

Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals

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Abstract

Endocrine disrupting chemicals and pharmaceuticals represent two classes of emerging contaminants that are ubiquitously present in municipal wastewater effluents. Some of these contaminants have been shown to impact aquatic organisms at trace concentrations (i.e., ng/L). Moreover, the public has expressed human health concerns regarding the presence of emerging contaminants in water reuse projects. The primary objective of this investigation was to determine the efficacy of various membranes and activated carbons for the removal of endocrine disruptors, pharmaceuticals, and personal care products. A suite of structurally diverse target compounds was selected for evaluation based largely upon occurrence and molecular structure. Several membrane types and applications were evaluated at pilot- and/or full-scale, including: microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electro dialysis reversal, membrane bioreactors, and combinations of membranes in series. Granular activated carbon was evaluated at bench-scale using rapid small scale column tests and at two full-scale utilities. Microfiltration and ultrafiltration were found to reject very few target compounds; however, some loss of steroidal type compounds was observed. Nanofiltration and reverse osmosis were capable of significant rejection of nearly all target compounds, though compounds were detectable at trace levels in permeates. Granular activated carbon was highly effective at removing all target chemicals. However, break-through curves clearly demonstrated that compounds with greater hydrophilicity breach activated carbon faster than hydrophobic compounds. In full-scale applications, the impact of regeneration was observed as activated carbon filters that received regular regeneration had minimal breakthrough of organic contaminants, while non-regenerated filters displayed no removal of target compounds. Findings confirm that membrane and carbon processes are capable of greatly reducing the

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concentrations of emerging contaminants; however, several compounds are detectable in membrane permeate and carbon effluent.

Keywords: Endocrine disruptor; Pharmaceutical; Treatment; Membrane; Reuse; GAC; Activated carbon; Reverse osmosis; Emerging contaminant

1. Introduction

Wastewater effluents contain significant amounts of organic carbon as a result of incomplete removal and formation of microbial products. A small portion of the total organic carbon consists of contaminants that are either not completely removed or were formed/added during treatment processes. While steroids and pharmaceuticals in wastewaters were first discovered in the United States in the 1960s and 1970s [1–4], the issue did not attract great interest until occurrence in wastewater was linked to impacts in fish living near outfalls [5–10]. It was immediately clear that conventional water treatment in some cases could not remove all organic constituents to levels less than the concentrations required to induce biological effects in fish.

The impacts demonstrated in fish exposed to wastewater effluents were characteristic of exposure to estrogenic compounds. Estrogenic (or anti-estrogenic) compounds are those which can mimic (or block) the effect of endogenous estrogen, and therefore represent one class of endocrine disruptors. There are three primary classes of endocrine disrupting chemicals, namely: estrogenic (or anti-estrogenic), androgenic (or anti-androgenic), and thyroidal. Interestingly, reports documenting that certain chemicals were capable of mimicking natural steroids were published as early as the 1930s [11–16]. In the past two decades, a plethora of reports has demonstrated that various pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) are ubiquitous contaminants in wastewater effluents at sub- $\mu\text{g/L}$ concentrations [17–25]. While not all PPCPs

are EDCs and vice-versa, it is clear that certain compounds fit both categories (i.e., certain oral contraceptive medications, thyroid hormones administered as medications, and estrogen replacement pharmaceuticals). A definitive list of EDCs does not exist, as most chemicals in commerce have not been tested for endocrine toxicity; however, screening programs are under development to determine the toxicological relevance of these compounds [26]. Despite sparse data on actual health risks from human exposure to trace levels of EDCs and PPCPs through water reuse, public perception likely will be a driving force in the implementation of more advanced treatment processes to further reduce the concentrations of these contaminants in water recycling projects. Additionally, continuing concerns regarding possible population-level impacts of EDCs/PPCPs in wastewater effluents also will contribute towards implementation and/or optimization of treatment processes for contaminant removal. The project described here evaluated several membrane and activated carbon processes for the removal of EDCs and PPCPs during both drinking water and reuse water treatment.

Implementation of membranes in water treatment is greatly increasing. It is well-known that low-pressure membranes are capable of removing microbial constituents without increasing disinfection by-products, thereby allowing compliance with the rules promulgated in response to the 1986 Surface Water Treatment Rule Amendments [27]. The efficacy of low-pressure membranes in removing pathogenic microorganisms including total coliform (TC) bacteria, *Giardia*, and *Cryptosporidium*, as well as viruses has been

very well demonstrated by several researchers [28,29]. Low-pressure membranes are also important as pre-treatment to tight membrane processes such as reverse osmosis (RO), nanofiltration (NF), and electrodialysis reversal (EDR) that are increasingly being utilized for softening of brackish groundwater and surface waters and removal of dissolved contaminants including trace organics for potable reuse applications [30–32]. Whether the purpose is desalination or water reuse, low-pressure membrane systems play an important role as RO pretreatment processes. Microfiltration/ultrafiltration (MF/UF) systems are strongly recommended when there are space limitations and/or variable feed water quality [27]. Recently, data have become available which demonstrate that membrane technology can be highly effective for the removal of emerging contaminants [33–38].

Activated carbon is a well-known process for removing various organic contaminants and organic carbon in general. Activated carbon is most commonly applied as a powdered feed or in a granular form in packed bed filters. Granular activated carbon (GAC) is used at many water treatment plants in the United States and Canada. The GAC can be used as a replacement for anthracite media in conventional filters, thus providing both adsorption and filtration. Alternatively, GAC can be applied post-conventional filtration as an adsorbent bed [39,40]. An estimated two thirds of all surface water treatment plants in the US and Canada have the capability to feed powdered activated carbon (PAC) intermittently. One of the more common uses of PAC is for controlling tastes and odors such as geosmin and methylisoborneol (MIB) [41]. Recently, researchers have developed tailored activated carbons for improving geosmin and MIB removal [42,43], and the work herein has appraised how this activated carbon also enhances the removal of pharmaceuticals and endocrine disrupting compounds. Several authors have demonstrated the efficiency of activated carbon, both as PAC

and GAC, for the removal of trace organic pollutants from water [44–50].

