therefore, medium-pressure UV systems are expected to remove a broader range of organic compounds and perhaps have higher removal efficiencies (AWWARF, 2005).

The addition of hydrogen peroxide for advanced oxidation increased the removal of the target compounds; however, the efficiency was highly dependent on hydrogen peroxide dose and UV dose. At a 5-mg/L H_2O_2 dose with a 671-mJ/cm² UV dose, excellent removal was observed for nearly all tested compounds (AWWARF, 2005). The removal efficiencies of the tested compounds via UV/AOP are provided in Attachment B.

Implementation Issues

UV disinfection is effective for inactivating pathogens but ineffective for removing CECs. However, UV/AOP is highly effective for removing pathogens as well as CECs and does not create known DBPs like the chlorination and ozonation processes. UV/AOP is expensive, and several factors need to be considered before implementing this process including:

- The size and the efficiency of UV/AOP are highly dependent on the UV transmittance of the water stream being treated. Transmittance should be at least 85 percent of the total UV to avoid costly investment and to operate the system efficiently. Concentrate has a low UV transmittance, which requires pretreatment to improve UV transmittance. If the stream is untreated, the efficiency of the system would be drastically reduced, and capital and O&M costs would increase.
- Free radical scavengers, such as NOM and iron, can reduce the efficacy of destruction of contaminants. Also, excessive dosages of chemical oxidizers could act as scavengers and reduce the destruction of contaminants.
- The aqueous stream to be treated by UV/AOP should be relatively free of ions of heavy metal (that is, less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling the quartz sleeves.
- O&M costs might be higher than competing technologies because of high energy requirements.
- High hardness in concentrate might require softening to reduce cleaning and maintenance frequency of the UV reactor and quartz sleeves.

• Handling and storage of hydrogen peroxide requires compliance with health and safety standards.

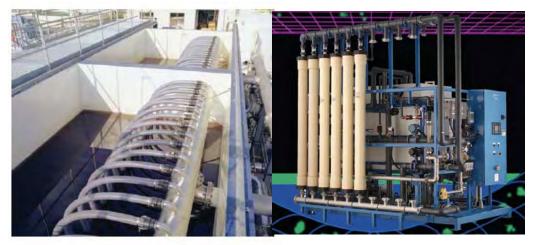
3.2.6 Membranes

Low-Pressure Membranes

Microfiltration (MF) and ultrafiltration (UF) are the low-pressure membrane filtration processes (that is, typical operating pressures range from 3 to 40 pounds per square inch [psi]) that are used to remove particulate and microbial contaminants, including turbidity, *giardia*, and cryptosporidium. The distinction between MF and UF is typically based upon or molecular weight cut-off (MWCO) or pore size. MWCO is a manufacturer specification that refers to the molecular mass of a macrosolute (for example, glycol or protein) for which a membrane has a retention capability of greater than 90 percent.

The pore size refers to the diameter of the micropores in a membrane surface. Although pore size is an important consideration in determining which contaminants an MF or UF membrane process can remove, it is not the only factor that affects the removal of compounds. Another factor that affects performance is the build-up of a cake layer on the membrane surface during the filtration cycle. Because of this, membrane rejection characteristics are assessed through "challenge" studies where the ability of a membrane to reject a specific contaminant is demonstrated through pilot testing. Figure 3.7 shows a submerged MF system (photograph on left) and a pressurized MF system (photograph on right).

FIGURE 3.7 SUBMERGED MF SYSTEM (LEFT), PRESSURIZED MF SYSTEM (RIGHT)



Low-pressure membranes have been increasingly employed in water and wastewater treatment and are effective in removing particulate material and pathogens (for example, *giardia* and cryptosporidium). CECs are soluble compounds with molecular size much smaller than pore sizes and the MWCOs of MF and UF membranes. As a result, low-pressure membranes are not generally effective in removing CECs from water. However, CECs that had been adsorbed onto colloids and particulate material were successfully removed (Huang and Sedlak, 2001). An

AWWARF study showed that UF membranes tended to remove more hydrophobic compounds (such as DDT and benzo(a)pyrene) as a result of adsorption, while other more polar compounds exhibited less efficient removal, which suggests that adsorption of CECs onto virgin membrane surfaces could be a factor in removal efficiency. Interaction of target compounds with NOM was found to be another mechanism affecting removal efficiencies (AWWARF, 2005). UF membranes are able to remove hydrophobic compounds mainly due to adsorption, so the efficiency of removal depends on the presence of colloidal or organic material in addition to the cleanliness of the membrane's surface. Attachment B provides a summary of the efficiency in removal of CECs using UF, as pilot tested on secondary effluent (AWWARF, 2005).

Implementation Issues

The capabilities of MF and UF membranes to remove emerging contaminants in brine-concentrate have never been explored. One property of concentrate that could benefit removal efficiency is that it contains NOM and colloidal material. However, this high organic content of concentrate could also rapidly foul MF and UF membranes, reducing membrane run times, requiring more frequent chemical cleaning, and resulting in increased costs for cleaning chemicals and membrane replacement.

To minimize membrane fouling and improve removal of organic material, a hybrid membrane system incorporating PAC and membrane filtration could be used. In PAC/membrane processes, the PAC is added to the recirculation loop of the membrane systems (AWWARF, 1996). Dissolved organic carbon (DOC) and natural DBP precursors are adsorbed on activated carbon particles, which are then separated from water by UF or MF membranes. Several studies have reported that the use of PAC can reduce membrane fouling, which could be due to the shear scouring effects induced by the larger-sized PAC particles. This technology has not been tested for CEC removal.

High-Pressure Membrane Systems

High-pressure membrane systems include NF and RO. NF and RO are pressuredriven processes that employ the principles of osmosis to remove dissolved contaminants (that is, TDS and organic compounds) from water. The amount of energy required to drive feedwater through the membrane depends on the membrane's thickness and tightness and on the osmotic pressure of the feedwater (AWWARF, 1996). Much higher pressures are required in RO applications than for NF applications. Desalination using RO requires 800 to 1,200 psi for seawater, and 200 to 450 psi for brackish water. Membrane softening using NF requires 75 to 150 psi.

NF is currently used as an alternative to lime softening for reducing the level of calcium and magnesium in hard water when TDS reduction is not a primary goal. The NF process is more effective than lime softening for removing naturally occurring color and dissolved organic species responsible for the formation of THMs and other DBPs regulated by the USEPA.

RO has been used for TDS reduction for desalination of seawater and brackish water. More recently, RO is being used for the removal of specific inorganic ions and organic compounds. The USEPA has classified RO as a best available technology (BAT) for removal of many of the contaminants listed under Phases II, III, and V of the Amendments to the 1986 SDWA. These contaminants include inorganic contaminants (IOCs) and radionuclides. RO is effective for removing specific SOCs from contaminated groundwater, such as herbicides and pesticides. Figure 3.8 shows the RO membranes used at the Eastern Municipal Water District (EMWD) Perris Desalination Facility.



FIGURE 3.8 EMWD PERRIS DESALINATION FACILITY RO MEMBRANES

Studies have shown that RO membranes are capable of removing nearly all compounds usually to below their detection limits (Bellona et al., 2005 Erdal et al., 2007; AWWARF, 2005). RO membranes removed more than 99 percent of TCEP, which cannot be effectively removed by any other treatment process. However, clear evidence exists that certain CECs are not completely removed using RO treatment. This is particularly true for low molecular weight (MW) organic compounds, such as neutral compounds with a MW of 200 Daltons (Da), which is greater than the reported MWCOs of the membranes tested (that is, 100 Da) (Drewes et al., 2003). In fact, studies have shown that polyamide membranes rejected branched and complex large molecules but varied in their rejection characteristics for smaller molecules, such as chlorinated solvents, base neutrals, and low MW acids (Reinhard et al., 1986). Another study demonstrated that low-molecular weight non polar compounds showed the poorest rejection during RO treatment (Levine et al., 1999).

More recent studies conducted at NF and RO full-scale applications report a partial rejection (removal) of CECs with MW below the MWCO of the membranes. Compounds with MW below MWCO include DBPs—specifically, NDMA, THMs, and HAAs (Bellona et al., 2005). Also, DBPs such as bromoform, bromodichloromethane, and dibromochloromethane have been shown to have consistently lower retention rates compared to other similar MW range solutes for all membranes (Agenson et al., 2003). Removal of compounds with RO membranes is complex, and higher removal rates are typically obtained for more hydrophobic molecules that are wider and longer than MWCO of RO membranes. The rejection of TOC represents a complex interaction of steric hindrance, electrostatic repulsion, solution effects on the membrane, and compounds or membrane properties (Bellona et al., 2005).

Some interactions are fairly well understood. For example, the major process in solute rejection by NF is physically sieving solutes larger than the membrane MWCO. Other mechanisms of rejection such as electrostatic exclusion and hydrophobic–hydrophobic interactions between membrane and solute are considered important but are not as well understood. In addition, solution chemistry and membrane fouling could considerably influence the rejection of organic solutes. A mechanistic model to predict removal efficiencies of organic compounds based on MWCO of membrane, membrane surface charge, solution pH, and p-chem properties of organic contaminants (that is, MW, molecular diameter, pKa, and Kow) has been developed (Bellona et al., 2005). A schematic for the model is shown in Figure 3.9.

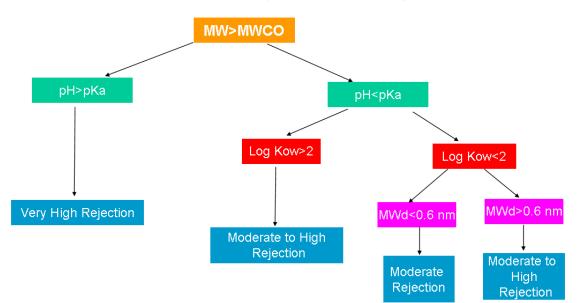
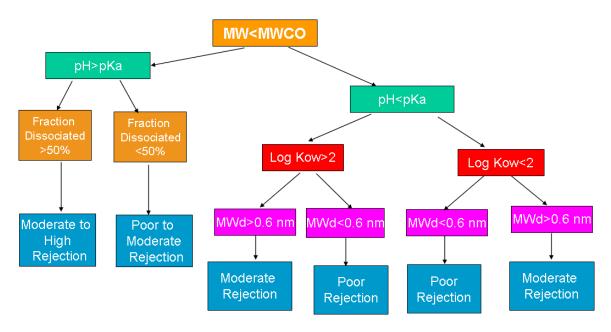


FIGURE 3.9 SCHEMATIC OF RO REJECTION MODEL (CONTINUED ON NEXT PAGE)



Source: Bellona et al., 2005)

According to the model, the efficiency in removing compounds generally will be high if the MW of the compounds is larger than MWCO of the RO due to size exclusion and/or electrostatic and steric exclusion. However, moderate to high removal efficiency might be observed if compounds with lower pKa and Kow are treated using RO membranes. Poor to moderate or moderate to high rejections can be expected for small organic compounds depending upon Kow and pKa values of the compounds.

