

Fate of Pharmaceuticals, Personal Care Products, and Endocrine-disrupting Chemicals in Water

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Introduction

Pharmaceuticals (both prescription- and non-prescription drugs) and personal care products (combined and termed as PPCPs, hereafter) and endocrine-disrupting chemicals (termed as EDCs, hereafter) have recently been identified as emerging organic contaminants in environmental waters (Xagorarakis and Kuo, 2008; Sanderson et al., 2004; Christensen, 1998; Schulman et al., 2002; Webb et al., 2003; Schwab et al., 2005; Bercu et al., 2008; Snyder, 2008; Cunningham et al., 2009). Personal care products (PCPs) represent a group of chemicals, which can be categorized based on their intended usages: (1) Cosmetics (e.g., triethyl citrate), (2) Antimicrobial activity (e.g., triclosan), (3) Deodorizer (e.g., 1,4-Dichlorobenzene), (4) Fragrance (e.g., 3-Methyl-1*H*-indole (skatol)), and (5) Flavorant (e.g., Camphor) (Stackelberg *et al.*, 2004). Endocrine-disrupting chemicals (EDCs) represent groups of chemicals which have been reported to result in increased incidences of breast, prostate, and testicular cancers, reproductive disorders, cognitive impairment, miscarriage, early puberty in girls, delayed puberty in boys, impaired fertility in men, cognitive impairment, behavior abnormalities in children, etc. (Birklett, 2003; Liu *et al.*, 2005; Rahman *et al.*, 2009). In general, these organic compounds can be categorized in five categories: (1) Pharmaceuticals, (2) Steroids, (3) Alkylphenols, (4) Flame retardants, and (5) Pesticides (Liu *et al.*, 2005; Stackelberg *et al.*, 2007). The presence of these organic compounds in wastewater effluent and source water for drinking water utilities may have implications on human and ecological health.

Water and wastewater treatment processes are capable of transforming PPCPs and EDCs, but each compound responds differently to treatment, making it difficult to predict the fate of these chemicals as a whole. A review of literature suggests that conventional water treatment may effectively remove the majority of tested chemicals. However, certain compounds appear to undergo treatment without transformation, thus requiring further treatment. Drinking water oxidants, such as chlorine, ozone, and advanced ultraviolet (UV) oxidation have been shown to degrade and transform a wide variety of PPCPs and EDCs. Chlorine and ozone are shown to react with these emerging contaminants during water treatment and often results in the formation of by-products that may or may not be harmful to humans and the environment. In most cases, UV irradiation does not degrade emerging contaminants unless an advanced oxidation process (AOP), such as H₂O₂/ozone is applied. Ozone appears to be the most effective at oxidizing different classes of emerging contaminants present in waters. Predictive quantitative-structure-activity-relationship (QSAR) models may be key to determining persistence of these chemicals during drinking water treatment. However, the current state of knowledge does not provide clear answers regarding potential human risks of exposure to emerging contaminants via water consumption and/or recreational activities.

Sources and Occurrences

Contamination of aquatic systems with PPCPs and EDCs has become an emerging important environmental issue for health of human-beings and environment. These organic

46 compounds are biologically active compound, which may produce adverse effects in humans,
47 animals, and plants. Increasing numbers of studies reveal that these chemicals have been found
48 in natural waters, wastewater effluents, and drinking water supplies. When water undergoes
49 treatment, such as coagulation/flocculation, adsorption, disinfection/oxidation, these chemicals
50 are either removed from water or transformed into compounds that are less or more harmful to
51 humans and the environment than the parent compound (Rahman *et al.*, 2009). Removal of these
52 compounds from water primarily depends on their initial concentrations, characteristics of water
53 matrix, sequence and conditions of different unit-processes at drinking and wastewater treatment
54 plants. In the United States there is more consumption of new pharmaceuticals and high-strength
55 or long-acting formulations than in other countries (Danzon and Furukawa, 2008). This suggests
56 that more persistent and/or newer man-made compounds may occur in U.S. waters. A recent
57 USGS survey of 139 streams in 30 states, conducted by Kolpin *et al.* (2002), reported detection
58 of 82 of 95 target compounds, including steroids, plasticizers, detergent metabolites, veterinary
59 medicines, and other organic water contaminants.

60

61 **Sources of PPCPs and EDCs in Environment**

62 There are several proposed pathways responsible for contamination of water with these
63 organic compounds. Pharmaceuticals consumed by humans in daily life are partially metabolized
64 and excreted into wastewater in forms of urine and fecal matter. Depending on removal
65 efficiencies of unit processes at wastewater treatment plant and contaminant's initial
66 concentrations, a portion of these contaminants, either transformed or unchanged, are released in
67 wastewater effluents and discharged in receiving water bodies. These contaminants are found in
68 surface water or groundwater bodies, depending on their persistence in environment. During the
69 use of surface stream as a source of raw water for supplying drinking water after treatment, these
70 contaminants enter into drinking water treatment system and are removed depending on removal
71 effectiveness of different unit processes present in the drinking water treatment system. At
72 drinking water treatment plant, these compounds are either removed or transformed to other
73 compounds (i.e., by-products). Upon distribution of drinking water for human consumption,
74 these compounds and their by-products are present in water, which finally results in exposure of
75 humans to these contaminants through ingestion of drinking water.

76 In addition to wastewater, animal waste, biosolids, and solid waste are other possible
77 sources of PPCPs and EDCs in environment. Animal production has been reported to contribute
78 significantly in dissemination of pharmaceuticals in water, particularly from industrialized
79 animal agriculture, or from concentrated animal feeding operations (CAFOs). Industrialized
80 animal agriculture is used to provide livestock for human consumption, typically with animals
81 living in dense populations. After a period of storage manure is often land-applied as plant
82 fertilizer, and as consequence the pharmaceuticals are discharged to surface and ground water via
83 surface runoff and percolation. Studies indicate application of swine manure to crops results in
84 temporary increases of antibiotic resistant bacteria (Sengelov *et al.*, 2003; Halling-Sorensen *et al.*,
85 2005).