This manuscript investigates the removal of a broad range of representative EDCs and PPCPs during drinking and wastewater treatment processes at bench, pilot, and full-scale. The processes investigated used a diversity of water qualities and membrane/carbon configurations. Removal efficiencies were evaluated by simultaneously measuring the target analytes in water spiked at environmentally relevant concentrations and in actual occurrence scenarios at pilot and full-scale facilities. These data provide a comprehensive evaluation of the efficacy of a variety of viable membrane and carbon processes to reduce the concentration of these emerging contaminants in water.

2. Methods and materials

2.1. Sample collection and preservation

One-liter ultra clean, pre-silanized, amber glass sample bottles were used for sample collection. It was determined that sample preservation was required to prevent microbial degradation of several target compounds [51]. Therefore, 1 g of sodium azide was added to each sample bottle prior to sample collection. Although not an issue for most experiments shown here, if any residual disinfectant was indicated during sample planning, 50 mg of ascorbic acid was added to sample bottles prior to collection to quench residual oxidants. Samples were kept on ice during transport to the laboratory. Once received, samples were stored at 4°C until solid-phase extraction (SPE). All samples were extracted within 14 days of collection.

2.2. Reagents and chemicals

All standards and reagents used were the highest purity commercially available. Target compounds and basic physical–chemical properties are shown in Table 1. All standards were obtained

Table 1
Target EDCs and PPCPs

	Class	Method	MRL (ng/L)	MW	p <i>K</i> _a	log <i>K</i> _{ow}	S (mg/L)
Acetaminophen	Pharmaceutical	LC	1	151.2	9.4	0.46	1.4E+04
Androstenedione	Steroid	LC	1	286.4	NA	2.75	58
Atrazine	Pesticide	LC	1	215.7	1.7	2.61	35
Benzo[a]pyrene	PAH	GC	10	252.3	NA	6.13	1.6E−03
Caffeine	PCP	LC	10	194.1	10.4	−0.07	2.2E+04
Carbamazepine	Pharmaceutical	LC	1	236.3	0.37	2.45	18
DDT	Pesticide	GC	10	354.5	NA	6.91	5.5E−03
DEET	PCP	LC	1	191.3	0.67	2.18	9.9
Diazepam	Pharmaceutical	LC	1	284.7	3.4	2.82	50
Diclofenac	Pharmaceutical	LC	1	294	4.51	0.7	2.4
Dilantin	Pharmaceutical	LC	1	252.3	8.33	2.47	32
Erythromycin-H ₂ O	Antimicrobial	LC	1	734.5	8.88	3.06	1.4
Estradiol	Steroid	LC	1	272.4	10.4	4.01	3.6
Estriol	Steroid	LC	10	288.4	10.4	2.45	441
Estrone	Steroid	LC	1	270.4	10.4	3.13	30
Ethinylestradiol	Steroid	LC	1	296.4	10.4	3.67	11
Fluorene	PAH	GC	10	166.2	NA	4.18	1.7
Fluoxetine	Pharmaceutical	LC	1	309.1	8.7	4.05	60
Galaxolide	Fragrance	GC	10	258.4	NA	5.9	1.8
Gemfibrozil	Pharmaceutical	LC	10	250.3	4.42	4.77	19
Hydrocodone	Pharmaceutical	LC	1	299.4	7.32	2.16	6.9E+03
Ibuprofen	Pharmaceutical	LC	1	206.3	4.91	3.97	21
Iopromide	Pharmaceutical	LC	1	791.1	10.2	−2.05	24
Lindane	Pesticide	GC	10	290.8	NA	3.72	7.3
Meprobamate	Pharmaceutical	LC	1	218.3	10.9	0.7	4.7E+03
Metolachlor	Pesticide	GC	10	283.8	−1.34	3.13	530
Musk Ketone	Fragrance	GC	10	294.3	NA	4.3	0.46
Naproxen	Pharmaceutical	LC	1	230.3	4.15	3.18	16
Oxybenzone	PCP	LC	1	228.1	7.77	3.79	69
Pentoxifylline	Pharmaceutical	LC	1	278.3	0.97	0.29	7.7E+04
Progesterone	Steroid	LC	1	314.5	NA	3.87	8.8
Sulfamethoxazole	Antimicrobial	LC	1	253.3	5.5	0.89	610
TCEP	PCP	LC	10	285.5	NA	1.44	7.0E+03
Testosterone	Steroid	LC	1	288.4	NA	3.32	23
Triclosan	Antimicrobial	LC	1	287.5	7.9	4.76	10
Trimethoprim	Antimicrobial	LC	1	290.3	7.12	0.91	400

NA = Not applicable; MRL = Method reporting limit.

from Sigma–Aldrich (St. Louis, MO) except polycyclic aromatic hydrocarbons (PAHs) and pesticides obtained from Ultra Scientific (North Kingstown, RI); mirex, atrazine, and DEET from

Accustandard (New Haven, CT); fluoxetine and iopromide from the United States Pharmacopeia (Rockville, MD); and hydrocodone from Cerillant (Round Rock, Texas). All solvents were trace

analysis grade and were obtained from Burdick and Jackson (Muskegon, MI) except formic acid and methyl-*t*-butyl ether (MTBE) from EM Science (Gibbstown, NJ).