Implementation Issues

With the exception of a few compounds (such as NDMA and certain DBPs), RO is effective in removing a variety of CECs. RO followed by UV/AOP is a doublebarrier process that is a proven, preferred treatment technology of CDPH. RO is beneficial for improving efficiency, reducing facility size, and reducing O&M costs of downstream processes such as UV, UV/AOP, ozone, or ozone/AOP. Because RO is the highly preferred technology for desalination and concentrate treatment, it will be well suited for the treatment of CECs in brine-concentrate streams. However, high TDS in RO concentrate might adversely affect removal efficiencies of CECs. Before implementing RO, capital and O&M costs, ultimate use of the recovered water, degree of treatment with RO (partial versus full treatment), final treatment, and ultimate disposal options for concentrate need to be evaluated.

3.2.7 Magnetic Ion Exchange

Magnetic ion exchange (MIEX) is a process that utilizes magnetic polymer microspheres as an ion exchange resin (AWWARF, 2005). The resin consists of a polymer and inorganic magnetic material, such as ferric oxides (Fe_2O_3 , Fe_3O_4), nickel, and cobalt and exhibits characteristics of ion exchange and magnetism. The ion exchange resin beads contain a magnetized component within their structure that allows the beads to act as weak, individual magnets. The magnetized component draws the beads of the resin together under settling conditions to form floc, allowing easy separation of the resin from the treated water. The base (cationic) exchange resin can remove negatively charged inorganic compounds such as sulfate, bicarbonate, and bromide, as well as NOM with acidic functional groups. The resin is introduced to water as slurry in applied doses, which are expressed in milliliters (mL) of resin per liter (L) of water (AWWARF, 2005). Figure 3.10 shows a process flow diagram of the MIEX process.

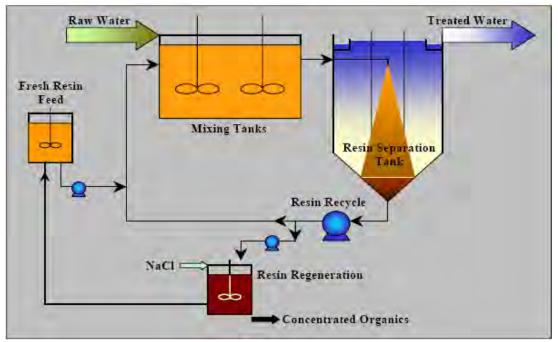


FIGURE 3.10 MIEX PROCESS FLOW DIAGRAM

MIEX resin can remove a majority of small hydrophilic compounds and a significant amount of hydrophobic compounds from biologically treated secondary effluent within a short contact time (less than 20 minutes) (Zhang et al., 2006). In a full-scale facility in Australia, MIEX increased DOC removals while reducing THM levels by approximately 60 percent. The removal capabilities of MIEX on emerging compounds were recently evaluated by AWWARF using a bench-scale test. In the test, 18 of 28 target compounds that were spiked showed less than 20 percent removal using a contact time of 10 minutes. Among the tested compounds, only triclosan and diclofenac were removed to a 90 percent or greater removal efficiency, which was most likely due to the fact that at ambient pH, these two compounds were negatively charged and have greater affinity to anion exchange.

The AWWARF testing also showed that most neutral compounds were poorly removed, but some removal was observed for compounds with large Kow values (that is, with a log Kow greater than 5). Increasing contact time to 20 minutes resulted in marginal improvement for the removal rates of the target compounds. The AWWARF report also showed that increasing MIEX dose and contact time did not result in linear increases in compound removal (AWWARF, 2005).

Implementation Issues

The capabilities of MIEX have been tested on drinking water and secondary wastewater effluent with a relatively low TDS. MIEX has exhibited poor removal efficiencies even under relatively good water quality conditions (that is, low ionic strength) (AWWARF, 2005). MIEX removal efficiency is generally limited to negatively charged compounds, although some removal has been observed for compounds with high Kow values. High TDS concentrations and the presence of highly diversified compounds in concentrates might further reduce the efficiency for removing CECs using MIEX.

3.2.8 Electrodialysis Reversal

Electrodialysis reversal (EDR) is a process that uses an electric current to remove salt ions from a solution. EDR is based on the property that salts in solution are dissociated into positively and negatively charged ions. EDR has been commonly used in groundwater desalination applications, especially groundwater with high silica concentrations. The EDR process uses a semipermeable barrier that allows passage of either positively charged ions (cations) or negatively charged ions (anions) but excludes passage of ions of the opposite charge. These semipermeable barriers are commonly known as ion-exchange, ion-selective, or electrodialysis membranes. The selective removal of cations and anions produces a concentrate stream and a demineralized product stream. Because the product water does not pass through a membrane barrier, CDHS does not recognize EDR as a barrier process for turbidity and/or pathogen removal; therefore, it is not allowed for reuse applications unless it is combined with filtration and disinfection processes. A package EDR unit is shown in Figure 3.11.

FIGURE 3.11 PACKAGE EDR UNIT



Source: GE-Water Technologies

Although it is an effective process in removing ions from solution, uncharged molecules and organic compounds cannot be effectively removed using EDR. In a pilot study, EDR was shown to be ineffective in removing any detectable CECs present in the MF effluent (Snyder et al., 2004).

Implementation Issues

EDR is a proven technology for desalination with TDS concentration of up to 8,000 mg/L. For TDS concentrations exceeding 8,000 mg/L, EDR is not economically feasible. The process has a limited capability to remove CECs; therefore, EDR is least suitable as a pretreatment process for CEC removal technologies where high TDS and hardness could limit the performance of the process (AWWARF, 2005).

3.3 Biological Treatment Processes

Biological processes rely on the metabolic activity of a diverse population of bacteria to degrade organic material in water. Most natural and organic compounds are biodegradable by microorganisms as part of their metabolism for energy and growth. One portion of organic material is converted to oxidized end-products through oxidation and reduction reactions (for energy production), and the rest of the organic material is synthesized into cellular material (growth). Such conversions can take place in aerobic, anoxic or anaerobic environments. An anoxic environment is a condition where oxidized forms of nitrogen (for example, nitrate) serve as electron acceptors in the absence of molecular oxygen. In anaerobic environments, neither oxygen nor an oxidized form of nitrogen is present. Microorganisms use inorganic and organic electron acceptors in anaerobic environments.

When bacteria use the CECs as a primary substrate (electron donor), they degrade these compounds, and the end-products and reaction rates can easily be determined. CECs usually are in trace quantities that are insufficient to provide primary substrate for the growth of microorganisms. Some natural compounds and SOCs are easy to biodegrade, while others have structures that resist biodegradation. The compounds that can be biotransformed often have structures that prevent the biotransformation from becoming a part of the microorganism's primary metabolic system for energy generation and growth (Ritmann and McCarty, 2002). Under this condition, removal and transformation of such specific compounds using biological treatment cannot be theoretically predicted but must instead be determined empirically for each application.

WWTPs are designed to meet effluent quality parameters, (that is, BOD, COD, or TOC) and not designed to remove specific organic compounds (that is, individual hormones and chlorinated organic compounds). Therefore, the removal of specific organic contaminants is unknown due to the exclusion of these specific parameters in NPDES permit limits. Most work on CEC removal rates in wastewater has been focused on parent compounds with little or no attention to oxidative daughter products, conjugates, or bioactive metabolites. Biodegradation of many CECs is known to result in partially degraded intermediates, some of which might be at least as bioactive, or more so, than the parent compound (Gröning et al., 2007).

In general, the body of literature related to wastewater treatment shows that many CECs are only partially removed by typical WWTP processes (Pickering and Sumpter, 2003). The main removal pathways for the removal of EDCs during wastewater treatment processes are the following (Birkett and Lester 2003):

- Adsorption onto suspended solids
- Aerobic and anaerobic biodegradation
- Hydrolysis
- Volatilization

Most of the research related to CEC removal has been done in activated sludge (i.e., suspended growth) systems (Holbrook, 2002; Stephenson and Oppenheimer, 2007; Drewes et al., 2006); however, limited information can be found on biological aerated filters (i.e., fixed-film systems). Although other attached growth systems, such as trickling filters, integrated fixed-film activated sludge systems, and rotating bioreactors, are expected to remove CECs, they are not included in this report due to insufficient information and study of these technologies for CEC removal. The biological treatment processes discussed in this report are focused on conventional activated sludge (CAS) systems, membrane bioreactors (MBR), and BAFs.

3.3.1 Conventional Activated Sludge System

The CAS system incorporates biological treatment processes that involve the conversion of organic matter and/or other constituents in wastewater to cell tissue and final products (that is, carbon dioxide and water) by a large mass of microorganisms maintained in suspension using mixing and aeration followed by clarification of treated water using sedimentation. CAS systems can be designed to achieve the following.

- BOD removal only; typical solids retention time (SRT) is 2 days or fewer; it includes aeration basins only; a pure oxygen system can be used instead of air.
- BOD and nitrogen removal system (BNR); typical SRT is between 6 and 15 days depending upon temperature; system includes anoxic and aerobic basins.
- Enhanced Biological Phosphorus System (EBPR); typical SRT is between 6 and 15 days depending upon temperature; system includes anaerobic and aerobic basins or anaerobic, anoxic, and aerobic basins for complete nutrient removal.

A process flow schematic of a CAS system designed to achieve BOD and nitrogen removal is presented in Figure 3.12.