86

87 **Occurrences**

88 *Pharmaceuticals and personal care products (PPCPs) in Water*

89 The presence of pharmaceuticals and personal care products (PPCPs) in raw and treated
90 wastewater has been well documented with concentrations averaging from less than 10 µg/L in
91 finished wastewater to greater than 100 µg/L in raw wastewater (Batt *et al.*, 2006; Boyd *et al.*,

92 2003; Brun *et al.*, 2006; Buser *et al.*, 1999; Buser *et al.*, 1998; Carballa *et al.*, 2004; Castiglioni
93 *et al.*, 2006; Wennmalm and Gunnarsson, 2005; Yang and Carlson, 2004; Zuccato *et al.*, 2006).
94 Examples of pharmaceuticals that have been detected in wastewater are common prescription
95 and veterinary drugs such as beta-blockers (*e.g.*, metoprolol, propranolol), analgesics (*e.g.*,
96 ibuprofen, naproxen), and antibiotics (*e.g.*, erythromycin, trimethoprim, ciprofloxacin,
97 tetracycline, clindomycin, sulfonamides, tetracycline, fluoroquinolone, macrolides, and
98 trimethoprim). For example, Santos *et al.*, (2007) detected ibuprofen in wastewater influent and
99 effluent at concentrations of 12.1 – 373 µg/L and 0.78 – 48.2 µg/L, respectively. Naproxen was
100 also detected at 1.1 – 27.4 µg/L in wastewater influent and 0.22 – 4.3 µg/L in effluent. Gomez *et*
101 *al.* (2007) detected acetaminophen, codeine, diclofenac, and ibuprofen in wastewater influent at
102 mean concentrations of 134, 5.2, 1.5, and 84 µg/L, and in wastewater effluent at mean
103 concentrations of 0.22, 3.7, 0.9, and 7.1 µg/L, respectively.

104 Although most of the published literature focuses on occurrence in sewage effluents,
105 PPCPs have also been detected in raw and treated drinking water, mostly at levels less than 1
106 µg/L (Boyd *et al.*, 2003; Heberer, 2002; Loraine and Pettigrove, 2006; Moll *et al.*, 2001; Perret
107 *et al.*, 2006; Petrovic *et al.*, 2003; Rodriguez-Mozaz *et al.*, 2004; Stackelberg *et al.*, 2004;
108 Stolker *et al.*, 2004; Ternes *et al.*, 2002; Vieno *et al.*, 2005; Zuhlke *et al.*, 2004). For example,
109 Loraine and Pettigrove (2006) detected ibuprofen in finished drinking water at a mean
110 concentration of 0.93 µg/L. In Italy, three sulfonamide antibiotics were detected in store-bought
111 mineral waters at concentrations ranging from 0.009 to 0.080 µg/L (Perret *et al.*, 2006). In 2004,
112 the US Geological Survey conducted a study on the fate of 106 contaminants throughout a
113 conventional drinking water treatment plant (Stackelberg *et al.*, 2004). Pharmaceuticals present
114 in raw water samples included carbamazepine, trimethoprim, erythromycin-H₂O, acetaminophen,
115 codeine, and sulfamethoxazole. Carbamazepine was detected at a maximum concentration of
116 0.258 µg/L in finished water samples (Stackelberg *et al.*, 2004).

117 The presence of PPCPs has been confirmed in surface waters (rivers and lakes) as well,
118 with concentrations generally less than 1 µg/L (Abuin *et al.*, 2006; Batt *et al.*, 2006; Bound and
119 Voulvoulis, 2006; Yang and Carlson, 2004; Zuccato *et al.*, 2006). For example, Bound and
120 Voulvoulis (2006) reported concentrations of ibuprofen and acetaminophen up to 3 and 0.56
121 µg/L, respectively. Rabiet *et al.* (2006) detected acetaminophen, carbamazepine, and diclofenac
122 in surface water at concentrations of 0.011 – 0.072, 0.024 – 0.056, and 0.001 – 0.033,
123 respectively. The U.S. Geological Survey conducted the first major study of pharmaceuticals
124 and personal care products in surface waters during 1999 and 2000 (Kolpin *et al.*, 2002). The
125 study focused on locations likely to be contaminated by wastewater effluent. Kolpin *et al.*
126 (2002) detected pharmaceuticals, steroids and hormones, veterinary and human antibiotics, and
127 other organic contaminants in 80% of 139 streams sampled. The most frequently detected
128 pharmaceuticals by Kolpin *et al.* in U.S. streams included trimethoprim, acetaminophen,
129 erythromycin, estriol, lincomycin, and sulfamethoxazole at detection frequencies of 27.4, 23.8,
130 21.5, 21.4, 19.2 and 19.0% and at median concentrations of 0.013, 0.11, 0.1, 0.019, 0.06, and
131 0.07 µg/L, respectively. Other pharmaceuticals that have been found in surface waters are
132 naproxen, clofibric acid, ketoprofen and clarithromycin. Frequencies of occurrences of these
133 chemicals, obtained from Kolpin *et al.* (2002). Among all PCPs, fragrances in surface waters
134 have been analyzed more in detail compared to other PCPs (Lee *et al.*, 2003a) and have been
135 found as high as 0.150 µg/L in surface waters and 0.1 µg/L in drinking waters. (Daughton and
136 Ternes (2002); Kolpin *et al.* (2002) ; Lee *et al.* (2003a); Stackelberg *et al.*, 2007)

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Table 1. Personal Care Products in Source and Finished Waters

Chemical	CASRN	Source water (µg/L)	Finished water (µg/L)	Reference
<i>Cosmetics</i>				
Triethyl citrate	77-93-0	0.085	0.013	Stackelberg <i>et al.</i> (2007)
<i>Antimicrobial</i>				
Triclosan	3380-34-5	0.05-0.15	ND	Daughton and Ternes (2002); Stackelberg <i>et al.</i> (2007)
<i>Deodorizer</i>				
1,4-Dichlorobenzene	106-46-7	0.09	ND	Kolpin <i>et al.</i> (2002); Stackelberg <i>et al.</i> (2007)
<i>Fragrance</i>				
3-Methyl-1 <i>H</i> -indole (skatol)	83-34-1	ND	ND	Stackelberg <i>et al.</i> (2007)
Acetyl hexamethyl tetrahydro naphthalene (AHTN)	21145-77-7	0.126	0.036	Stackelberg <i>et al.</i> (2007)
Musk Ketone	81-14-1	0.001-0.023	ND	Lee <i>et al.</i> (2003a)
<i>Flavorant</i>				
Camphor	76-22-2	0.004	0.003	Stackelberg <i>et al.</i> (2007)
<i>Insect Repellent</i>				
N,N-diethyltoluamide	134-62-3	0.06-0.082	0.003	Kolpin <i>et al.</i> (2002)

CASRN-Chemical Abstracts Services Registry Number, ND-Not detected

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141 *Endocrine-disrupting Chemicals in Water*

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143 Endocrine-disrupting chemicals (EDCs) have been found in stream water and wastewater
 144 effluents, along with other organic compounds. The USGS study of national streams (Kolpin *et*
 145 *al.*, 2002) found occurrences of EDCs with other organic compounds. Similar observations of
 146 co-occurrence of EDCs with other wastewater organic compounds were also noted by
 147 Stackelberg *et al.* (2007). This study found presence of different EDCs such as bisphenol A
 148 (BPA), 4-Nonylphenol (NP), Diethoxyoctylphenol (OP₂EO), Tris(dichloroisopropyl)phosphate
 149 (TDIP), and Tris(2-chloroethyl)phosphate (TCEP) with organic compounds in wastewater.
 150 Concentrations of EDCs in source water vary between 0.038 and 0.342 µg/L and vary between
 151 0.004 and 0.092 µg/L in finished water. Also, these compounds have been found in settled
 152 sludge and filter-backwash sediments, which are of cause of concern as these sediments are
 153 generally digested, dewatered, and finally used as a soil amendment.