2.3. Analytical methodology and data reporting

Analytical methods were selected to encompass the vast diversity of compound structures. As shown in Table 1, gas chromatography and liquid chromatography, each coupled to tandem mass spectrometers (GC-MS/MS and LC-MS/MS, respectively), were utilized for all sample analyses. An ion-trap mass spectrometer was used for the GC-MS/MS system, while a linear triple-quadrupole mass spectrometer was used for all LC-MS/MS analyses. Detailed descriptions of the methods employed have been published previously [51,52]. Stable isotope internal and surrogate standards were used for each sample, and a travel blank, laboratory blank, and spike/recovery sample were processed with each batch of samples. Reporting limits are shown in Table 1. Data are presented in ng/L concentrations and/or percent removal. A few compounds were ubiquitous in blanks at trace levels; in these cases, reporting limits were raised to reduce the probability of false-positives. Overall, recoveries were quite good and variability low [51,52]. Despite low analytical variability, percent removal differences of less than 15% may be due to

analytical and experimental variability as opposed to actual removal. In several instances, calculation of percent removal produced a negative number (i.e., effluent concentrations greater than influent concentrations). Negative removals can result from analytical/experimental variability (including improper calculation of hydraulic retention time, or HRT, or improper sampling), from binding of compounds to particles in influent samples which are largely absent in effluent samples, and possibly from biological or chemical deconjugation of metabolites to regenerate the parent compound. Often a contaminant is detected in the influent but the concentration is less than the detection limit in the effluent. In these cases, the percent removal is reported as greater than the maximum calculated removal based upon the method reporting limit (MRL). For example, if the influent concentration is 2 ppb and the effluent concentration is less than the detection limit of 1 ppb, the percent removal is reported as >50%.

3. Membrane testing

All membrane evaluations were performed in dynamic flow-through pilot skids or in operational full-scale treatment plants. Table 2 summarizes the tests performed with the corresponding membrane types and source of feed water. A variety of membrane types and configurations were used; therefore, each experiment will

Table 2
Membrane and carbon experiments

Membrane type	Manufacturer	Feed water	Spiked
MBR	US Filter	Primary effluent	No
MBR/RO	Zenon/Saehan	Primary effluent	No
MBR/RO	Osmonics/Saehan	Raw wastewater	No
MF/RO	US Filter/Hydranautics	Tertiary effluent	No
MF/RO	US Filter/Hydranautics	Secondary effluent	No
MF/RO/EDR	US Filter/Dow/Aquamite	Tertiary effluent	No
RO	Koch	Saline groundwater	Yes
UF	Ionics	Secondary effluent	Yes
UF/RO	Zenon/Saehan	Tertiary effluent	No

be described individually with corresponding results provided. Likewise, each plant handled unique water qualities, which are provided where available.

3.1. Ultrafiltration using secondary wastewater effluent

An Ionics™ ultrafiltration (UF) pressure-vessel skid using secondary effluent from a municipal wastewater treatment plant (WWTP) was evaluated for EDC/PPCP removal. This system used a single 8-inch vessel containing two Norit membrane cassettes. This system had been in service for several weeks, so the membranes were partially fouled. This skid was fed from an 1100-L head tank, which was spiked with the target analytes then filled and mixed with secondary effluent for a final concentration of approximately 100 ng/L for each analyte. Resulting concentrations in the feed water vary, and several are greater than the nominal dose due to occurrence of the analyte in the secondary effluent (Table 3). After the head tank was fully homogenized, water was passed through the UF membranes until a minimum of three complete vessel volumes had been voided. Three samples of the membrane influent were collected from a tap located just prior to the pressure vessel. Finally, three membrane effluent samples were collected from a tap located in the permeate stream. As shown in Table 3, the vast majority of compounds were not rejected by this UF system. While no obvious trends were observed to explain why some compounds were significantly removed, it is interesting that steroids were well-removed. This may be a function of their relatively lower water solubility; however, other compounds did not follow this pattern.

3.2. Membrane bioreactor using primary WWTP effluent

A membrane bioreactor (MBR) system, US Filter Jet Tech, was tested at pilot scale using

Table 3
Results of ultrafiltration pilot testing (ng/L)

Analyte	Ave. INF	Ave. EFF
Acetaminophen	18	17
Androstenedione	77	22
Atrazine	61	52
Benzo[a]pyrene	87	<10
Caffeine	85	79
Carbamazepine	191	161
DDT	67	<10
DEET	249	228
Diazepam	58	9
Diclofenac	38	37
Dilantin	130	98
Erythromycin-H ₂ O	289	245
Estradiol	87	<1
Estriol	108	64
Estrone	98	9
Ethinylestradiol	78	<1
Fluorene	38	<10
Fluoxetine	45	14
Galaxolide	1601	1718
Gemfibrozil	82	89
Hydrocodone	105	90
Ibuprofen	39	36
Iopromide	75	79
Lindane	68	<10
Meprobamate	561	529
Metolachlor	108	47
Musk ketone	147	93
Naproxen	24	21
Oxybenzone	32	5
Pentoxifylline	49	44
Progesterone	64	<1
Sulfamethoxazole	66	63
TCEP	169	156
Testosterone	81	23
Triclosan	32	4
Trimethoprim	138	113

INF = influent; EFF = effluent.

primary effluent as the feed water. No spiking was performed for this experiment; therefore, compounds shown are limited to those detectable in the primary effluent samples that were

collected. Additionally, no GC-MS/MS analyses were performed for this experiment. The pilot used a 3-mm pre-screen, influent holding tank, pumps, a membrane tank, and a backwash tank. The system was also equipped with a self-priming pump used to pump mixed liquor from the full-scale plant aeration basin to the membrane pilot unit. The membranes, under a light suction, filtered a portion of the mixed liquor from the membrane tank with the remaining mixed liquor overflowed back to the feed tank. This operation resulted in a cross-flow velocity across the membrane surface to prevent fouling. Four membrane modules were submerged in the membrane tank. Each membrane module was comprised of hollow fibers with a nominal pore size of 0.2 μm . Technical information on the membranes is provided in Table 4. During operation, air and mixed liquor were continuously pumped into the membrane tank to scrub and shake the membrane fibers. Samples were collected from the WWTP influent,

MBR influent (essentially primary effluent), and MBR effluent. The MBR effluent sample was collected after the calculated HRT from the time the influent sample was collected. Smaller sample volumes were processed for this experiment, since raw wastewater analysis was desired and dilution of sample extracts was expected. Therefore, reporting limits are greater than in other experiments. For this reason, fewer of the target analytes were detectable, and those compounds that were not detected in any sample are not reported. The results of this MBR experiment are shown in Table 5. These data show that some compounds are well-removed by the MBR while others are not. In some cases, particularly meprobamate, concentrations appear to increase through the MBR. While this phenomenon has been mentioned previously, it is important to note that this has been documented on several occasions (see following sections).