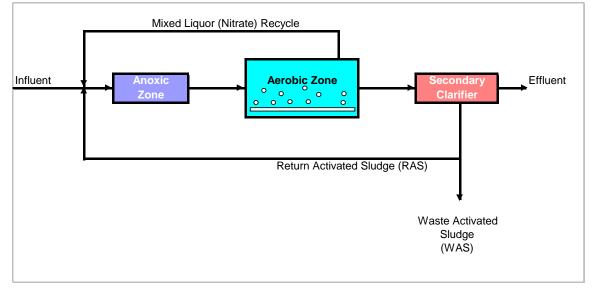


FIGURE 3.12 PROCESS FLOW SCHEMATIC OF A CAS SYSTEM

Impacts of operational parameters on removal of CECs have been the focus of recent research, where SRT has been the operating parameter most studied. For example, there have been several studies reporting that activated sludge systems with longer SRTs remove greater amounts of CECs (Ternes and Joss, 2004; Oliver et al., 2007; Jones et al., 2007). A critical SRT (minimum SRT) for the removal of some target CECs can be determined (Clara et al., 2005). If a facility operated below its critical SRT, the removal of the target CECs would be minimal or primarily due to adsorption. For example, one recent study determined that the critical SRT for bisphenol A, 17b-estradiol, estrone, and estriol was approximately 10 days. Almost complete removal of EDCs was reported for a CAS system operated at an SRT of 10 days or longer (Lee et al., 2003). One facility having the longest HRT and employing nitrification/denitrification, as well as biological phosphorus removal, achieved the highest removal of EDCs among all the plants (Drewes et al., 2006). However, other studies have been unable to find a significant correlation between EDC removal rates and operating SRTs.

More recently, the removal efficiencies of 20 target CECs using CAS with SRTs ranging from 3 to 30 days was investigated (Stephenson and Oppenheimer, 2007). The study results indicate that nearly half of the targeted compounds (easily biodegradable compounds) have a greater than 80 percent removal rate with an SRT of 5 days or less. Some slowly biodegradable materials, such as triclosan and benzophenone, required an SRT of at least 10 days to obtain removal efficiencies of between 50 and 80 percent. Musk ketone and TCEP were the most resistant compounds to biodegradation, but a removal rate of 50 percent was achieved using an SRT of fewer than 30 days. No significant correlation between EDC removal and the operating SRT for the target compounds and investigated SRT ranges were found, but the study indicated that higher SRTs have improved the removal efficiencies of slowly biodegradable CECs such as triclosan and benzophenone (Stephenson and Oppenheimer, 2007). Nitrifying bacteria are capable of transforming EE2 into daughter compounds due to the cometabolic activity of

ammonia monooxygenase (AMO) that can concurrently degrade EE2 and ammonianitrogen (NH₃-N) (Yi and Harper, 2007). Since nitrifiers are slow-growing autotrophic bacteria, this finding might support the benefit of long SRTs on the removal of CECs in the activated sludge system.

Unlike the previous studies, a few researchers have emphasized the impact of adsorption on EDC removal in activated sludge systems. Most naturally occurring hormones can be removed efficiently (that is, 90 percent or higher) using a CAS system (Holbrook, 2002). No significant difference exists for the removal of tested hormones using an SRT of between 2 and 10 days, and sorption of EDCs on colloidal organic material was found more important than SRT for enhancing removal using a CAS system (Holbrook et al., 2002). Hormones can be adsorbed onto biosolids, as the primary removal mechanism, with the 17b-estradiol concentration of the biosolids three orders of magnitude greater than the secondary effluent concentration (Takigami et al., 2000). Because the highest estrogenic activity was found in the digested biosolids, it is suggested that these compounds sorb to suspended solids before significant biodegradation occurs (Holbrook et al., 2002). It appears that biodegradation and adsorption are the two main mechanisms responsible for the removal of CECs during the activated sludge treatment process. Attachment B provides removal efficiencies of target CECs using four different SRT operations (Stephenson and Oppenheimer, 2007).

Implementation Issues

Implementation includes the following issues associated with a CAS system.

- A CAS system is able to remove a majority of CECs in concentrate but cannot remove TDS. Therefore, if recovery and reuse of water are considered, the CAS system needs to be coupled with a desalination process (such as RO or EDR).
- High TDS in concentrate might result in floc dispersion and an increase in effluent TSS concentration. The treatability studies on agricultural wastewater showed that a TDS concentration exceeding 16,000 mg/L significantly deteriorated effluent TSS concentrations (Eckenfelder et al, 1992). Similarly, significant increases in effluent turbidity were reported when sodium chloride concentrations in treated wastewater was increased to 30,000 mg/L (Ng et al., 2005). Organic removal efficiencies were considerable, however, even with concentrations under 60,000 mg/L TDS if there was proper acclimation of microorganisms to the high TDS wastewater.
- High TDS concentrations (for example, a TDS concentration greater than 20,000 mg/L) reduce the oxygen transfer efficiency of the CAS system thereby affecting the efficiency of the activated sludge process. For this reason, shock TDS loading should be avoided by providing flow equalization or over-sizing the aeration system capacity.
- Organisms that nitrify are sensitive to a wider range of organic and inorganic compounds at concentrations below those that affect other aerobic microorganisms. Compounds that are inhibitory to nitrifying organisms even at

threshold concentrations include solvent organic chemicals, amines, phenolic compounds, alcohols, cyanates, ethers, and benzene.

- Metals are inhibitory at lower concentrations (for example, nickel at 0.25 mg/L, chromium at 0.25 mg/L, and copper at 0.10 mg/L). If nitrogen removal is important, treatability testing is needed to determine the toxicity of the concentrate stream.
- Inhibition of nitrification at sodium chloride concentrations as low as 35,000 mg/L has been reported; however, studies in which TDS acclimation was provided showed very good nitrification and organic removal efficiencies.

3.3.2 Membrane Bioreactor

MBRs combine activated sludge biological treatment with an integrated membrane system to provide enhanced removal of organic materials and removal of suspended solids. MBR uses a low-pressure membrane system (that is, MF or UF) and eliminates the need for secondary clarifiers and tertiary filtration for solid-liquid separation. The membranes are typically immersed in the aeration tank; however, some applications use a separate membrane tank. One of the key benefits of using an MBR system is that it effectively overcomes the limitations associated with poor settling of sludge in CAS systems. The technology permits bioreactor operation with considerably higher mixed-liquor suspended solids (MLSS) concentration than CAS systems, which are limited because sludge must be allowed time to settle. Also, operating with higher MLSS concentrations (for example, as high as 8,000 to 10,000 mg/L compared to 2,000-3,500 mg/L) results in a much smaller aeration tank volume compared to CAS systems. The combination of a relatively high SRT, typically 10 days or more depending upon temperature, and superior solids removal capability results in the production of good effluent quality (that is, with a concentration of TSS of less than 1.0 mg/L and BOD of less than 5 mg/L) in MBR systems. Also, elimination of secondary clarifiers and filters reduces the overall footprint of the facility.

Although external pressure-driven membranes have gained attention recently, the most commonly used configuration is external submerged membranes. In external submerged systems, membranes are subjected to a vacuum that draws product water (permeate) through the membrane (from the outside to the inside) while retaining solids in the membrane separation tank. To clean the exterior of the membranes, air is introduced below the membranes. As air bubbles rise to the surface, they scour the membrane surface and solids are returned to the mixed liquor. Figure 3.13 provides a process flow schematic for an MBR system with a separate membrane tank.

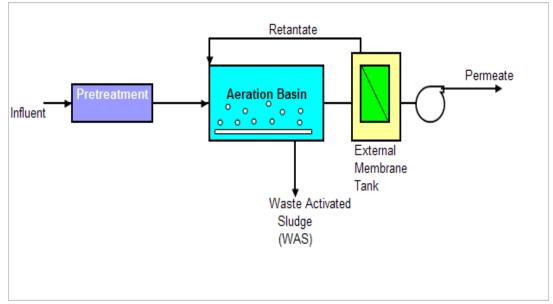


FIGURE 3.13 PROCESS FLOW SCHEMATIC OF AN MBR SYSTEM

Because the operating SRT is the primary driver behind biodegradability of CECs, no differences are expected in the efficiency of CEC removal using CAS and MBR systems. This is true because these systems are operated at similar SRTs. However, improved CEC removal has been reported with MBR (Stephenson and Oppenheimer, 2007; Holbrook, 2002). The main reason for the improved CEC removal is the capability of an MBR to more efficiently remove suspended and colloidal particles (maintaining a TSS concentration of less than 1.0 mg/L) and the CECs are sorbed onto these materials. Attachment B has additional information on the efficiency of CEC removal using MBR systems.

Implementation Issues

Implementation issues for MBR systems are similar to those identified for CAS systems. Three major advantages exist for using MBR over CAS systems.

- MBR systems are more resilient to shock loads (that is, organic and TDS) compared to CAS systems because MBR operates at a higher MLSS concentration.
- MBR efficiently captures particulate materials so floc dispersion and sludge settleability are not issues in MBR systems.
- MBR systems provide superior pretreatment for desalting technologies such as NF, RO, and EDR.

3.3.3 Biological Aerated Filters and Biologically Active Carbon

BAFs are down-flow or up-flow submerged attached growth systems. Microorganisms attach to the media matrix and form a biofilm layer where biodegradation (and, depending on system configuration, oxidation) of organic and inorganic material take place. The media used in BAFs have a high ratio of surface area to volume; thus, large amounts of biomass can be supported in a relatively small space. To a lesser extent, biomass also grows in suspension in the interstitial spaces between media particles. The media used in these systems is a relatively coarse rounded filter media, which is optimal due to the self-cleaning characteristics it has during backwashing. This system has two major advantages over suspended growth systems:

- High volumetric loading rates are achievable
- Biomass can be retained for long periods of time at a relatively high biomass density independent of recycle rates, which aids in the development of slow-growing bacteria

Similar to MBRs, BAF provides filtration at the same time that the biological treatment is occurring, so typically no requirement exists for separate clarification or filtration. A photograph of a BAF system is shown in Figure 3.14.



FIGURE 3.14 BAF SYSTEM AT A WWTP

In an aerated BAF system, an air header is used to ensure that oxygen is provided throughout the entire media bed, as well as the packing material. Packing material used in BAF systems includes activated carbon, clay material, sand, and anthracite. BAF systems have been used in wastewater and reuse treatment for BOD removal and combined BOD removal and nitrification. The system is efficient because the inner part of the biofilm is oxygen deficient allowing nitrate formed through nitrification to be converted into nitrogen gas (Tchobanoglous et al, 2003). BAF systems are generally suited for treatment of wastewater with a high content of BOD.

In addition to the BAF systems, granular-activated carbon is used in conjunction with ozone in an advanced water treatment process known as the biologically activated carbon (BAC) process. The basis of this process is the breakdown, by oxidation using ozone, of a wide range of organic species into compounds that are degraded biologically on bacterial biomass that has developed on the surface of the activated carbon, and the adsorption of the nonbiodegraded organic species, by conventional adsorption processes. The biomass that is fixed to the carbon occurs naturally in water, and its growth is promoted by the biodegradable matter in the water as a result of ozonation. This growth is controlled by periodic backwashing. The major advantages of the BAF process provide the following benefits.