153

Table 2 Endocrine disrupting chemicals in stream water (Kolpin et al., 2002)

Chemical	CASRN	Use	Frequency of detection (%)
Triclosan	3380-34-5	antimicrobial disinfectant	57.6
4-nonylphenol	251-545-23	nonionic detergent metabolite	50.6
Bisphenol A	80-05-7	Plasticizer	41.2
Diazinon	333-41-5	Insecticide	25.9
Methyl parathion	298-00-0	Disinfectant	24.7
Carbaryl	63-25-2	Insecticide	16.5
Benzo(a)pyrene	50-32-8	PAH	9.4
Lindane	58-89-9	Insecticide	5.9
<i>cis</i> -chlordane	5103-71-9	Insecticide	4.7
Dieldrin	60-57-1	Insecticide	4.7
2,6-di- <i>tert</i> -butylphenol	128-39-2	Antioxidant	3.5
3- <i>tert</i> -butyl-4-hydroxy anisole	25013-16-5	Antioxidant	2.4
<i>Prescription drugs</i>			
Fluoxetine	54910-89-3	Antidepressant	1.2
<i>Steroids and hormones</i>			
Estriol	50-27-1	reproductive hormone	21.4
17 α -ethynyl estradiol	57-63-6	ovulation inhibitor	15.7
<i>cis</i> -androsterone	53-41-8	urinary steroid	14.3
19-norethisterone	68-22-4	ovulation inhibitor	12.8
17 β -estradiol	50-28-2	reproductive hormone	10
mestranol	72-33-3	ovulation inhibitor	10
Estrone	53-16-7	reproductive hormone	7.1
17 α -estradiol	57-91-0	reproductive hormone	5.7
progesterone	57-83-0	reproductive hormone	4.3
equilenin	517-09-9	estrogen replacement	2.8
testosterone	58-22-0	reproductive hormone	2.8
Equilin	474-86-2	estrogen replacement	1.4

Table 3. Other chemicals (Non-EDC) in stream water (Kolpin et al., 2002)

Chemical	CASRN	Use	Frequency of detection (%)
<i>Veterinary and human antibiotics</i>			
erythromycin-H ₂ O	114-07-8	erthromycin metabolite	21.5
Lincomycin	154-21-2	Antibiotic	19.2
Tylosin	1401-69-0	Antibiotic	13.5
sulfamethoxazole	723-46-6	Antibiotic	12.5
trimethoprim	738-70-5	Antibiotic	12.5
roxithromycin	80214-83-1	Antibiotic	4.8
sulfamethazine	57-68-1	Antibiotic	4.8
ciprofloxacin	8585721-33-1	Antibiotic	2.6
chlortetracycline	57-62-5	Antibiotic	2.4
sulfamerazine	122-11-2	Antibiotic	1.2
Tetracycline	60-54-8	Antibiotic	1.2
sulfamethizole	144-82-1	Antibiotic	1
Norfloxacin	70458-96-7	Antibiotic	0.9
<i>Steroids and hormones</i>			
coprostanol	360-68-9	fecal steroid	85.7
Cholesterol	57-88-5	plant/animal steroid	84.3
<i>Prescription drugs</i>			
Dehydronifedipine	67035-22-7	Antianginal	14.3
Diltiazem	42399-41-7	antihypertensive	13.1
Codeine	76-57-3	Analgesic	10.6
Cimetidine	51481-61-9	Antacid	9.5
Metformin	657-24-9	Antidiabetic	4.8
Gemfibrozil	25812-30-0	antihyperlipidemic	3.6
Enalaprilat	76420-72-9	eantihypertensive metabolite	1.2
<i>Other organics</i>			
N,N-diethyltoluamide	134-62-3	insect repellent	74.1
tri(2-chloroethyl)phosphate	115-96-6	fire retardant	57.6
ethanol,2-butoxy-phosphate	78-51-3	Plasticizer	45.9
Fluoranthene	206-44-0	PAH	29.4
Pyrene	129-00-0	PAH	28.2
1,4-dichlorobenzene	106-46-7	Deodorizer	25.9
4-methyl phenol	106-44-5	disinfectant	24.7
tetrachloroethylene	127-18-4	solvent,degreaser	23.5
phthalic anhydride	85-44-9	plastic manufacturing	17.6
<i>Non-prescription drugs</i>			
Caffeine	58-08-2	Stimulant	61.9
Cotinine	486-56-6	nicotine metabolite	38.1
<u>1,7-dimethylxanthine</u>	611-59-6	caffeine metabolite	28.6
acetaminophen	103-90-2	Antipyretic	23.8
ibuprofen	15687-27-1	antiflammatory	9.5

158 **Removal of PPCPs and EDCs in Drinking Water Utilities**

159 The fate of pharmaceuticals and personal care products (PPCPs), and endocrine-
160 disrupting chemicals (EDCs) during water treatment depends on the compound's
161 physicochemical properties and the types and sequences of processes used in the treatment plant.
162 Physical processes, such as settling, coagulation/flocculation, and filtration show varying
163 removal efficiencies of pharmaceuticals (Gobel *et al.*, 2007; Nakada *et al.*, 2007; Stackelberg *et*
164 *al.*, 2007; Peng *et al.*, 2006; Clara *et al.*, 2005; Ternes *et al.*, 2002). Disinfection processes, such
165 as chlorine oxidation and ozonation are expected to degrade these organic compounds or
166 transform them into byproducts, which may or may not be toxic to humans and environment.
167 PPCPs and EDCs are organic substances which are expected to be highly susceptible to
168 oxidation, depending on their physicochemical properties, such as octanol-water partition
169 coefficient, presence of aromatic rings and functional groups. Full-scale treatment studies
170 indicate that an appropriate combination of processes may effectively reduce their concentrations
171 in water leaving a drinking water treatment plant (Nakada *et al.*, 2007; Stackelberg *et al.*, 2007;
172 Boyd *et al.*, 2003; Ternes *et al.*, 2002).

173

174 **PPCPs and EDCs in Full-scale Drinking Water Treatment Plants**

175 **PPCPs.** Few studies have looked at removal of pharmaceuticals during full-scale
176 drinking water treatment. Full-scale treatment studies are valuable because they provide
177 information regarding the effectiveness of individual processes on pharmaceutical removal, as
178 well as concentrations of pharmaceuticals in source and finished waters.