Table 4
Membrane specifications for MBR pilot

	Units	Value
Manufacturer		US Filter
Element size (L \times D)	mm	1850 \times 100
Membrane area/Module	m ²	9.2
Number of fibers		\approx 2000
Inside fiber diameter	mm	0.65
Outside fiber diameter	mm	1
Length of fiber	m	1.5
Flow direction		Outside-in
Nominal pore size	μm	0.08
Absolute pore size	μm	0.2
Membrane material		PV dF
Surface characteristic		Hydrophilic
Membrane charge		Neutral
Design flux	gfd	14.4
Designed pH range	pH	2–11
Vacuum pressure	kPa	50
Oxidant tolerance	ppm h/yr	100,000

Table 5
Removal of target compounds by a pilot MBR (ng/L)

Analyte	WWTP INF	MBR INF	MBR EFF
Acetaminophen	172,000	<10	<10
Androstenedione	150	<10	<10
Caffeine	72,200	68	<10
Carbamazepine	189	281	<10
DEET	150	213	171
Diclofenac	<100	16	<10
Dilantin	210	192	184
Erythromycin-H ₂ O	1050	800	34
Fluoxetine	<100	44	<10
Gemfibrozil	2210	74	<10
Hydrocodone	118	168	<10
Ibuprofen	12,000	27	43
Meprobamate	966	652	1340
Naproxen	12,500	70	<10
Oxybenzone	3810	<10	<10
Sulfamethoxazole	1110	23	<10
Triclosan	1280	17	<10
Trimethoprim	693	42	<10

3.3. Reverse osmosis with virgin and fouled membranes using saline groundwater

Removal of EDCs and PPCPs using reverse osmosis and a saline groundwater feed was evaluated. This pilot system was evaluated with both virgin and fouled membranes. Feedwater was pumped from the equalization basin by a low-pressure pump and dosed with antiscalant ahead of a static mixer. Initial testing for EDC and pharmaceutical target compounds indicated that only one or two compounds were detectable in the saline groundwater. Therefore, the equalization basin was used as a head tank where a limited number of target contaminants (based on mass available) were spiked and thoroughly mixed before pumping the spiked water through the RO system. After the static mixer, the feedwater was filtered through two 5- μm cartridge filters to protect the membranes from damage by debris. After filtration, the feed pressure was boosted by the high-pressure pump for delivery to the first stage of the RO skid. RO permeate was discharged to a permeate holding tank and used for membrane cleaning and flushing procedures. During normal operation, permeate was discharged to the permeate tank continually. A constant level was maintained in the permeate tank by an overflow orifice, and overflow permeate was discharged by gravity flow to a reject tank.

The pilot skid contained two stages of pressure vessels in a 2:2:1:1 array. Each vessel contained three 4-inch diameter, 40-inch long RO elements. The elements were Koch model TFC-HR thin film composite (TFC) polyamide elements. The first stage included the first two pairs of pressure vessels in series and the second stage comprised the last two vessels in series. Flux and recovery were controlled automatically by the operator from a central control panel.

Results from the spiking study using virgin membranes and fouled membranes are shown in Tables 6 and 7. From these data, it appears that all

Table 6
RO treatment using virgin membranes (ng/L)

	Feed tank	Post antiscalant	Brine recycle	Final permeate
Androstenedione	284	306	315	<25
Caffeine	311	324	344	52
Diclofenac	26	32	31	<25
Dilantin	259	275	287	<25
Estradiol	125	66	57	<25
Estriol	128	78	58	<25
Estrone	167	57	78	<25
Ethinylestradiol	125	65	58	<25
Fluoxetine	263	284	499	<25
Gemfibrozil	230	211	218	<25
Ibuprofen	259	244	251	<25
Iopromide	165	170	158	<25
Naproxen	118	129	119	<25
Oxybenzone	218	176	192	<25
Pentoxifylline	458	483	471	45
Progesterone	285	324	312	<25
Triclosan	246	185	180	<25
Trimethoprim	265	294	268	<25

Table 7
RO treatment using fouled membranes (ng/L)

	Feed tank	Post antiscalant	Brine recycle	Final permeate
Androstenedione	247	250	243	<25
Caffeine	196	193	219	<25
Dilantin	239	242	225	<25
Estradiol	27	<25	<25	<25
Estrone	83	<25	<25	<25
Ethinylestradiol	51	<25	<25	<25
Fluoxetine	564	441	451	<25
Gemfibrozil	234	234	221	<25
Ibuprofen	302	275	284	<25
Iopromide	125	115	133	72
Naproxen	91	73	77	<25
Oxybenzone	221	34	<25	<25
Pentoxifylline	169	154	160	<25
Progesterone	250	251	250	<25
Triclosan	166	105	90	<25
Trimethoprim	278	309	371	<25