- Enhanced removal of dissolved organics due to combining adsorption and biological treatment
- Biodegradation even in an organic and nutrient-deficient environment
- Adsorption of toxic compounds, which minimizes process upsets
- Reduction in disinfectant doses
- Reduction of DBP formation
- Reduced potential for regrowth of microorganisms

The efficiency of removal of emerging contaminants using BAF and BAC has not been extensively investigated. AWWARF has pilot-tested the capability to remove CECs using BAF filters containing BAC or biologically active sand (BAS) packing with an empty bed contact time of 2 minutes. The results of the study showed that only 5 of the 36 target compounds tested exhibited greater than 40 percent removal with the use of BAS; however, 18 of the target compounds tested exhibited greater than 90 percent removal using BAC. The better removal rate using BAC is due to the adsorptive properties of carbon in addition to those that occur during the biological removal (AWWARF, 2005).

Implementation Issues

The major issues associated with implementing for processes include:

- No full-scale implementation of the BAC process in water or wastewater treatment plants exists
- No design criteria have been developed for these processes
- No capital or O&M cost data are available for cost comparison with other technologies

3.4 Natural Treatment Systems

3.4.1 Riverbank Filtration

During high river flow conditions, water naturally percolates from rivers, into aquifers; during low river flow conditions, water naturally percolates from aquifers into rivers. Pumping action in connected aquifers can create a pressure head difference between the river and the aquifer, which induces the river water to flow through the riverbed toward the pumping well. The well extracts a mixture of groundwater originally present in the aquifer and riverbank-filtered surface water. This process is known as riverbank filtration (RBF).

RBF removal mechanisms are filtration, sorption, and attenuation through mixing, chemical precipitation, oxidation reduction, bioaccumulation and biodegradation. If no other contaminants are present in the aquifer, the quality of water in the aquifer is generally better than that found in the river or lake. Figure 3.15 shows the schematic of an RBF system.

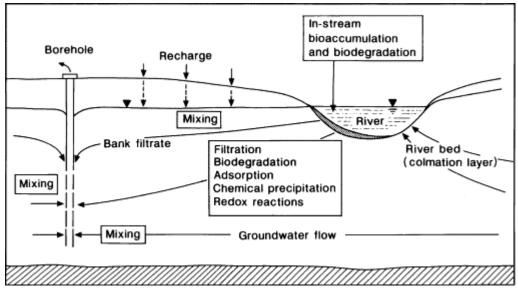


FIGURE 3.15 PROCESS SCHEMATIC OF AN RBF SYSTEM

RBF holds promise as a simple, low-cost technology to remove particulates and microorganisms from surface water to facilitate subsequent treatment. RF might attenuate concentration peaks, and it is effective under aerobic and anaerobic conditions. Additionally, RBF can be easily coupled with another technology, and it requires minimal maintenance and operation efforts and expenditures.

RBF is a well-established technology in Germany and is most often used as a component of a multiple-barrier treatment approach. The combination of filtration, biodegradation, sorption, and contaminant attenuation provides natural treatment. Depending upon the ultimate purpose of use, as well as the degree of filtering and contaminant attenuation required, additional treatment processes such as disinfection may or may not be required prior to distribution of water. One limitation of RBF is that polar, persistent, organic substances are not typically removed using this process. Elimination rates of these substances vary with residence time and length of the subsoil passage, and can also depend on redox potential. For this reason, RBF is often coupled with additional treatment barriers (such as disinfection, oxidation, and adsorption at water treatment plants) to provide a multiple barrier system.

RBF has been shown effective in reducing metals found in a contaminated river (Schmidt et al., 2003) and had efficiency of DOC removal of between 50 and 85 percent. Removal of DOC at the 85 percent level required long detention times (greater than 100 days) in the aquifer. Studies showing CEC removal using RBF are limited; however, AWWARF has investigated this technology using pilot RBF units. This study showed very good removal efficiencies for a majority of the target compounds tested (AWWARF, 2005).

Implementation Issues

Implementation issues associated with RF include:

- RBF is not effective for TDS removal; therefore, a desalination process should reduce the TDS to an acceptable level (that is, less than 1,000 mg/L) to pretreat the water before an RF system.
- RBF is typically used for polishing groundwater or treated wastewater effluent. No demonstration or testing of the use RF for treating concentrate streams has occurred.
- The use of RBF depends on subsurface geologic conditions and is therefore is highly site specific, so it is difficult to size and cost the RF facilities until site-specific characteristics are known.
- An RBF system might require a large footprint, depending on the quantity and quality of flow.
- Due to concerns over the environmental impacts of CECs, permitting could be difficult for RF systems that treat concentrate.

3.4.2 Constructed Wetlands

Wetlands represent a form of natural treatment that utilizes the ability of a range of fauna and flora, with a small input of energy, to remove and stabilize pollutants from water. These systems can be low cost, technologically simple facilities that provide habitat value and recreational opportunities. The habitat and recreation opportunities can make constructed wetlands (CW) particularly appealing for the treatment of wastewater in small to medium-sized communities and in developing countries (Brix, 1993). Depending upon the application objective, CWs can be configured as vertical flow, surface flow, or submerged aquatic vegetation. An example of a surface flow CW is presented in Figure 3.16.



FIGURE 3.16 EXAMPLE OF A SURFACE FLOW CONSTRUCTED WETLAND

Traditionally, plants were thought to have an active role in the removal of pollutants in wetlands systems. However, recent studies have shown that bio-degradation, biotransformation, and adsorption are the most important mechanisms for the removal of pollutants from wastewater. Studies conducted using sediments from rivers indicate that estrogenic hormones (log Kow 4 to 4.2) can sorb to suspended and bed sediments (Bowman et al., 2002); therefore, in engineered wetlands, sorption is a potentially important mechanism for removal of hormones from the aqueous phase. Although sorption might result in the removal of hormones from the aqueous phase, the compounds will eventually pass through the wetland if transformation does not occur.

Engineered treatment wetlands provide an environment with surface areas for biofilms, which are conducive to biotransformation of organic compounds. Sorption coupled with biodegradation has been invoked as an explanation for the removal pesticides including atrazine, azinphosmethyl, and chlorpyrifos in wetlands (Moore et al., 2002; Schulz and Peall, 2001; Schulz et al., 2001). Furthermore, experiments using columns packed with freshwater sediments demonstrate sorption coupled with degradation of E2 at rates significantly faster than columns packed with sand or soil (Das et al., 2004). Bacteria present in municipal wastewater treatment systems (Ternes et al., 1999) and in surface waters (Jurgens et al., 2002) also can transform E2 to E1 and other metabolites.

Limited information is available to understand the removal efficiencies and mechanisms of CECs through CWs. Some studies have shown, however, that E2 and EE2 were attenuated during a wetland test experiment, and overall hormone removal ranged from 36 to 41 percent (Gray and Sedlak, 2005). CW also can remove 60 to 70 percent of detected PAHs, such as naphthalene, phenanthrene, fluoranthene, and pyrene (Masi et al., 2005). Accumulation of these compounds, 2 to 7 milligrams per kilogram (mg/kg), in a solid phase, indicates that sorption is an important mechanism for the removal of CECs in CWs. Removal efficiencies of 47, 58, and 89 percent have been found for ibuprofen, gemfibrozil, and tris-3-chloropropyl-phosphate (Gross et al., 2004).

Implementation Issues

Implementation of CW includes the following associated issues.

- The capability of CW to remove CECs is still unknown because no detailed pilot testing has been performed to evaluate the feasibility of this process to remove CECs in concentrate streams.
- The feasibility of implementing a CW system can be affected by the quality and flow rate of the concentrate stream, its geographical location and climate, and its hydrology and water balance. Also, high TDS and the presence of toxic material can diminish growth of plant and microorganisms.
- Sizing and cost of CW systems are case specific.
- CW systems require large facility footprints. CW systems generally would have to be coupled with other technologies, such as a volume-reduction technology, to

reduce the amount of concentrate that requires treatment so that the land required would be feasible.

• Shallow wetlands enhance adsorption of the compounds but require larger footprints.

In coastal areas, where ocean discharge is available, removal of CEC might be of primary interest. Although TDS removal is not necessary in some instances (that is, ocean discharge), a pretreatment might be needed as a precursor to a CW system to improve the removal of CECs and reduce the costs and size requirements.

4 Regulatory Status and Treatment Requirement for CECs

This section of the report contains the following subsections:

- Regulatory Status for CECs
- Treatment Requirements for CECs

4.1 Regulatory Status for CECs

Under the SDWA, the USEPA is required to publish a Contaminant Candidate List (CCL) every 5 years. The list is of contaminants known or anticipated to occur in public water supplies. As part of this effort, the Endocrine Disruptors Screening and Testing Program (EDSTP) was established. EDSTP issued a final report in 1998 outlining a multi-tiered approach for screening, testing, and assessing approximately 87,000 compounds.

The EDSTP report calls for the USEPA to prioritize potential contaminants and validate public health concerns for selected compounds through screening and testing to identify any adverse affects and establish a dose-response relationship for CECs. This process is ongoing.

Based on the large number of potential EDCs, future regulations could shift toward regulating compounds on a class basis by focusing on a common mechanism, such as toxicity or similar chemical structure, rather than regulating individual compounds (AWWARF, 2005). Another possible regulatory approach could require identification of specific treatment technologies (such as GAC or high-pressure membrane systems) for an array of chemicals, instead of setting standards for a class of chemicals.

CDPH recommends monitoring of additional constituents including pharmaceuticals, EDCs, PCPs, and other indicators of municipal wastewater contaminants for GRRPs. Although these CECs are not currently regulated, a majority of the compounds have been detected at least once in drinking water supplies. The most updated Groundwater Recharge Reuse Draft Regulation (August 2008) does not specifically identify monitoring parameters for GRRP, but it recommends that GRRP investigate chemicals presented in Table 4.1 or use surrogates that could represent one or more constituents in each category. This revision to the regulation was made based upon the limited availability of analytical methods for identification and detection of emerging contaminants. In either case, the information is useful for providing insight on the most frequently detected CECs.