179 Stackelberg *et al.* (2007) sampled water from a drinking water treatment plant (DWTP) in
180 the United States that utilized screening, clarification, primary chlorine disinfection,
181 sand/granular activated carbon (GAC) filtration, and secondary chlorine disinfection. The
182 DWTP treated 235 million liters per day. The degree of removal by each process varied for each
183 organic compound investigated. Forty-five organic compounds were detected in the source
184 water, including pharmaceuticals, flame retardants, plasticizers, pesticides, and others. Overall,
185 GAC filtration resulted in an average percent removal of 53% for all compounds, disinfection
186 resulted in 32% removal, and clarification resulted in 15% removal. Only some of the
187 pharmaceuticals, such as acetaminophen, carbamazepine, erythromycin, and sulfamethoxazole
188 were detected in at least 25% of source water samples. After primary disinfection,
189 sulfamethoxazole and acetaminophen were not detected, while carbamazepine and erythromycin
190 were removed by 20% and 92%, respectively. The initial concentrations of acetaminophen,
191 carbamazepine, erythromycin, and sulfamethoxazole compounds before primary disinfection
192 were 30, 15, 191, and 10 ng/L, respectively. The combination of clarification, chlorine
193 disinfection, and sand/GAC filtration was effective at reducing the studied pharmaceuticals.
194 These results were similar to a previous study, which Stackelberg *et al.* (2004) conducted at the
195 same DWTP. The utility was located in a very urbanized area, with at least 50 wastewater
196 treatment plants discharging into streams or tributaries supplying source water to the DWTP. In
197 the original study, the treatment process train followed screening, the addition of powdered
198 activated carbon (PAC), coagulation, primary disinfection, flocculation, sedimentation,
199 sand/GAC filtration, and secondary disinfection. Several changes were made to the treatment
200 process before the second study (i.e., Stackelberg *et al.*, 2007), including discontinuing the
201 addition of PAC, adding microsand to the clarification process, and reversing the order of
202 clarification and primary disinfection. Similar to the second study (i.e., Stackelberg *et al.*, 2007),
203 carbamazepine was the only investigated pharmaceutical that was not entirely removed by

204 conventional drinking water treatment (i.e., Stackelberg *et al.*, 2004). Observed removal of
205 organic compounds during drinking water treatment was attributed to hydrophilicity and
206 reactivity of organic compounds and conditions at unit processes, such as oxidant dose, contact
207 time, and presence of co-ions and co-organic compounds, etc.(Stakelberg *et al.*, 2007). GAC
208 removed both hydrophilic and hydrophobic pharmaceuticals, such as carbamazepine (Octanol-
209 water partition coefficient: $\log K_{OW} = 2.45$) compared to chlorination, which only oxidized
210 hydrophilic compounds.

211 A treatment train consists of clarification, disinfection, and filtration steps was observed
212 to be effective in removing only one personal care product (PCP) out of 4 PCPs studied during a
213 monitoring study which Stackelberg *et al.* (2007) conducted at a DWTP . Only triethyl citrate
214 was observed to removed ~90% from water compared to other PCPs, such as acetyl hexamethyl
215 tetrahydro naphthalene (AHTN) and hexahydrohexamethyl cyclopentabenzopyran (HHCB),
216 which were observed to removed <20%. Further, they also observed that the same treatment train
217 was able to remove >50% EDCs from water. Summary of performance effectiveness of overall
218 treatment train of the DWTP in removing EDCs, such as bisphenol A (BPA), tris(2-
219 chloroethyl)phosphate (TCEP), 4-nonylphenol (NP), diethoxyoctylphenol (OP₂EO), and
220 tris(dichloroisopropyl)phosphate (TDIP) from water. EDCs such as TCEP, OP₂EO, and TDIP
221 were observed to be completely removed from water in the DWTP (i.e., 100% removal), whereas
222 BPA and NP were observed to be removed only by 87% and 68%, respectively.

223 Boyd *et al.* (2003) took samples at various stages of treatment from two different
224 drinking water treatment plants. The first plant situated in Louisiana, USA, used PAC addition,
225 coagulation, flocculation, sedimentation, chlorination, filtration, and chloramination steps for
226 drinking water treatment. Only naproxen was detected at 68 ng/L, but it was completely removed
227 after going through a combination of unit processes, consists of chlorination, filtration, and
228 chloramination steps. The second plant, located in Windsor, Ontario, used ozonation,
229 coagulation, flocculation, sedimentation, filtration, and chlorination steps for drinking water
230 treatment. In this plant, clofibrac acid and naproxen were detected in the influent raw water at
231 103 ng/L and 63 ng/L, respectively. Neither of the compounds was detected in the final effluent.

232 Ternes *et al.* (2002) also monitored selected pharmaceuticals from two different drinking
233 water treatment plants. The first DWTP used pre-ozonation, flocculation, main ozonation,
234 multiple-layer filtration, and GAC filtration steps for the treatment train, while the other plant
235 used sedimentation, flocculation, GAC filtration, underground passage, bank filtration, and slow
236 sand filtration steps. During the study, Ternes *et al.* (2002) observed the combination of
237 ozonation and GAC filtration steps effective at reducing carbamazepine, diclofenac, and clofibrac
238 acid compounds, with all three compounds removed by greater than 90% in the first treatment
239 plant (initial concentrations of these compounds ranged from 10 to 180 ng/L).

240 Bundy *et al.* (2007) studied effects of drinking water treatment processes, such as
241 flocculation, sedimentation, dual-media filtration (anthracite and sand), GAC, and chlorine
242 disinfection removal of pharmaceuticals and pharmaceuticals-like compounds, such as caffeine
243 (1µg/L), trovafloxacin (38 µg/L), 17β-Estradiol (1µg/L), and salicylic acid (3 µg/L) from water.
244 During this study, the filtration step was observed to partially some of the compounds studied. It
245 was observed to provide 0.62 to 7.7% removal of caffeine and estradiol and 3.3 to 27.1%
246 removal for trovafloxacin compounds. For these chemicals, the disinfection was not observed to
247 be effective. Addition of a GAC adsorber to unit processes resulted in increase in overall
248 removal of PPCPs and EDCs to more than 90% for all chemicals tested.