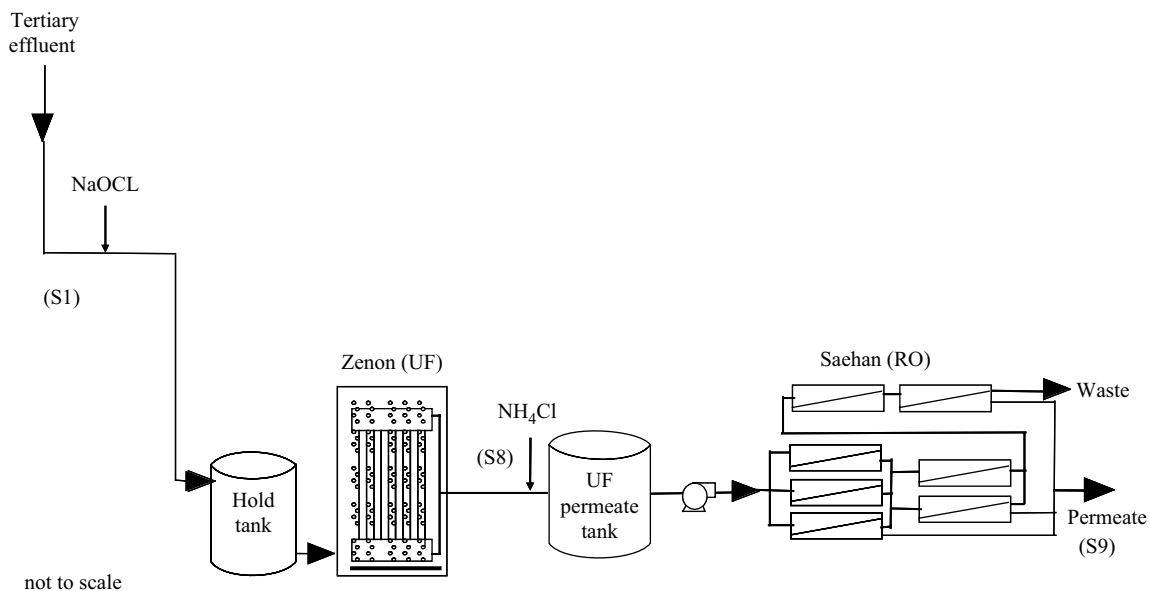


Fig. 1. Process flow diagram for UF/RO pilot.

target analytes were well-rejected and that membrane fouling had a minimal effect on removal. Interestingly, the antiscalant appeared to remove a significant portion of the phenolic steroids (i.e., estradiol, estrone, ethinylestradiol).

3.4. Ultrafiltration followed by reverse osmosis using secondary wastewater

A pilot system consisting of a submerged UF unit followed by a multi-pass RO unit was evaluated using secondary effluent feed water without spiking. A Zenon ZeeWeed™ 1000 (ZW1000) UF pilot system was used during the study to provide pretreatment to downstream Sachan RO membranes. A process flow diagram of this pilot system is provided in Fig. 1. Specifications for the ZW1000 membrane are provided in Table 8. Operational parameters for the UF/RO skid are provided in Table 9 while general water quality data are provided in Table 10. A multi-stage RO pilot system was used during this study. The system was configured as a 2-1 array. Stage 1 consisted of four pressure vessels

arranged as two parallel 1-1 arrays. Stage 2 contained two single vessels arranged in series. Each vessel houses 3 RO elements with nominal dimensions of 4" × 40". The stages were arranged in series, to allow concentrate from Stage 1 to serve as feed water for Stage 2. Samples were collected of the secondary effluent, UF effluent, RO permeate, and the RO retentate. Results of contaminant removal using this pilot are shown in Table 11. In general, UF had little effect on target compounds while RO removed nearly all target analytes to below or very near the MRLs.

3.5. Membrane bioreactor followed by reverse osmosis pilot

The ability of a pilot scale MBR followed by RO to reduce EDC/PPCP concentrations was evaluated at two WWTPs. Table 12 summarizes the influent source water and pilot equipment installed at each participating location. The advanced primary treatment at full scale Facility #1 consisted of influent screening, grit removal,

Table 8
UF membrane properties from UF/RO pilot

Parameter	Unit	Value
Manufacturer		Zenon Environmental
Element size	m	0.68 × 0.62 × 0.10
Membrane area	m ²	32.5
Number of fibers per element		30,000
Number of elements		3
Inside diameter of fiber	mm	0.35
Outside diameter of fiber	mm	0.6
Length of fiber	m	0.6
Flow direction		Outside-in
Nominal molecular weight cutoff	Daltons	100,000
Nominal membrane pore size	Micron	0.02
Absolute membrane pore size	Micron	0.1
Membrane material/construction		PVDF
Membrane surface characteristics		Hydrophilic
Membrane charge		Non-ionic
Design operating pressure	psi	1.0–10.0
Design flux	gfd	5–50
Range of pH		2–9.5
Maximum permissible turbidity	NTU	>2000
Chlorine/oxidant tolerance	ppm	>2000

chemical coagulation, flocculation, and sedimentation. The MBR samples were obtained for the following range of MBR operating conditions: flux range of 15–22 gfd; HRT of 2–6 h and MLSS range of 4,000–13,000 mg/L. Two sampling events were conducted at Facility #2, while samples were only collected once at Facility #1. The Osmonics and Saehan RO membranes are both made of polyamide thin-film composite material with similar spiral wound configurations as shown in the specifications provided in

Table 9
UF/RO pilot operational parameters

Process	Operating parameters
Ultrafiltration	Flux = 35 gfd @ 20°C Transmembrane pressure = 1–10 psi Backwash frequency = 30 min Backwash pressure = 90 psi (Air) Flow direction = direct flow
Reverse osmosis	Flux = 12 gfd @ 25°C Recovery = 85% Feed pH = 7–8 Antiscalant dose = 2 mg/L