Endocrine-Disrupting and Other Chemicals*	
Ethinyl estradiol (Hormone)	Caffeine (Other Indicators)
17b-Estradiol (Hormone)	Carbamazepine (Pharmaceutical)
Estrone (Hormone)	Ciprofloxacin (Pharmaceutical)
Bisphenol A (Industrial EDC)	Ethylenediamine Tetra Acetic Acid (EDTA)
Nonylphenol (Industrial EDC)	Gemfibrozil (Pharmaceutical)
Nonylphenol polyethoxylate (Industrial EDC)	Ibuprofen (Pharmaceutical)
Octylphenol (Industrial EDC)	Iodinated Contrast Media (Other Indicators)
Octylphenol polyethoxylate (Industrial EDC)	Lipitor (Pharmaceutical)
Polybrominated diphenyl ethers (Industrial EDC)	Methadone (Pharmaceutical
Acetaminophen (Pharmaceutical)	Morphine (Pharmaceutical)
Amoxicillin (Pharmaceutical)	Salicylic Acid (Pharmaceutical)
Azithromycin (Pharmaceutical)	Triclosan (Personal Care Product)

TABLE 4.1

RECOMMENDED EMERGING CONTAMINANTS FOR GRRP MONITORING

Note:

*Contaminants listed are from the January 2007 Title 22 California Code of Regulations, Groundwater Recharge Reuse Draft Regulations.

Source: CDPH, 2007

Also, the State of Pennsylvania is working with the USGS to develop a list of unregulated potential drinking water contaminants. This work, along with CDPH efforts, might eventually lead to the development of a regulatory framework through which some CECs could be regulated. However, regulation of CECs will require a well-grounded understanding of their occurrence, of how treatment affects these compounds, of the demographics of a utility's service area, and of the public perception.

4.2 Treatment Requirements for CECs

In current practice, concentrate is most commonly discharged into the ocean, especially in coastal areas that have existing ocean outfalls or access to outfalls via brine pipelines. There has been some implementation of deep well injection, evaporation ponds, or other zero-liquid discharge systems in inland areas where brine line and ocean discharge are not viable options. The Groundwater Replenishment System (GWRS) in Orange County and the West Basin Municipal Water District "boutique" water operations are two examples of coastal discharge of concentrate to the ocean. Laguna County Sanitation District and Fort Irwin are examples of inland areas with management of concentrate using deep well injection and ZLD systems, respectively. These examples do not address treatment of CECs because these constituents are not regulated. Because of the lack of regulatory requirements for CECs, this report has developed the following definitions for removal rates for treatment technologies:

- A moderate degree of treatment; 50 to 70 percent of CECs are removed; presented in Section 3.
- A high degree of treatment; greater than 85 percent of CECs are removed; presented in Section 3.

We assumed these two treatment requirements to capture moderate and high levels of removal. The removal rate for the moderate case was selected so that treatment technologies, such as GAC/PAC and biological treatment system (conventional activated sludge systems), that have removal rates of 50 to 70 percent would be considered in the analysis. These technologies provide alternative treatment with a reasonable cost although they do not provide complete removal of CECs. The high-level case provides higher removal rates at increased costs (that is, RO, ozonation, and UV/AOP).

5 Technology Selection and Cost Estimate

This section of the report contains the following subsections.

- Technology Overview
- Technologies with Moderate Removal Efficiency
- Technologies with High-Level Removal Efficiency

5.1 Technology Overview

Technologies that can remove CECs to a moderate extent (that is, a 50 to 70 percent removal rate for more than 67 percent of the compounds tested) include activated carbon adsorption, UV irradiation (at greater than 580 mJ/cm²), conventional activated sludge systems, and MBR. Technologies that can remove CECs to a great extent (that is, at least an 85 percent removal rate for more than 67 percent of the compounds tested) include RO, ozone, ozone/AOP, UV/AOP, and BAC.

Table 5.1 shows the treatment technologies and their removal efficiencies for the tested CECs. The green and yellow highlighted cells in Table 5.1 indicate that the selected technology exhibits moderate and high removal efficiency for the specified CEC. Blank areas in the table indicate that CEC removal efficiency is unknown for the selected technology. Brown highlighted areas indicate that the selected technology exhibits unsatisfactory removal (less than 50 percent removal) of the specified CECs.

According to Table 5.1, BAS and BAC are highly effective technologies for CEC removal; however, these findings are based on limited bench- and pilot–scale studies.

Because concentrate water quality could significantly vary between brackish groundwater and WWTP streams, the quality of each water source needs to be defined. Table 5.2 summarizes concentrate water quality for brackish groundwater and WWTP facilities that were used in this analysis. Brackish groundwater and WWTP concentrate data were obtained from the EMWD Menifee Brackish Groundwater Desalination Plant and the City of Oxnard Advanced Water Purification Facility.

Percentage Removal (%) Biologically Biologically Activated UV Carbon Active Active Compound Sub Category Adsorption Ozone UV AOP Irradiation CAS MBR NF RO Sand Carbon 1,4-Dioxane $(C_4H_8O_2)^a$ Industrial <20 <35 >95 <20 <20 <20 20-40 20-50 <20 <20 Acetaminophen ($C_8H_9NO_2$) N/A^b 78 >95 >97 73 >99 25-50 79 95 Analgesics >90 Androstenedione $(C_{19}H_{26}O_2)$ 70 >80 96 89 N/A >98 50-80 >61 96 97 Steroids Atrazine (C₈H₁₄CIN₅) 20-50 80 92 N/A 50-80 Pesticides 63 N/A N/A 54 83 Benzon(a)pyrene (C₂₀H₁₂) PAH 72 N/A N/A N/A >80 >85 N/A >90 N/A 89 Caffeine (C₈HYN₄O₂) Stimulant 59 >80 89 44 >97 >85 50-80 >99 77 93 Carbamazepine (C₁₅H₁₂N₂O) Analgesics, 72 >95 >88 60 N/A 20 50-80 >99 54 90 stimulant

TABLE 5.1

TREATMENT TECHNOLOGIES THAT EXHIBIT MODERATE OR HIGH-LEVEL EFFICIENCY FOR REMOVAL OF CECS

TABLE 5.1

TREATMENT TECHNOLOGIES THAT EXHIBIT MODERATE OR HIGH-LEVEL EFFICIENCY FOR REMOVAL OF CECS

					Per	centage Re	emoval (%	%)			
Compound	Sub Category	Activated Carbon Adsorption	Ozone	UV AOP	UV Irradiation	CAS	MBR	NF	RO	Biologically Active Sand	Biologically Active Carbon
DDT (C ₁₄ H ₉ Cl ₅)	Pesticides	70	N/A	N/A	N/A	N/A	N/A	>80	N/A	N/A	85
DEET (C ₁₂ H ₁₇ NO)	Pesticides	54	50-80	89	52	N/A	20	50-80	>95	37	80
Diazepam (Valium) (C ₁₆ H ₁₃ ClN ₂ O)	Anticonvulsant	67	50-80	93	52	<20	N/A	50-80	N/A	82	84
Diclofenac (C ₁₄ H ₁₁ Cl ₂ NO ₂)	Analgesics	49	>95	>98	>98	N/A	>50	50-80	>97	67	75
Dilantin (C ₁₅ H ₁₂ N ₂ O ₂)	Anticonvulsant	56	50-80	97	96	N/A	4	50-80	>99	77	80
Erythromycin (C ₃₇ H ₆₇ NO ₁₃)	Antimicrobials	52	>95	50-80	39	N/A	96	>80	>98	79	78

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TABLE 5.1

TREATMENT TECHNOLOGIES THAT EXHIBIT MODERATE OR HIGH-LEVEL EFFICIENCY FOR REMOVAL OF CECS

					Per	centage Re	emoval (%	%)			
Compound	Sub Category	Activated Carbon Adsorption	Ozone	UV AOP	UV Irradiation	CAS	MBR	NF	RO	Biologically Active Sand	Biologically Active Carbon
Estradiol (C ₁₈ H ₂₄ O ₂)	Steroids	55	>95	>98	93	60-80	N/A	50-80	N/A	85	94
Estriol (C ₁₈ H ₂₄ O ₃)	Steroids	58	>95	>99	90	>85	>98	50-80	N/A	81	92
Estrone (C ₁₈ H ₂₂ O ₂)	Steroids	77	>95	>99	94	80	82	50-80	>95	62	95
Ethinyl Estradiol (C ₂₀ H ₂₄ O ₂)	Steroids	70	>95	>98	93	N/A	N/A	50-80	N/A	73	91
Fluorene (C ₁₃ H ₁₀)	PAH	94	N/A	N/A	N/A	N/A	N/A	>80	N/A	N/A	>94
Fluoxetine (Prozac) (C ₁₇ H ₁₈ F ₃ NO)	Antidepressant	91	>95	>98	>98	N/A	40	>80	>96	98	>99
Galaxolide (C ₁₈ H ₂₆ O)	Fragrance	59	50-80	N/A	N/A	<20	N/A	50-80	>98	N/A	74

TREATMENT TECHNOLOGIES THAT EXHIBIT MODERATE OR HIGH-LEVEL EFFICIENCY FOR REMOVAL OF CECS Percentage Removal (%) Biologically Biologically Activated UV Carbon Active Active Compound Sub Category Adsorption Ozone UV AOP Irradiation CAS MBR NF RO Sand Carbon Gemfibrozil (C₁₅H₂₂O₃) Heart 38 95 N/A 74 >95 57 >86 50-80 >99 54 Medication Hydrocodone (C₁₈H₂₁NO₃) Analgesics 72 >95 >98 64 N/A >94 50-80 >98 47 92 Ibuprofen (Advil) (C₁₃H₁₈O₂₎ 26 50-80 94 70 >80 95 50-80 >99 66 83 Analgesics ≻. lopromide (C₁₈H₂₄I₃N₃O₈) X-Ray Contrast 31 20-50 91 99 N/A 20 >80 >99 28 42 Media Lindane (a-BHC) (C₆H₆Cl₆) 70 N/A N/A N/A N/A Pesticides N/A 50-80 N/A N/A 91 Meprobamate (C₉H₁₈N₂O₄₎ Anticonvulsant 36 20-50 75 29 N/A <1 50-80 >99 36 71 Metolachlor (C₁₅H₂₂CINO₂) 50 N/A N/A 79 Pesticides N/A N/A N/A 50-80 N/A N/A