249

250 **Table 4. Overall Removal of Pharmaceuticals during Full-Scale Drinking Water Treatment**

Pharmaceutical	Frequency of detection in stream water (>10%)	Influent Concentration (ng/L)	Effluent Concentration (ng/L)	Overall Removal (%)	Treatment Process Train	Reference
Carbamazepine		191 ^a 200 ^{a,b} 80 80 - 180 ^b	29 ^a 126.5 ^{a,b} BDL BDL – 30 ^b	85 36.7 ^a >99 83 – 100 ^c	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination Screening, PAC and sulfuric acid addition, coagulation, chlorination, flocculation, sedimentation, GAC filtration, secondary chlorination DWTP1: Pre-ozonation, flocculation, main ozonation, layer and GAC filtration DWTP2: Sedimentation, flocculation, GAC, underground passage, bank and sand filtration	Stackelberg <i>et al.</i> , 2007 ^c Stackelberg <i>et al.</i> , 2004 Ternes <i>et al.</i> , 2002
Bezafibrate		80 ^b ND	BDL	100 ^c	DWTP1: Pre-ozonation, flocculation, main ozonation, layer and GAC filtration DWTP2: Sedimentation, flocculation, GAC, underground passage, bank and sand filtration	Ternes <i>et al.</i> , 2002
Clofibric Acid		~10 ^b ~10-15 ^b	BDL BDL	100 ^c 100 ^c	DWTP1: Pre-ozonation, flocculation, main ozonation, layer and GAC filtration DWTP2: Sedimentation, flocculation, GAC, underground passage, bank and sand filtration	Ternes <i>et al.</i> , 2002
Diclofenac		~35 ^b ~65 ^b	BDL BDL	100 ^c 100 ^c	DWTP1: Pre-ozonation, flocculation, main ozonation, layer and GAC filtration DWTP2: Sedimentation, flocculation, GAC, underground passage, bank and sand filtration	Ternes <i>et al.</i> , 2002
Naproxen		63-65 64	ND ND	100 100	DWTP1: PAC addition, coagulation/flocculation/sedimentation, chlorination, filtration, chloramination DWTP2: Ozonation, coagulation/flocculation/sedimentation, filtration, chlorination	Boyd <i>et al.</i> , 2003
Veterinary and						

human antibiotics						
Erythromycin	21.5 (Kolpin et al., 2002)	10 ^a	ND	100	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg <i>et al.</i> , 2007 ^c
Sulfamethoxazole	19% (Kolpin et al., 2002)	30 ^a	ND	100	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg <i>et al.</i> , 2007 ^c
Prescription drugs						
Codeine	10.6% (Kolpin et al., 2002)					
Dehydronifedipine	14.3% (Kolpin et al., 2002)					
Diltiazem	13.1% (Kolpin et al., 2002)					
Non-prescription drugs						
Acetaminophen	23.8 (Kolpin et al., 2002)	15 ^a	0.3 ^a	98	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg <i>et al.</i> , 2007 ^c
Cotinine	38.1 (Kolpin et al., 2002)					

Note: BDL: below detection limits; NA: not available; ND: pharmaceutical not detected in sample; NM: not measured

^a Value represents average.

^b Approximated from figure.

^c Removal calculated by authors.

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257 **Table 5. Overall Removal of Endocrine-disrupting chemicals during Full-Scale Drinking Water Treatment**

Pharmaceutical	Frequency (%) (Kolpin et al., 2002)	Influent Concentration (ng/L)	Effluent Concentration (ng/L)	Overall Removal (%)	Treatment Process Train	Reference
<i>Other organics</i>						
Triclosan	57.6	ND	ND	-	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg et al., 2007
4-nonylphenol	50.6	342	92	73	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg et al., 2007
Bisphenol A	41.2	107	26	76	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg et al., 2007
Diazinon	25.9	47	ND	100	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg et al., 2007
Methyl parathion	24.7					
Carbaryl	16.5	55	ND	100	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg et al., 2007
Chlorpyrifos	15.3					
Diethylphthalate	11.1					
bis(2-ethylhexyl)phthalate	10.6					
2,6-di-tert-butyl-1,4-benzoquinone	9.4					
Benzo(a)pyrene	9.4	ND	ND	-	Screening, clarification, chlorination, sand/GAC filtration, secondary chlorination	Stackelberg et al., 2007

Note: BDL: below detection limits; NA: not available; ND: pharmaceutical not detected in sample; NM: not measured

^a Value represents average.

^b Approximated from figure.

^c Removal calculated by authors.

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Table 6. Removal of Pharmaceuticals during Individual Processes in Full-Scale Drinking Water Utilities

Chemical	Influent Conc. (ng/L)	Primary Treatment (Coagulation, flocculation, settling)		Filtration			Disinfection			Reference
		ng/L	% Removal	Ng/L	% Removal	Type	ng/L	% Removal	Oxidant	
Carbamazepine	191 ^a 200 ^{a,d} 80-180 ^d	186 ^a 82.3 ^{a,d} 100 – 180 ^d	3 ^b 59.9 ^{a, b} 0 to 14 ^b	4 ^a 106 ^{a,d} 0 - 10 ^d	97 ^b 0 ^{a, b} >90 ^b	Sand/GAC GAC GAC	149 ^a 126.5 ^{a,d} NA	20 ^b 0 ^{a,b} >99 ^e	NaOCl NaOCl Ozone	Stackelberg <i>et al.</i> , 2007 ^c Stackelberg <i>et al.</i> , 2004 Ternes <i>et al.</i> , 2002
Bezafibrate	80 ^d	73 ^d	8.8 ^b	BDL	>95 ^b	GAC	NM	NM	Ozone	Ternes <i>et al.</i> , 2002
Clofibric Acid	9 - 10 ^d	10 ^d	0 ^b	5 ^d	50 ^b	GAC	NA	77 ^c	Ozone	Ternes <i>et al.</i> , 2002
Diclofenac	35 – 65 ^d	60 ^d	7.7 ^b	BDL	>95 ^b	GAC	NA	>99 ^e	Ozone	Ternes <i>et al.</i> , 2002
Naproxen	63-65	63-68	0 ^b	NA	NA	NA	ND ^e	100 ^b	NaOCl	Boyd <i>et al.</i> , 2003
Veterinary and human antibiotics										
Erythromycin	10 ^a	5.3 ^a	47 ^b	ND ^a	100 ^b	Sand/GAC C	0.4 ^a	92 ^b	NaOCl	Stackelberg <i>et al.</i> , 2007 ^c
Sulfamethoxazole	30 ^a	20 ^a	33 ^b	ND ^a	NA	Sand/GAC C	ND ^a	100 ^b	NaOCl	Stackelberg <i>et al.</i> , 2007 ^c

Note: Percent removals were calculated based on pharmaceutical concentration before and after each treatment process (eg. primary treatment, filtration, disinfection).

BDL: below detection limit; NA: not available; ND: pharmaceutical not detected in sample; NM: not measured

^a Value represents average.

^b Authors calculated removals from given concentrations.

^c Filtration followed primary disinfection.

^d Approximated from figure.