Table 13. The RO systems were operated in a 2-1 array at a flux range of 10–12 gfd and a 75% feed water recovery rate. Samples were collected from the MBR influent, MBR effluent, and RO permeate. Tables 14 and 15 present the results of these MBR/RO investigations. The data show that while the MBR is effective for reducing the concentration of many EDC/PPCPs, several compounds are unaffected and very few compounds are reduced to below the MRL. The removal is likely related to biodegradability of

Table 10
Water quality data from UF/RO pilot

Parameter	Unit	Tertiary	UF EFF	RO EFF
Aluminum	µg/L	16.4	13.3	ND
Alkalinity	mg/L	146	147	9.01
Arsenic	µg/L	2.03	1.93	ND
Boron	µg/L	365	353	283
Chloride	mg/L	268	276	7.93
Conductivity	µmh/cm	2420	2550	0.91
Hardness	mg/L	352	356	4.4
Manganese	µg/L	119	115	ND
Silica	mg/L	18.4	18.2	0.714
Sulfate	mg/L	233	234	0.769
TOC	mg/L	8.13	7.8	ND
TDS	mg/L	934	1020	77
Turbidity	NTU	–	0.25	0.1

Table 11
EDC/PPCP removal by UF/RO pilot (ng/L)

	Secondary EFF	UF EFF	RO permeate	Retentate
Acetaminophen	<20	<10	<1.0	16
Caffeine	<20	14	<10	298
Carbamazepine	110	147	<1.0	278
DEET	104	103	<1.0	293
Diclofenac	<20	37	<1.0	59
Dilantin	126	191	<1.0	416
Erythromycin-H ₂ O	336	357	<1.0	940
Estrone	35	<10	<1.0	78
Fluoxetine	<20	<10	<1.0	17
Galaxolide	968	816	<10.0	2180
Gemfibrozil	100	142	<1.0	329
Hydrocodone	87	89	<1.0	215
Iopromide	<20	58	1.1	89
Meprobamate	693	715	<1.0	1610
Musk ketone	97	106	<10.0	329
Naproxen	<20	17	<1.0	33
Oxybenzone	48	26	<1.0	20
Sulfamethoxazole	90	56	1.2	121
TCEP	189	219	<10	426
Triclosan	29	<10	<1.0	14
Trimethoprim	186	158	<1.0	403

Table 12
Source water and pilot facilities for MBR/RO

	Facility 1	Facility 2
Source water	Advanced primary	Raw wastewater
MBR system	Mitsubishi Sterapore HF	Zenon ZW 500C
RO system	Saehan 4040 FL	Osmonics AK4040
	Dual stage operated at a 75% feed water recovery rate	Dual stage operated at a 75% feed water recovery rate

the individual compound. For instance, in each experiment naproxen, acetaminophen, ibuprofen, and caffeine experienced significant removal through the MBR. These compounds were previously shown to be rapidly biodegraded [53]. While individual differences were observed for removal efficiency between the two MBR systems evaluated, the two sampling events at

Facility #2 demonstrate that influent and effluent concentrations can be quite variable.

3.6. Microfiltration followed by reverse osmosis and electro dialysis reversal

Treatment trains consisting of microfiltration (MF) followed by RO and electro dialysis

reversal (EDR) were evaluated at pilot scale using unspiked tertiary treated wastewater. This wastewater is characterized by relatively high levels of total dissolved solids, hardness and alkalinity, with moderate levels of organic material and low turbidity. Table 16 presents typical feed water quality at the pilot site. Microfiltration was accomplished using a submerged hollow fiber membrane skid provided by US Filter (Memcor CMF-S 16S10T). Reverse osmosis trial equipment consisted of a modified US Filter “H” series RO skid (model number ROSLH 3180). This pilot system was capable of using

Table 13
RO membrane characteristics

	Osmonics	Saehan
Model	AK4040	RE 4040-FRM
Material	Polyamide-TFC	Polyamide-TFC
Operating pH range	4–11	3–11
Maximum turbidity	1 NTU	<1 NTU
Maximum pressure	600 psi	600 psi
Nominal surface area	85 ft ²	85 ft ²
Configuration	Spiral wound	Spiral wound
Element length	40.0 inches	40.0 inches
Element diameter	4.0 inches	4.0 inches

Table 14
Results of MBR/RO — Facility #1 (ng/L)

	WWTP INF	Primary EFF	MBR A EFF	MBR B EFF	RO Feed	RO Permeate
Acetaminophen	21,950	4095	<1.0	<1.0	11.4	<1.0
Androstenedione	<100	60	<1.0	<1.0	<1.0	<1.0
Atrazine	<100	<1.0	<1.0	<1.0	<1.0	<1.0
Caffeine	58,550	6775	<10	<10	16.5	<10
Carbamazepine	299	138	205	171	181	<1.0
DEET	690	168	37	46	45	2.3
Diazepam	<100	1.1	2.8	2.4	2.6	<1.0
Diclofenac	<100	5.6	15	17	1.1	<1.0
Dilantin	143	21	72	67	72	<1.0
Erythromycin-H ₂ O	479	9.4	96	54	42	<1.0
Estradiol	<100	<1.0	<1.0	<1.0	<1.0	<1.0
Estriol	226	67	<1.0	<1.0	<1.0	<1.0
Estrone	<100	36	8.5	<1.0	6	<1.0
Ethinylestradiol	<100	<1.0	<1.0	<1.0	<1.0	<1.0
Fluoxetine	<100	4.4	4.8	9.8	6.9	<1.0
Gemfibrozil	<100	331	36	270	<1.0	<1.0
Hydrocodone	<100	32	46	39	44.5	<1.0
Ibuprofen	70,350	641	4	5.3	8.9	<1.0
Iopromide	<100	<1.0	4.1	3.5	2.6	<1.0
Meprobamate	520	92	236	216	238	1.3
Naproxen	21,000	599	26	1.3	<1.0	<1.0
Oxybenzone	896	181	3.1	9.4	4.9	<1.0
Pentoxifylline	<100	6.9	<1.0	<1.0	<1.0	<1.0
Progesterone	<100	22	<1.0	<1.0	<1.0	<1.0
Sulfamethoxazole	234	103	265	33	15.5	<1.0
TCEP	464	151	186	171	186	6.5
Testosterone	<100	23	<1.0	<1.0	<1.0	<1.0
Triclosan	4030	176	7.6	11	6.9	<1.0
Trimethoprim	699	144	15	7.4	<1.0	<1.0