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TABLE 5.1

TREATMENT TECHNOLOGIES THAT EXHIBIT MODERATE OR HIGH-LEVEL EFFICIENCY FOR REMOVAL OF CECS Percentage Removal (%) Biologically Activated Biologically UV Carbon Active Active Compound Sub Category Adsorption Ozone **UV AOP** Irradiation CAS MBR NF RO Sand Carbon Musk Ketone (C₁₄H₁₈N₂O₅) Fragrance N/A N/A N/A <20 83 69 N/A >80 N/A N/A Naproxen (C₁₄H₁₄O₃) Anti-Inflammatory 60 >95 >99 99 N/A >86 20-50 80 82 >99 Agent, Analgesics N-Nitrosodimethylamine $(NDMA) (C_2H_6N_2O)^{a}$ DBPs <20 40-70 <20 <20 <20 20-50 30-70 <20 >95 <20 **~**_0 Oxybenzone (C₁₄H₁₂O₃) Sun Screen 92 >95 50-80 50 >85 95 >80 >93 83 98 Pentoxifylline (C₁₃H₁₈N₄O₃) Heart 71 >80 90 50 N/A 85 50-80 >96 91 90 Medication Progesterone (C₂₁H₃₀O₂) 84 >80 98 92 N/A 95 50-80 N/A N/A 99 Steroids Sulfamethoxazole (C₁₀H₁₁N₃O₃S) 43 >95 >99 >99 N/A 20 50-80 >99 77 63 Antimicrobials

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TABLE 5.1

TABLE 5.1 TREATMENT TECHNOLOGIES THAT	EXHIBIT MODERATE	OR HIGH-LEVEL	EFFICIENCY	FOR REMOV	AL OF CECS						
						centage Re	emoval (%	%)			
Compound	Sub Category	Activated Carbon Adsorption	Ozone	UV AOP	UV Irradiation	CAS	MBR	NF	RO	Biologically Active Sand	Biologically Active Carbon
TCEP (C ₉ H ₁₅ O ₆ P)											
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Flame Retardant	60	<20	16	10	<20	20	50-80	>91	53	80
Testosterone (C ₁₉ H ₂₈ O ₂ )											
and the set of the set	Androgenic Steroids	71	>80	97	91	N/A	96	50-80	N/A	92	96
Triclosan (C ₁₂ H ₇ Cl ₃ O ₂ )											
	Antimicrobials	90	>95	>97	>97	70	70	>80	>97	97	97
Trimethoprim (C14H18N4O3)											
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Antimicrobials	69	>95	94	<5	N/A	>76	50-80	>99	24	94

Notes:

^a Notification levels for NDMA and 1,4 Dioxane are 10 and 3000 ng/L respectively ^b N/A = Information Not Available

Parameter	Units	Brackish Water RO Concentrate	Reuse RO Concentrate
рН	mg/L CaCo₃	7.0	8.0
Total Alkalinity	mg/L CaCo₃	650	1,820
Hardness	mg/L	3,500	2,300
Total Organic Carbon	mg/L	1.5	77
Total Suspended Solids	mg/L	18	6
Total Dissolved Solids	mg/L	5,700	12,200
Ammonia-N	mg/L	1.0	176
Nitrate-N	mg/L	20	11
Nitrite-N	mg/L	<0.1	9
Total Kjeldahl Nitrogen	mg/L	1.5	193
Total Nitrogen	mg/L	21.5	213
Total Phosphate-P	mg/L	0.4	18
Reactive Silica	mg/L	180	182
Chloride	mg/L	2,440	3,380
Fluoride	mg/L	<0.1	13
Sulfate	mg/L	470	3,800
Calcium	mg/L	990	827
Magnesium	mg/L	234	57
Potassium	mg/L	26	409
Sodium	mg/L	890	2,900
Strontium	mg/L	5.1	16
Barium	µg/L	660	159
Total Iron	µg/L	26	197
Total Manganese	µg/L	8	56

TABLE 5.2 BRACKISH AND REUSE RO CONCENTRATE WATER QUALITY

As shown in Table 5.2, although TOC, nitrogen, and phosphorus concentrations significantly vary between brackish groundwater and WWT concentrate streams, a high TDS concentration is common to each concentrate type.

5.2 Technologies with Moderate Removal Efficiency

5.2.1 Activated Carbon Adsorption

Activated carbon is a proven technology for removing a variety of organic compounds including CECs. However, there is limited application and experience for activated carbon as a treatment mechanism beyond drinking water applications that have relatively low ionic strength and TDS. Implementation of the use of activated carbon adsorption for CEC removal includes the following potential issues.

- High TOC in concentrate and suspended solids in brackish groundwater concentrate can block the pores within the activated carbon structure and reduce efficacy of the activated carbon system. Pretreatment for TOC and TSS might be required to improve process efficiency and to reduce facility size and costs.
- Concentrate might contain highly diverse organic compounds. Some of these compounds might have very high solubility in water, which can break through the GAC column relatively quickly and limit the run time of GAC.
- High ionic strength of the solution can interfere with GAC performance because certain ions can be precipitated and block the activated carbon pores.
- Spent activated carbon might contain hazardous substances that require special handling and have high disposal costs.
- Air quality permitting for GAC regeneration might be complex because of concerns associated with the presence of hazardous volatile compounds in concentrate.
- At a minimum, TDS removal and disinfection technology should be used in conjunction with CEC treatment.

GAC will provide good treatment for CECs; however, in areas where the treated water will be reused, adequate treatment for TDS and disinfection will be needed.

5.2.2 UV Irradiation

UV irradiation at typical disinfection UV doses of 50 to 80 mJ/cm² is not effective for CEC removal (AWWARF, 2005). At increased UV doses of 600 to 700 mJ/cm², however, UV was found to be effective in removing a majority of the CECs tested. Implementation of the use of UV includes the following potential associated issues.

- The UV transmittance through RO concentrate might be very low (20 to 30 percent for concentrate), which would dramatically increase the costs and size of the UV facility while reducing efficiency of the UV treatment process. Pretreatment is required to improve UV transmittance or the use of UV systems becomes cost prohibitive.
- Metals and inorganic compounds that are able to be oxidized exert UV demands. Higher UV demands result in higher UV doses and costs.

- Hardness greater than 300 mg/L in concentrate might require softening to minimize cleaning and maintenance of the UV reactor and quartz sleeves.
- At a minimum, the UV process should be coupled with filtration and TDS removal to allow treatment of concentrate.

One of the advantages of implementing a UV system is that it provides excellent inactivation of pathogens, thereby eliminating the need for additional disinfection facilities. UV also provides very good removal of NDMA at the proposed UV dose of 650 mJ/cm².

5.2.3 Conventional Activated Sludge

Most CECs (not all) are biodegradable. CAS systems provide good removal for a majority of the CECs listed in Table 2.6. Also, operating CAS systems at high TDS and nitrogen concentrations is not uncommon; however, care should be given to ensure process performance and avoid process upsets. Potential issues that could affect removal efficiencies of CAS systems for treating concentrate include:

- Acclimation of the CAS microbial community is essential in an environment with a high TDS concentration. A proper acclimation period should be given at plant startup to ensure that no process upset occurs.
- Concentrate could contain heavy metals and other inhibitory substances (phenolic substances) that can inhibit process performance at very low concentrations. A bench-scale treatability test is highly recommended to determine the feasibility of using a CAS system.
- TDS concentrations of greater than 20,000 mg/L reduce the efficiency of oxygen transfer and the ability of sludge to settle, which might result in poor process performance.
- Fluctuations in feedwater quality and flows have adverse impacts on process performance.
- CAS systems could require a large footprint; therefore, the available footprint for the facility needs to be evaluated before considering a CAS system as a CEC removal technology.
- CAS systems are not effective for the removal of NDMA, perchlorate, and 1,4 dioxane. If one of these compounds is of concern, additional treatment will be required using additional technologies.

Although CAS is a proven technology in treating a variety of industrial wastewaters with high TDS concentrations, there are no applications of CAS systems for treating concentrate. Therefore, it is recommended that the fraction of biodegradable organic material and treatability of the concentrate be determined before considering implementation of CAS. In coastal areas where ocean discharge is available, the treated stream can be discharged into the ocean without further treatment. On the other hand, filtration, TDS removal, and disinfection technology need to be coupled with the CAS if reuse of the treated water is desired. Incorporation of these technologies will further increase the footprint of the facility, as well as capital and O&M costs.

5.3 Technologies with High-Level Removal Efficiency

5.3.1 Membrane Bioreactor

MBR combines CAS treatment systems with membrane filtration providing a superior treatment of organics and improved solids removal. Certain CECs can be absorbed into the solids particles and more efficiently removed by MBR than by a CAS system. As a result, MBR provides better treatment for the CECs. MBR has the potential to provide some removal of CECs by adsorption, as well as biodegradability. MBR and CAS provide a similar degree of treatment using biodegradability at a given SRT so the implementation issues outlined in Section 5.2.3 also are applicable to the MBR systems. The major advantages that MBR has over a CAS system is that the ability of sludge to settle is no longer an issue in the MBR system.

One disadvantage of MBR is that no existing applications of this technology for treating concentrate exists. Therefore, the biodegradable fraction of organic material, presence of inhibitory substance, and treatability of RO concentrate should be determined before considering implementation of MBR for RO concentrate treatment.

5.3.2 Ozonation

Ozone reacts with organic contaminants through either the direct reaction with molecular ozone or through the formation of HO* radical (AWWARF, 2005). Both molecular ozone and hydroxyl radical pathways were found effective for the removal of organic compounds including CECs (AWWARF, 2005). An AWWARF study indicated that an applied dose of 2 to 5 mg/L ozone with a detention time of less than 5 minutes significantly reduced target CECs in drinking water (AWWARF, 2005).

The study focused on drinking water applications that have a relatively low concentration of TOC and other compounds that can be oxidized; therefore, the actual ozone dose might be 10 to 20 times higher for treating concentrate streams. In addition, no studies have been done to evaluate the fate of CECs and by-product formation in concentrate during ozonation. The use of ozonation to treat concentrate includes the following implementation issues.

- Accurate determination of ozone decay and other key design parameters might be a challenging task especially when dealing with a complex water quality matrix such as that found in concentrate.
- High organics, ammonia-nitrogen, and other oxidizable material exert ozone demands and dramatically increase capital and O&M costs of the ozonation facilities. Initial ozone demand and ozone decay kinetics will need to be determined via bench-scale studies prior to implementation of a project.

• Ozone is not effective for removal of NDMA, 1,4-dioxane, perchlorate, and nitrate. If removal of these compounds is required, then an additional treatment process needs to be implemented in conjunction with ozonation.

Because TOC and ammonia-N concentrations are very high in concentrate, capital and O&M facility costs will be higher.

Since brackish groundwater concentrate has low TOC concentrations, pretreatment is not necessary. Ozonation eliminates the need for additional disinfection facilities, if treated water needs to be disinfected; however, ozonation might have to be coupled with additional filtration and TDS removal technologies to treat concentrate from WWTPs.