^e Removal after main ozonation

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273 **Table 7. Removal of EDCs during Individual Processes in Full-Scale Drinking Water Utilities**

Chemical	Influent Conc. (ng/L)	Clarification		Disinfection			Filtration			Reference
		ng/L	% Removal	ng/L	% Removal	Oxidant	ng/L	% Removal	Type	
Other organics										
Tris(2-chloroethyl)phosphate (TCEP)	95	94	-0	92	2.1	Chlorine	ND	100	Sand/GAC	Stackelberg <i>et al.</i> (2007)
Diethoxyoctylphenol (OP ₂ EO)	38	17	55.3	15	11.7	Chlorine	ND	100	Sand/GAC	Stackelberg <i>et al.</i> (2007)
Tris(dichloroisopropyl) phosphate (TDIP)	102	102	0	101	0	Chlorine	ND	100	Sand/GAC	Stackelberg <i>et al.</i> (2007)
Triclosan										
4-nonylphenol	342	342	-0	100	70.8	Chlorine	108	0	Sand/GAC	Stackelberg <i>et al.</i> (2007)
Bisphenol A	107	108	0	45	58.3		14	68.9	Sand/GAC	Stackelberg <i>et al.</i> (2007)

Note: Percent removals were calculated based on pharmaceutical concentration before and after each treatment process.
 ND: pharmaceutical not detected in sample

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278 **Removal Effectiveness of Unit Processes in Removing PPCPs and EDCs from Water**

279 This section presents descriptions of removal effectiveness of different unit processes at
280 DWTP, such as (a) lime softening, coagulation/flocculation, sedimentation, (b) filtration
281 (adsorptive, sand, and membrane filtration), and (c) oxidation (chlorination, ozonation,
282 H₂O₂/ozonation, and ultraviolet Irradiation) in reducing concentrations of PPCPs and EDCs in
283 drinking water. Also, a discussion about possible water quality indicators, to be used in
284 ascertaining removal effectiveness of different treatment trains employed at different DWTPs, is
285 presented at the end of this chapter.

286

287 *a. Lime Softening, Coagulation, Sedimentation*

288 Several studies have investigated the effects of coagulation/flocculation, lime softening,
289 and sedimentation on removal of PPCPs and EDCs from water. Sedimentation by
290 coagulation/flocculation and lime softening are not expected to remove these organic compounds
291 due to their hydrophilic nature (Ternes *et al.*, 2002; Westerhoff *et al.*, 2005; Kimura *et al.*, 2005;
292 Vieno *et al.*, 2007; Stackelberg *et al.*, 2007; Choi *et al.*, 2008). Ternes *et al.* (2002) observed
293 little or no removal of carbamazepine, diclofenac, and clofibrac acid after coagulation with iron
294 chloride during full-scale drinking water treatment. Similarly, Stackelberg *et al.* (2007) observed
295 incomplete removal of acetaminophen, carbamazepine, erythromycin, and sulfamethoxazole
296 during coagulation with iron chloride at a DWTP. Clarification resulted in percent removals of
297 3%, 33%, 47%, and 60% for carbamazepine, sulfamethoxazole, erythromycin, and
298 acetaminophen, respectively (Stackelberg *et al.*, 2007). During a bench-scale study, Adams *et al.*
299 (2002) did not observe any removal of antibiotics during coagulation and lime softening
300 processes (experimental conditions: aluminum sulfate concentration: 20-107 mg/L; ferric sulfate
301 concentration: 35-169 mg/L; antibiotics types: carbadox, sulfachlorpyridazine, sulfadimethoxine,
302 sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim; antibiotic concentration: 50
303 µg/L; lime dosage: 232 mg/L; soda ash dosage: 191 mg/L; pH 11.3). Westerhoff *et al.* (2005)
304 also observed similar results during coagulation and lime softening experiments involving 22
305 different pharmaceuticals. In a pilot-scale study, the average removal of 13 different
306 pharmaceuticals was 3% during coagulation with ferric sulfate (Vieno *et al.*, 2007). Choi *et al.*
307 (2008) conducted coagulation experiments on tetracycline antibiotics using poly-aluminum
308 chloride (dosage: 5 - 60 mg/L, mixing time: 5 min) and observed that removal of antibiotics
309 increased with increasing coagulant dose. However, removal was observed to decrease at very
310 high dosage, i.e., 40 mg/L, which was attributed to the possibility of charge neutralization of
311 antibiotics at high coagulant dosage, resulting in re-stabilization of antibiotics in water. Analysis
312 of these studies indicates that lime softening and coagulation processes are not effective in
313 completely reducing concentrations of PPCPs in water.

314

315 *b. Filtration*

316 Three different types of filtrations are considered in this work: (1) Adsorptive filtration,
317 (2) Sand filtration, and (3) Membrane filtration. Following sections present descriptions of
318 performance effectiveness of these filtration types in removing PPCPs and EDCs from drinking
319 water.

320 **Adsorptive Filtration.** Adsorption by activated carbon is commonly used in drinking
321 water treatment for removal of organic chemicals, associated with taste and odor and natural
322 organic matter (NOM), either in powdered activated carbon (PAC) or granular activated carbon

323 (GAC) forms. The adsorption of organic compounds to activated carbon depends on its chemical
324 structure, polarity, and hydrophobicity (expressed in terms of octanol-water partition coefficient,
325 K_{ow}); porosity of activated carbon (i.e., media), activated carbon dosage, and presence of NOM
326 in solution during adsorptive filtration (Choi *et al.*, 2008; Mestre *et al.*, 2007; Vieno *et al.*, 2007;
327 Westerhoff *et al.*, 2005; Yoon *et al.*, 2003; Yu *et al.*, 2003; Bundy *et al.*, 2007).

328 Adsorption by GAC may be effective for removing pharmaceuticals with high octanol-
329 water partitioning coefficients (K_{ow}), such as estradiol, ethinylestradiol, fluoxetine, bezafibrate,
330 carbamazepine, and diclofenac compounds (Ternes *et al.*, 2002; Vieno *et al.*, 2007). During a
331 pilot study, Vieno *et al.* (2007) observed that most of the pharmaceuticals studied were removed
332 after a two-step GAC filtration process except those pharmaceuticals having high hydrophilicity
333 (or K_{ow}), such as atenolol, sotalol, and ciprofloxacin. Choi *et al.* (2008) found the use of a coal-
334 based GAC column more effective than coagulation in removing tetracycline (> 68% removal
335 was observed using GAC) and reported that coal-based carbon exhibits slightly better removal
336 than coconut-based carbon for removing pharmaceuticals from water. During a batch adsorption
337 study of removal of bezafibrate, carbamazepine, diclofenac, and clofibrac acid compounds from
338 water using a coal-based GAC (chemical concentration range: 0.1-100 $\mu\text{g/L}$; sorbent
339 concentration: <0.2 g/L; equilibrium time: 24 h), Ternes *et al.* (2002) also observed similar
340 removals and suggested the possibility of application of a coal-based GAC adsorber in drinking
341 water treatment plants.