Table 15
Results of two MBR/RO sampling events — Facility #2 (ng/L)

	Event-1			Event-2		
	MBR INF	MBR EFF	RO EFF	MBR INF	MBR EFF	RO EFF
Acetaminophen	199	<5.0	<1.0	392	<10	<1.0
Androstenedione	30	<5.0	<1.0	25	2.6	<1.0
Caffeine	2270	223	<10	7140	1650	<10
Carbamazepine	243	199	<1.0	367	410	<1.0
DEET	74	16	<1.0	365	20	<1.0
Diclofenac	28	32	<1.0	32	38	<1.0
Dilantin	236	206	<1.0	259	310	<1.0
Erythromycin-H ₂ O	34	50	<1.0	50	90	<1.0
Estradiol	8.1	<5.0	<1.0	17	<1.0	<1.0
Estrone	72	13	<1.0	70	21	<1.0
Ethinylestradiol	<5.0	<5.0	<1.0	32	<1.0	<1.0
Fluoxetine	15	9.0	<1.0	17	23	<1.0
Gemfibrozil	660	357	<1.0	701	698	<1.0
Hydrocodone	76	54	<1.0	81	85	<1.0
Ibuprofen	1980	33	<1.0	1990	169	<1.0
Iopromide	233	186	<1.0	564	1230	<1.0
Meprobamate	251	205	<1.0	309	339	<1.0
Naproxen	1710	66	<1.0	2660	467	<1.0
Oxybenzone	37	5.7	<1.0	50	16	<1.0
Progesterone	<5.0	<5.0	<1.0	6.4	<1.0	<1.0
Sulfamethoxazole	883	667	<1.0	1490	1800	<1.0
TCEP	218	180	<10	291	334	30
Triclosan	44	17	<1.0	50	33	<1.0
Trimethoprim	92	101	<1.0	199	250	<1.0

up to 12 vessels, but for the purposes of this study, 3 vessels were used. Each vessel housed four RO membrane elements placed in series in each of the three pressure vessels in a two-stage 2:1 array configuration with a feed water recovery of 50–75 percent at a 10–15 gpm permeate flow. The membrane elements were Dow Filmtec brackish water membranes (part number BW30-4040). Membrane pretreated water was continuously fed to the RO pilot system at a flow rate of approximately 20 gpm. Sodium bisulfite and antiscalant were added to the MF pretreated water to control RO membrane fouling and to protect the membrane elements from chemical damage due to free chlorine or chloramines. The

EDR equipment consisted of an Aquamite V with a bipolar membrane stack. The capacity of the Aquamite V is 15,000–35,000 gpd. The maximum feed flow for this unit was 60,000 gpd. For this experiment, the EDR operated at a range of flows (22–27 gpm) to continually produce demineralized water without constant chemical addition during normal operation. Current was supplied at 2–4 amps depending on the specific water quality goals to be achieved. Membrane fouling and scaling was controlled by using electrical polarity reversal every 15 min. Typically, EDR systems are configured using multiple stages to provide the maximum membrane surface area and retention time to remove

Table 16
Water quality at MF/RO/EDR pilot site

Parameter	Unit	Value
Chloride	mg/L	188
Nitrate-N	mg/L	7.1
Sulfate	mg/L	96
Calcium	mg/L	59.1
Magnesium	mg/L	31.7
Silica	mg/L	24
Sodium	mg/L	156.0
TOC	mg/L	9
Hardness-Ca	mg/L	250
Alkalinity-Ca	mg/L	190
TDS	mg/L	720
Conductivity	μS/cm	1200
pH		7.3
Turbidity	NTU	0.7
UV-254	Abs/cm	0.109

a specified fraction of salt from the demineralized stream. Two types of staging are used: hydraulic and electrical. For this study, the Aquamite V pilot unit operated as a single stack with two electrical stages that could be independently controlled to achieve a desired water quality. Electrical staging was accomplished by inserting additional electrode pairs into the membrane stack to provide maximum salt removal rates while avoiding polarization and hydraulic pressure limitations. Samples from the WWTP raw influent, tertiary effluent, MF effluent, EDR effluent, and RO effluent were collected and analyzed. Results of EDC/PPCP removal using this system are provided in Table 17.

3.7. Full-scale microfiltration followed by reverse osmosis and UV advanced oxidation

A 10 million gallon per day (MGD) MF/RO water reuse facility equipped with a UV advanced oxidation process (AOP) was evaluated for EDC/PPCP removal. The facility is provided tertiary treated wastewater and uses a US Filter

submerged hollow fiber MF membrane system as a pretreatment for the RO process. Hydranautics ESPA 2 membranes are used for the RO process. After RO, the water is exposed to UV light in the presence of hydrogen peroxide. Feed water was not spiked and samples were collected between each unit process. Results from the MF/RO/AOP facility are provided in Table 18.

3.8. Full-scale microfiltration followed by double-pass reverse osmosis

A 37 MGD water reuse facility equipped with MF and double-pass RO was evaluated for EDC/PPCP removal. The facility is provided non-disinfected secondary treated wastewater and uses a US Filter Memcor pressure-vessel MF membrane system as a pretreatment for Hydranautics ESPA 2 RO membranes. Feed water was not spiked and samples were collected between each unit process. All samples were collected in duplicate or triplicate, so results shown are averages (Table 19). Variability in replicate measurements generally was less than 10%.