5.3.3 Reverse Osmosis

RO is one of the most effective treatment technology and is capable of removing soluble inorganic and organic compounds from water including CECs. Very few compounds are not fully removed by RO; however, NDMA and DBPs are only moderately removed by RO. One major challenge of using RO for treating concentrate is that the high TDS would result in lower water recovery. In many cases, concentration of sparingly soluble compounds, such as silica and salts (that is, barium sulfate, calcium carbonate, and calcium sulfate), limits the RO recovery rates. Sample water quality data used in this analysis and summarized in Table 5.2 have high concentrations of silica (180 mg/L) that will limit RO recovery at approximately 35 percent even if state-of-the-art scale inhibitors are used to push the super-saturation of silica to 280 mg/L (King Lee Technologies, 2009). Precipitative softening reverse osmosis (PSRO) facilities are designed to remove hardness caused by calcium and magnesium. PSRO facilities retard silica precipitation by the addition of caustic or lime-soda, thereby increasing water recoveries. In this report, PSRO was considered for the treatment of RO concentrates. The use of PSRO systems includes the following major implementation issues.

- Complex operation that requires a good control strategy and highly skilled operational personnel.
- High capital and operating costs.
- Requires pH adjustment after RO.
- Even with increased recovery rates significant quantity of concentrate is produced.
- Requires disinfection if treated water from WWTP concentrate is to be reused.

Unlike the other treatment processes, RO provides superior treatment for a wide range of compounds including TDS, CECs, nitrogen, TOC, and perchlorate. Despite its high cost, RO treatment might be the most suitable solution for the treatment of RO concentrate in inland areas where deep well injection and surface water discharge are not feasible brine management options.

5.3.4 UV/AOP

UV/AOP relies on the addition of hydrogen peroxide that absorbs UV light and generates highly reactive HO* radicals, which react indiscriminately with most organic pollutants including recalcitrant contaminants such as 1,4 dioxane, TCE, and MTBE, and NDMA. The efficiency of UV/AOP depends on water quality (i.e., UV transmittance and presence of free radical scavengers), compound type (i.e., recalcitrant versus readily oxidizable compounds), and UV dosage. Pretreatment is necessary for removing TOC and enhancing UV transmittance of concentrate to keep capital and O&M costs feasible. GAC was used for pretreatment to provide TOC and UV transmittance improvement. The use of UV/AOP treatment of concentrate includes the following major implementation issues.

- Inorganic material that is not removed in the GAC system acts as scavenger for OH* radical.
- High hardness fouls UV sleeves and increases the need for frequent cleaning.
- UV/AOP needs to be coupled with a TDS removal technology (that is, EDR or RO) if the treated water is reused.

TCEP and X-ray contrast media are only moderately removed using UV/AOP.

One of the challenges for treating concentrate with UV/AOP is the low UV transmittance value of the water (that is, less than 55 percent). Improving UV transmittance is essential, but it requires costly investment. One way to reduce cost is to consider media regeneration with GAC. Despite its relatively high cost, UV/AOP is the most effective technology for removal of CECs including NDMA and 1,4 dioxane while preventing the formation of DBPs. Therefore, depending upon treatment objectives, UV/AOP might be the most suitable technology.

6 Summary, Conclusions and Recommendations

CECs are a diverse group of compounds and include hormones, PhACs, PCPs, and pesticides, as well as industrial and household chemicals. Because some of these compounds can cause developmental and reproductive changes in fish and amphibians, and evidence exists that mammals might be sensitive to extremely low concentrations of these CECs, there is a growing concern about these compounds. In addition, hormones, PhACs, and PCPs are being studied for possible health effects by USEPA (AWWARF, 2005). Although no firm evidence for association between low-dose exposure to CECs and adverse human health effects has been found, CECs have become a popular issue because of public perception and attention of the scientific and environmental communities. CECs are not currently regulated; however, monitoring of several CECs has been done, and additional studies and monitoring are underway in California, Pennsylvania, and other states. Depending upon the findings regarding occurrence, frequency, and detectability, some CECs might be regulated in the future.

CECs are also present in concentrate streams. In this report, treatment technologies for CECs were evaluated. Since treatment regulatory requirements do not exist for CECs, this evaluation was based upon assumed standards for CEC removal. Two standards were used for technologies that provide removal of a majority of CECs at water treatment plans and WWTPs:

- A moderate degree of treatment; 50 to 70 percent of CECs are removed; presented in Section 3.
- A high degree of treatment; greater than 85 percent of CECs are removed; presented in Section 3.

One of the major challenges for each treatment technology is that the water quality matrix has high concentrations of TOC, TDS, and nitrogen, which might interfere with the process performance and result in the need for pretreatment. For this analysis, two types of concentrate streams were used for two sample facilities—brackish groundwater concentrate from EMWD Menifee Desalination plant and WWTP concentrate from the City of Oxnard Advanced Water Purification Pilot Facility. In this evaluation, selection of technology was based on CEC removal capabilities and potential costs of the technologies.

For moderate CEC removal treatment technologies, the most cost-effective option is GAC for brackish groundwater and WWTP concentrate treatment. CAS was the least cost-effective technology.

To attain efficient removal of CECs, the most cost-effective option is ozonation; however, pretreatment of WWTP concentrate is essential for ozonation, which

makes ozonation unfeasible from a cost perspective. UV/AOP could be a costcompetitive option if the UV transmittance of the water is around 95 percent. Sparingly soluble salts such as silica limit the RO recovery to around 35 percent, which necessitates incorporation of softening facilities to increase water recoveries. Despite the high cost, PSRO is the only technology that removes not only CECs but also TDS. The feasibility of implementing PSRO really depends upon treatment objectives, requirements, and project constraints.

Approximately 87,000 emerging compounds have been identified as possible EDCs (USEPA, 2008). CECs are diverse compounds whose characteristics (that is, pKa and Kow) vary even within the same subcategory (that is, PhACs and PPCs). Because of this diversity, no single technology, including RO, can treat all CECs effectively. Multiple barrier treatment will be the most effective approach and is recommended by CDPH for groundwater recharge projects. Before selecting a CEC removal technology:

- Carefully determine the need and objective of the CEC removal facility.
- Determine if there is a need to remove specific CECs or all CECs listed in Table 2.6.
- Identify constituents that are of particular concern and have been detected in water.

In addition, consideration should be given to:

- The willingness of the public to pay for potentially costly mitigation efforts.
- The importance of CECs in surface water and drinking water relative to other public health and environmental concerns.
- The potential loss or gain related to waiting for more information or taking action despite uncertainties regarding CECs.

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Attachment A Physical-Chemical Properties

Compound	Chemical Formula	Molecular Weight (gram/mole)	Solubility (mg/L)	Acid Solubility Constant -pKa	Octanol Water Partition Coefficient-logKow	Molecular Volume (gram/mole)
Acetaminophen	$C_8H_9NO_2$	151	14,000	9.38	0.46	559
Androstenedione	$C_{19}H_{26}O_2$	286	75	N/A	2.75	968
Atrazine	$C_8H_{14}CIN_5$	216	35	1.70	2.61	761
Benzo(a)pyrene	$C_{20}H_{12}$	252	3	N/A	6.13	825
Caffeine	$C_8H_{10}N_4O_2$	194	21,600	10.4	-0.01	646
Carbamazepine	$C_{15}H_{12}N_2O$	236	18	13.9	2.45	775
DDT	$C_{14}H_9CI_5$	355	1	N/A	6.91	910
DEET	$C_{12}H_{17}NO$	191	449	0.67	2.18	759
Diazepam (Valium)	$C_{16}H_{13}CIN_2O$	284	50	3.40	2.82	888
Diclofenac	$C_{14}H_{11}CI_2NO_2$	296	19,400	4.40	0.70	830
Dilantin	$C_{15}H_{12}N_2O_2$	252	32	8.33	2.47	782
Erythromycin	$C_{37}H_{67}NO_{13}$	734	1	8.88	3.06	2,016
Estradiol	$C_{18}H_{24}O_2$	272	4	10.4	4.01	907
Estriol	$C_{18}H_{24}O_3$	288	441	10.4	2.45	930
Estrone	$C_{18}H_{22}O_2$	270	30	10.4	3.13	903
Ethinyl Estradiol	$C_{20}H_{24}O_2$	296	4	10.4	3.67	983
Fluorene	$C_{13}H_{10}$	166	2	N/A	4.18	625
Fluoxetine (Prozac)	$C_{17}H_{18}F_3NO$	309	50,000	10.3	4.05	1,007
Galaxolide	C ₁₈ H ₂₆ O	258	2	N/A	4.80	919

TABLE A-1 PHYSICAL-CHEMICAL AND MOLECULAR PROPERTIES OF TARGET CECS

Compound	Chemical Formula	Molecular Weight (gram/mole)	Solubility (mg/L)	Acid Solubility Constant -pKa	Octanol Water Partition Coefficient-logKow	Molecular Volume (gram/mole)
Gemfibrozil	$C_{15}H_{22}O_3$	250	11	4.42	3.80	945
Hydrocodone	$C_{18}H_{21}NO_3$	299	797	7.32	2.16	911
Ibuprofen (Advil)	$C_{13}H_{18}O_2$	206	21	4.91	3.97	797
lopromide	$C_{18}H_{24}I_3N_3O_8$	791	24	10.2	-2.05	1,462
Lindane (a-BHC)	C ₆ H ₆ Cl ₆	291	7	N/A	3.72	670
Meprobamate	$C_9H_{18}N_2O_4$	218	4,700	10.9	0.70	781
Metolachlor	$C_{15}H_{22}CINO_2$	284	530	-1.34	3.13	948
Musk Ketone	$C_{14}H_{18}N_2O_5$	294	3,200	N/A	4.3	907
Naproxen	$C_{14}H_{14}O_3$	230	16	4.15	3.18	785
Oxybenzone	$C_{14}H_{12}O_3$	228	69	7.77	3.79	772
Pentoxifylline	$C_{13}H_{18}N_4O_3$	278	7700	0.97	0.29	949
Progesterone	$C_{21}H_{30}O_2$	315	9	N/A	3.87	1,032
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	253	610	5.50	0.89	769
TCEP	$C_9H_{15}O_6P$	286	310,000	N/A	1.30	819
Testosterone	$C_{19}H_{28}O_2$	288	23	N/A	3.32	960
Triclosan	$C_{12}H_7CI_3O_2$	290	10	7.90	4.76	782
Trimethoprim	$C_{14}H_{18}N_4O_3$	290	400	7.12	0.91	922