342 Addition of powdered activated carbon (PAC) adsorber to drinking water treatment train
343 may also be effective, but is often only used seasonally to control taste and odor causing organic
344 compounds and NOM. PAC adsorber appears to be effective in removing antibiotics from
345 surface water. Adams *et al.* (2002) observed more than 90% removal of antibiotics, such as
346 carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole,
347 trimethoprim (antibiotic concentration: 50 $\mu\text{g/L}$; PAC concentration: 50mg/L) from both pure
348 water and surface water (alkalinity: 7 mg/L as CaCO_3 ; total hardness: 268 mg/L as CaCO_3 ; pH
349 7.7). Westerhoff *et al.* (2005) also found that increasing PAC dosage resulted in greater removal
350 of pharmaceuticals and EDCs, such as bisphenol A (BPA), 17 β -estradiol (E2) and 17 α -
351 ethinylestradiol (EE2) from water, with a dosage of 20 mg/L PAC removing more than 80% of
352 organic compounds studied. They observed trends of compounds with protonated bases having
353 greater removal than other compounds, particularly compounds with deprotonated functional
354 groups having low K_{ow} values. Yoon *et al.* (2003) investigated the adsorption of EDCs, such as
355 E2 and EE2 onto six different PAC brands, tested at 5 and 15 mg/L dosages and a 4 hour contact
356 time (hormone concentration: 100 nM). For the model water, more than 99% of the hormones
357 were observed to be removed by all brands except for one, which had the lowest point of zero
358 charge (pH_{ZPC}) value. Removals of hormones were observed to lower in raw drinking water
359 because of the presence of NOM, which might have influenced adsorption of hormones on PAC.
360 Snyder *et al.* (2006) studied removal of spiked pharmaceutical compounds from natural waters in
361 bench- and pilot- scale experiments and observed that majority of compounds tested were
362 removed by more than 90% with a PAC dose of 35 mg/L and 5 hour contact time.

363 The adsorption of organic compounds on activated carbon depends on its chemical
364 structure, polarity, and hydrophobic nature; activated carbon type and dosage, solution pH and
365 presence of co-solutes, such as natural organic matter (NOM) during adsorption (Stackelberg *et al.*
366 *et al.*, 2004; Mestre *et al.*, 2007; Suntisukaseam *et al.* 2007). Solution pH is one of the most
367 important parameters, which influence adsorption of organic compounds and thus removal from
368 water. Depending on solution pH, surface characteristics (i.e., pH_{ZPC}) and the extent of

369 protonation/deprotonation of organic compounds vary. Mestre *et al.* (2007) studied the effect of
370 pH on adsorption of ibuprofen on activated carbon prepared from cork powder, and observed a
371 decrease in removal of ibuprofen with an increase in solution pH, suggesting the role of
372 electrostatic bonding between ibuprofen compound and activated carbon. As ibuprofen has a pK_a
373 value of 4.91, electrostatic repulsion is expected to occur between ibuprofen anion and activated
374 carbon surface at solution $pH > 5$, resulting in reduction of adsorption of ibuprofen compounds
375 on activated carbon surface. The second most important factor influencing the extent of
376 adsorption is the surface characteristics of media (i.e., activated carbon in this case). To study the
377 effect of surface characteristics of activated carbon on adsorption of acetaminophen and nalidixic
378 acid (a quinolone antibiotic with a carboxylic functional group), Suntisukaseam *et al.*, (2007)
379 used neutral polymeric resin as a polar adsorbent and powdered activated carbon as a nonpolar
380 adsorbent and observed higher adsorption on activated carbon (adsorption isotherm: Freundlich
381 type) compared to polymeric resins (adsorption isotherm: Langmuir type). Also, due to higher
382 water solubility and polarity, acetaminophen was observed to be adsorbed more on both media
383 compared to nalidixic acid. Another important factor influence adsorption of target compounds
384 on GAC is present of co-solutes, specifically NOM, which have been reported to decrease extent
385 of adsorption of organic compounds on GAC. Ternes *et al.* (2002) observed competitive effects
386 of NOM on adsorption of pharmaceuticals on GAC and adsorption of clofibrac acid on GAC was
387 observed to be lower in the natural groundwater (dissolved organic carbon: 2.0 mg/L) compared
388 to that in the deionized water. Stackelberg *et al.* (2004) also observed similar effects of NOM in
389 decreasing extent of adsorption of pharmaceuticals, such as carbamazepine and other organic
390 wastewater-related contaminants (OWCs), on GAC adsorber.

391 Previous studies have used different types of activated carbons, prepared from different
392 raw materials, such as bituminous carbon, coconut shell, and waste cork powder (Yu *et al.*, 2003;
393 Mestre *et al.*, 2007) for studying removal of PPCPs and EDCs from water. Yu *et al.* (2003)
394 compared adsorption of naproxen and carbamazepine on activated carbon, prepared from
395 bituminous carbon and coconut shell, using an adsorption isotherm (i.e., Freundlich isotherm)
396 and observed higher adsorption of carbamazepine on carbon than naproxen. Adsorption
397 capacities of these compounds were observed to differ depending on carbon type. Naproxen
398 showed greater adsorption affinity for bituminous carbon than coconut shell, while
399 carbamazepine did not display a significant difference, which was attributed to ionic forms of
400 compounds studied (at experimental conditions studied, naproxen is present in anionic form,
401 whereas carbamazepine is present in a neutral form). Mestre *et al.* (2007) prepared activated
402 carbon using cork powder and studied removal of ibuprofen from water. They observed higher
403 adsorption of ibuprofen on activated carbon prepared using chemical activation method
404 compared to that prepared using physical activation method, and attributed to the effect of
405 porous nature of chemically-activated activated carbon on adsorption.

406 **Sand Filtration.** Removal of organic compounds by sand filtration depends on its
407 hydrophilic or hydrophobic characteristics (or octanol-water partition coefficient). For example,
408 Nakada *et al.* (2007) observed lower removal (<50%) for hydrophilic compounds, such as
409 carbamazepine, sulfapyridine, sulfamethoxazole, and estriol after sand filtration compared to
410 hydrophobic compounds, such as ibuprofen, which were removed more than 80% in some cases.
411 During monitoring of a DWTP, Stackelberg *et al.* (2007) observed complete removal of
412 erythromycin, and carbamazepine (~97% removal) during sand/GAC filtration, employed
413 between primary and secondary chlorine disinfection. Ternes *et al.* (2002) also observed similar
414 observations of removal of pharmaceuticals from drinking water in a full-scale DWTP and

415 reported more than 95% removal of diclofenac and bezafibrate, 75% removal of carbamazepine,
416 and 20% removal of clofibrac acid compounds. Not all compounds have been observed to be
417 removed completely by filtration. During the study of removal of pharmaceuticals and
418 pharmaceuticals-like compounds, such as caffeine (1µg/L), trovafloxacin (38 µg/L), 17β-
419 estradiol (1µg/L), and salicylic acid (3 µg/L) from water, Bundy *et al.* (2007) observed dual-
420 step filtration (consists of anthracite and sand) to provide 0.62 to 7.7% removal of caffeine and
421 estradiol compounds and 3.3 to 27.1% removal of trovafloxacin compounds from water. The
422 filtration step was observed to be more effective than other treatment steps in partially removing
423 some of the compounds studied from water. It appears that sand filtration has a capability of
424 removing these compounds from water, which depends on surface chemical characteristics of
425 organic compounds in water, solution pH, and types and concentrations of co-solutes, however,
426 the treated water requires further treatment to remove low concentrations of different organic
427 compounds in the treated water.

428 **Membrane Filtration.** Removal of organic compounds by membrane filtration, similar
429 to sand filtration, also depends on its hydrophilic or hydrophobic nature (or octanol-water
430 partition coefficient), surface characteristics (i.e., pH_{ZPC}), and particle size, and surface
431 characteristics of membrane filters (Yoon *et al.*, 2006; Snyder *et al.*, 2006; Verliefe *et al.*,
432 2007). Depending on filtration type, such as nanofiltration (NF) or ultrafiltration (UF), removal
433 effectiveness of a membrane filtration step for treating water varies (Yoon *et al.*, 2006). Yoon *et*
434 *al.*, (2006) observed that NF membranes retained pharmaceuticals based on its hydrophobic
435 nature and particle size, whereas UF membranes retained pharmaceuticals mainly based on their
436 hydrophobic nature alone. During a study of removal of 20 pharmaceuticals from surface water
437 by a bench-scale nanofiltration (NF) membrane (1500 L/h feed flow, 10% recovery) and by a NF
438 membrane with subsequent GAC column (80% recovery), Verliefe *et al.* (2007) observed
439 rejection values (i.e., removal from water) to be lower for positively charged pharmaceuticals
440 compared to negatively charged pharmaceuticals, for which higher rejection values were
441 observed. Neutral compounds exhibited intermediate removal, likely due to negatively charged
442 membrane surface, or hydrophobic nature of neutral compounds (Verliefe *et al.*, 2007).
443 Addition of a GAC adsorber after nanofiltration step was observed to improve overall removal of
444 these compounds from drinking water.

445 Performance effectiveness of membrane filtration also depends on extent of fouling on
446 membrane filters (or pressure drop across the membrane). Snyder *et al.* (2006) observed very
447 less rejection of pharmaceuticals from feed water by a partially fouled UF membrane.
448 Compounds that were well-removed included steroid hormones, such as estradiol, estrone,
449 ethinylestradiol, and progesterone. During a pilot-study of removal of pharmaceuticals using a
450 reverse osmosis (RO) system, Snyder *et al.* (2006) found that all pharmaceuticals, spiked into
451 feed water, were well-rejected by both virgin and fouled membranes. Similarly, Adams *et al.*
452 (2002) also observed more than 90% rejection rate for antibiotics using a cellulose acetate-based
453 membrane and suggested this to be a viable unit processes for removal of PPCPs from water.
454 However, retentate water, consists of high concentrations of organic compounds, require further
455 treatment prior to being discharged in environment.

456
457 *c. Disinfection*

458 Disinfection processes, generally used for reducing microbial concentrations in drinking
459 water, have also been reported to degrade organic compounds, including some of the PPCPs and
460 EDCs. Chlorination and ozonation have been extensively used in improving drinking water

461 quality microbiologically. Different oxidants react differently with organic compounds, such as
462 NOM, and PPCPs and EDCs and reduce their concentrations or transform them into other
463 byproducts (Adams *et al.*, 2002; Ternes *et al.*, 2002; Westerhoff *et al.*, 2005; Kumar *et al.*, 2006;
464 Saroj *et al.*, 2005a & 2005b). The extent and rate of reaction of PPCPs and EDCs primarily
465 depends on solution characteristics (pH, co-solutes), chemical's characteristics (aromatic content,
466 octanol-water partition coefficient), and oxidant type, dosage, and contact time (Adams *et al.*,
467 2002; Ternes *et al.*, 2002; Westerhoff *et al.*, 2005). For example, Westerhoff *et al.* (2005)
468 observed different extent and rate of reactions of chlorine with PPCPs and EDCs. They observed
469 that some compounds, such as acetaminophen, diclofenac, estradiol, estriol, estrone,
470 ethynlestradiol, naproxen, oxybenzone, sulfamethoxazole, and triclosan were highly reactive
471 with chlorine and removed in higher concentrations, whereas, some other compounds, such as
472 DEET, meprobamate, TCEP, BHC, fluorine or heptachlor epoxide were observed to be partly
473 removed. Some functional groups, such as phenol, urea, amino, primary or secondary amine
474 groups were observed to be more reactive with chlorine compared to chlorine-substituted
475 molecules or compounds with conjugated carbon bonds. Similar observations of dependence of
476 extent and rates of reactions of ozone with PPCPs and EDCs were also observed (Adams *et al.*,
477 2002; Ternes *et al.*, 2002; Westerhoff *et al.*, 2005). Ozonation was observed to be more effective
478 in reacting with organic compounds with phenolic groups or aromatic moieties, but less
479 effective for compounds with ketone, carboxyl functional groups with nonaromatic rings or
480 conjugated bonds (Adams *et al.*, 2002; Westerhoff *et al.*, 2005).

481 In addition to chlorination and ozonation processes, water utilities have started using
482 other disinfection processes, such as advanced oxidation process (i.e., H₂O₂/ozonation),
483 ultraviolet irradiation, photodegradation, and electrochemical treatment, etc. depending on their
484 performance effectiveness and drinking water quality requirements (Westerhoff *et al.*, 2005;
485 Korshin *et al.*, 2006).

486

487 **CONCLUSIONS**

488 The presence of PPCPs and EDCs in wastewater, drinking water and surface water is
489 well documented. Primary sources of these organic compounds in surface water are likely from
490 human usage and land application of animal manure. Upon partial removal of these organic
491 compounds in drinking water treatment plant, humans are exposed to low concentrations of these
492 compounds via ingestion of drinking water. Drinking water treatment consists of a train of
493 physicochemical processes, which may or may not remove or transform PPCPs and EDCs into
494 less reactive and toxic compounds. Certain combinations of processes are more effective than
495 others, and bench-scale studies indicate that many factors influence the degree at which these
496 organic compounds are transformed.

497 Analysis of performance effectiveness of different unit processes in drinking water
498 treatment plant for PPCPs and EDCs indicate that lime softening, coagulation, and sedimentation
499 processes are not effective at removing PPCPs and EDCs. Adsorptive, sand, and membrane
500 filtration processes are effective at removing some of the PPCPs and EDCs compounds, but
501 depends on compound's chemical structure and properties, and filtration media and conditions.
502 Addition of disinfection process, especially chlorination and ozonation processes are very much
503 effective in decreasing remaining concentrations of PPCPs and EDCs from water after
504 coagulation/flocculation and filtration steps at drinking water treatment plant.

505

506

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