TABLE A-1 PHYSICAL-CHEMICAL AND MOLECULAR PROPERTIES OF TARGET CECS

N/A: Not available

Attachment B CEC Removal Efficiencies

	Activated Adsorp		Oxidation ^a			UV Irra		Advanced Oxidation ^a		
Compound	PAC	GAC	Chlorine	Chloramines	56 mJ/cm ²	290 mJ/cm ²	548 mJ/cm ²	806 mJ/cm ²	Ozone	UV AOP
Acetaminophen	99	78	>80	>80	34	31	45	73	>95	>97
Androstenedione	61	70	<20	<20	32	39	58	89	>80	96
Atrazine	3	63	<20	<20	19	35	55	92	20-50	80
Benzo(a)pyrene	N/A	72	>80	50-80	N/A	N/A	N/A	N/A	N/A	N/A
Caffeine	16	59	<20	<20	18	11	19	44	>80	89
Carbamazepine	16	72	<20	<20	17	18	27	60	>95	>88
DDT	N/A	70	<20	<20	N/A	N/A	N/A	N/A	N/A	N/A
DEET	63	54	<20	<20	16	15	31	52	50-80	89
Diazepam (Valium)	N/A	67	<50	<20	18	17	25	52	50-80	93
Diclofenac	69	49	>80	50-80	58	>98	>98	>98	>95	>98
Dilantin	23	56	<20	<20	26	48	69	96	50-80	97
Erythromycin	7.9	52	>80	<20	14	<1	11	39	>95	50-80
Estradiol	N/A	55	>80	>80	38	37	62	93	>95	>98
Estriol	<1	58	>80	>80	39	38	62	90	>95	>99
Estrone	N/A	77	>80	>80	42	64	>99	94	>95	>99
Ethinyl Estradiol	N/A	70	>80	>80	38	38	63	93	>95	>98
Fluorene	N/A	94	<20	<20	N/A	N/A	N/A	N/A	N/A	N/A
Fluoxetine (Prozac)	N/A	91	<20	<20	40	69	90	>98	>95	>98
Galaxolide	N/A	59	<50	<50	N/A	N/A	N/A	N/A	50-80	N/A
Gemfibrozil	8.2	38	50-80	<20	<1	15	35	57	>95	95
Hydrocodone	56	72	>80	<50	17	25	35	64	>95	>98

TABLE B-1 PHYSICAL-CHEMICAL TREATMENT PROCESSES (ACTIVATED CARBON ADSORPTION, OXIDATION, UV IRRADIATION AND ADVANCED OXIDATION) FOR CECS REMOVALS

_	Carbon otion ^a	n Oxidation ^a			UV Irra	Advanced Oxidation ^a				
Compound	PAC	GAC	Chlorine	Chloramines	56 mJ/cm ²	290 mJ/cm ²	548 mJ/cm ²	806 mJ/cm ²	Ozone	UV AOP
Ibuprofen (Advil)	16	26	<20	<20	5	24	42	70	50-80	94
lopromide	72	31	<20	<20	<1	49	75	99	20-50	91
Lindane (a-BHC)	N/A	70	<20	<20	N/A	N/A	N/A	N/A	N/A	N/A
Meprobamate	13	36	<20	<20	17	9	14	29	20-50	75
Metolachlor	N/A	50	<20	<20	N/A	N/A	N/A	N/A	N/A	N/A
Musk Ketone	N/A	69	>80	<20	N/A	N/A	N/A	N/A	N/A	N/A
Naproxen	6.3	60	>80	<20	15	65	84	99	>95	>99
Oxybenzone	N/A	92	>80	50-80	<1	<1	3	50	>95	50-80
Pentoxifylline	26	71	<50	<20	19	10	22	50	>80	90
Progesterone	N/A	84	<20	<20	31	41	61	92	>80	98
Sulfamethoxazole	84	43	>80	<20	36	78	93	>99	>95	>99
TCEP	N/A	60	<20	<20	14	<1	4	10	<20	16
Testosterone	74	71	<20	<20	32	38	61	91	>80	97
Triclosan	N/A	90	>80	>80	44	95	>97	>97	>95	>97
Trimethoprim	64	69	>80	<20	23	18	29	20-50	>95	94

TABLE B-1 PHYSICAL-CHEMICAL TREATMENT PROCESSES (ACTIVATED CARBON ADSORPTION, OXIDATION, UV IRRADIATION AND ADVANCED OXIDATION) FOR CECS REMOVALS

N/A: Not available

^aSnyder et al., 2007

		Membrane Processes ^a								
Compound	Magnetic Ion Exchange (MEIX) ^a	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)					
Acetaminophen	<20	N/A	6	25-50	>90					
Androstenedione	<20	N/A	72	50-80	>61					
Atrazine	<20	N/A	15	50-80	N/A					
Benzo(a)pyrene	N/A	N/A	>89	>80	>90					
Caffeine	<20	4	7	50-80	>99					
Carbamazepine	<20	8	16	50-80	>99					
DDT	N/A	N/A	>85	>80	N/A					
DEET	<20	23	9	50-80	>95					
Diazepam (Valium)	<20	N/A	84	50-80	N/A					
Diclofenac	>80	N/A	2	50-80	>97					
Dilantin	20-50	N/A	25	50-80	>99					
Erythromycin	N/A	5	15	>80	>98					
Estradiol	20-50	N/A	>99	50-80	N/A					
Estriol	<20	N/A	41	50-80	N/A					
Estrone	<20	N/A	91	50-80	>95					
Ethinyl Estradiol	20-50	N/A	>99	50-80	N/A					
Fluorene	N/A	N/A	>74	>80	N/A					
Fluoxetine (Prozac)	<20	N/A	69	>80	>96					
Galaxolide	N/A	400	<1	50-80	>98					
Gemfibrozil	20-50	N/A	<1	50-80	>99					
Hydrocodone	<20	5	14	50-80	>98					

TABLE B-1 PHYSICAL-CHEMICAL TREATMENT PROCESSES (MAGNETIC ION EXCHANGE AND MEMBRANE PROCESSES) FOR CECS REMOVALS CONT'D.

		Membrane Processes ^a									
Compound	Magnetic Ion Exchange (MEIX) ^a	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)						
Ibuprofen (Advil)	20-50	N/A	8	50-80	>99						
lopromide	<20	N/A	<1	>80	>99						
Lindane (a-BHC)	N/A	N/A	>85	50-80	N/A						
Meprobamate	<20	15	6	50-80	>99						
Metolachlor	N/A	N/A	56	50-80	N/A						
Musk Ketone	N/A	N/A	37	>80	N/A						
Naproxen	50-80	N/A	10	20-50	>99						
Oxybenzone	20-50	36	85	>80	>93						
Pentoxifylline	<20	15	11	50-80	>96						
Progesterone	<20	N/A	>98	50-80	N/A						
Sulfamethoxazole	20-50	2	5	50-80	>99						
TCEP	<20	9	7	50-80	>91						
Testosterone	<20	N/A	71	50-80	N/A						
Triclosan	>80	53	88	>80	>97						
Trimethoprim	<20	8	18	50-80	>99						

N/A: Not available

^aSnyder et al., 2007

			Biological Treatme	ent	Biological Treatment					
Compound	MBR ^a	CAS⁵	Biologically Aerated Filter (BAF) ^a	Biologically Active Sand ^a	Biologically Active Carbon ^a	River Bank Filtration ^a	Constructed Wetlands			
Acetaminophen	78	99	6	79	95	>98	N/A			
Androstenedione	70	61	41	96	97	>99	N/A			
Atrazine	63	3	15	54	83	4	N/A			
Benzo(a)pyrene	72	N/A	89	N/A	89	N/A	N/A			
Caffeine	59	16	8	77	93	97	N/A			
Carbamazepine	72	16	5	54	90	13	N/A			
DDT	70	N/A	>87	N/A	85	N/A	N/A			
DEET	54	63	8	37	80	91	N/A			
Diazepam (Valium)	67	N/A	15	82	84	42	N/A			
Diclofenac	49	69	13	67	75	>99	N/A			
Dilantin	56	23	19	77	80	22	N/A			
Erythromycin	52	7.9	31	79	78	98	N/A			
Estradiol	55	N/A	1	85	94	>99	36-41 [°]			
Estriol	58	<1	<1	81	92	>99	N/A			
Estrone	77	N/A	<1	62	95	>99	36-41 [°]			
Ethinyl Estradiol	70	N/A	1	73	91	>99	N/A			
Fluorene	94	N/A	28	N/A	>94	N/A	N/A			
Fluoxetine (Prozac)	91	N/A	97	98	>99	>99	N/A			
Galaxolide	59	N/A	19	N/A	74	N/A	N/A			
Gemfibrozil	38	8.2	13	54	74	>99	58 ^d			
Hydrocodone	72	56	14	47	92	97	N/A			

TABLE B-2 BIOLOGICAL (CAS, MBR, BAS, BAF AND BAC) AND NATURAL TREATMENT (RIVER BANK FILTRATION AND CONSTRUCTED WETLANDS) FOR CECS REMOVALS

	Biological Treatment					Natural Treatment	
Compound	MBR ^a	CAS⁵	Biologically Aerated Filter (BAF) ^a	Biologically Active Sand ^a	Biologically Active Carbon ^a	River Bank Filtration ^a	Constructed Wetlands
Ibuprofen (Advil)	26	16	30	66	83	>99	47 ^d
lopromide	31	72	11	28	42	93	N/A
Lindane (a-BHC)	70	N/A	7	N/A	91	N/A	N/A
Meprobamate	36	13	4	36	71	71	N/A
Metolachlor	50	N/A	4	N/A	79	N/A	N/A
Musk Ketone	69	N/A	10	N/A	83	N/A	N/A
Naproxen	60	6.3	3	80	82	>98	N/A
Oxybenzone	92	N/A	14	83	98	>97	N/A
Pentoxifylline	71	26	13	91	90	>99	N/A
Progesterone	84	N/A	52	N/A	99	>99	N/A
Sulfamethoxazole	43	84	5	77	63	N/A	N/A
TCEP	60	N/A	10	53	80	32	N/A
Testosterone	71	74	35	92	96	>99	N/A
Triclosan	90	N/A	37	97	97	>98	N/A
Trimethoprim	69	64	20	24	94	>99	N/A

TABLE B-2 BIOLOGICAL (CAS, MBR, BAS, BAF AND BAC) AND NATURAL TREATMENT (RIVER BANK FILTRATION AND CONSTRUCTED WETLANDS) FOR CECS REMOVALS

N/A: Not available

^aSnyder et al., 2007

^bStephenson and Oppenheimer, 2007

^cGray and Sedlak, 2005

^dGross et al., 2004