4. Activated carbon testing

Activated carbon, as both powdered activated carbon (PAC) and as granular activated carbon (GAC), was evaluated for removal of target EDCs and PPCPs in both surface and water reuse applications. Table 20 shows the various experiments performed as well as carbon type utilized.

4.1. Powdered activated carbon

Detailed results from bench-scale testing of PAC in natural waters was published previously [54]. Briefly, two commercially available activated carbons were evaluated, namely AC800 (Acticarb, Dunnellon, FL, USA) and WPM (Calgon Carbon

Table 17
Results from MF/RO and MF/EDR testing (ng/L)

	Raw INF	Tert. EFF	MF EFF	EDR EFF	RO EFF
Acetaminophen	14,200	2.5	2.4	3.4	<1.0
Androstenedione	52	5.8	5.2	5.2	<1.0
Caffeine	32,500	<10	<10	<10	<10
Carbamazepine	78	19	17	18	<1.0
DEET	154	122	100	112	4.2
Dilantin	51	52	31	47	<1.0
Erythromycin-H ₂ O	79	<1.0	<1.0	<1.0	<1.0
Estradiol	33	<1.0	<1.0	<1.0	<1.0
Estriol	137	<5.0	<5.0	<5.0	<5.0
Estrone	49	<1.0	<1.0	<1.0	<1.0
Fluoxetine	10	8.5	4.7	5.8	<1.0
Galaxolide	931	544	617	587	<10
Gemfibrozil	1220	<1.0	<1.0	<1.0	<1.0
Hydrocodone	35	<1.0	<1.0	<1.0	<1.0
Ibuprofen	2270	6.0	2.7	5.4	<1.0
Iopromide	17	42	34	51	<1.0
Meprobamate	124	75	67	71	<1.0
Musk ketone	119	65	45	45	<10
Naproxen	4480	<1.0	<1.0	<1.0	<1.0
Oxybenzone	657	5.8	4.9	3.8	<1.0
Sulfamethoxazole	360	<1.0	<1.0	<1.0	<1.0
TCEP	244	133	127	127	2.3
Testosterone	47	<1.0	<1.0	<1.0	<1.0
Triclosan	564	1.2	1.2	<1.0	<1.0
Trimethoprim	213	<1.0	<1.0	<1.0	<1.0

Corp., Pittsburgh, PA, USA). These PACs were chosen because they were shown to have different capabilities for removing certain EDCs [48]. PAC was hydrated for 24-h in purified laboratory water prior to use and added to the samples as a slurry. Experiments were performed in a six-place jar tester using 2-L glass beakers filled with 1.5-L of source water. The doses and contact times were based on full-scale treatment plants that frequently use PAC. Therefore, a contact time of 4 h followed by 1 h of settling and PAC doses of 1, 5, and 50 mg/L were evaluated. Supernatant was collected and filtered (ashed Whatman GF/F) to remove residual PAC. Four natural waters were spiked to achieve nominal

concentrations of 100 ng/L for target EDC/PPCPs. Fig. 2 shows the average results from the 4 spiked natural waters using a 5 mg/L WPM PAC dose.

PAC was also evaluated at pilot-scale using a dynamic spike and flow-through conditions. A positive-displacement diaphragm pump was used to introduce the target compounds into the process stream. A static mixer followed the injection to assure adequate mixing. Coagulant chemicals were injected upstream of a second static mixer before entering the flocculation basin. Norit Hydrodarco B, which is produced by steam-activation of lignite based coal, was used for all pilot experiments. The PAC slurry

Table 18
Results from full-scale MF/RO/AOP plant (ng/L)

	MF INF	MF EFF	RO EFF	UV AOP EFF
Caffeine	1037	994	<10	<10
Carbamazepine	258	237	<1.0	<1.0
DEET	3167	2430	4.4	2.2
Diclofenac	49	59	<1.0	<1.0
Dilantin	175	180	<1.0	<1.0
Erythromycin-H ₂ O	191	181	<1.0	<1.0
Estradiol	11	14	<1.0	<1.0
Estrone	137	158	<1.0	<1.0
Galaxolide	1130	1084	11	<10
Gemfibrozil	2740	3750	2.4	1.1
Hydrocodone	54	51	<1.0	<1.0
Ibuprofen	379	500	<1.0	<1.0
Iopromide	127	131	<1.0	<1.0
Meprobamate	308	260	<1.0	<1.0
Musk ketone	61	68	<10	<10
Naproxen	516	621	1.2	<1.0
Oxybenzone	121	77	6.1	2.1
Pentoxifylline	39	33	<1.0	<1.0
Sulfamethoxazole	1050	1030	1.9	<1.0
TCEP	407	370	7.4	2.6
Triclosan	136	64	<1.0	<1.0
Trimethoprim	248	227	<1.0	<1.0

was fed at the flocculation basin influent at concentrations of both 5 and 35 mg/L. Samples for analysis were collected from the spiked raw water and after 5 h of PAC contact time. Results are presented in Fig. 3. These results show a clear dose-response relationship. Various contact times were also investigated, with greater contact times leading to significantly greater removal (data not shown).

4.2. Granular activated carbon adsorption

Bench-scale testing was conducted using rapid small-scale column tests (RSSCTs) to predict GAC performance. Tests compared two lignite-based GACs manufactured by NORIT Americas: HYDRODARCO 4000 (HD4000) and Superdarco (SUPER). The Superdarco has been adapted to have considerably more micropore and mesopore volume than the HYDRODARCO;

and it also hosts a more stable surface that will not become oxygenated and acidified to the extent as HYDRODARCO and other commercial carbons. The Superdarco has been manufactured at full-scale in Marshall, Texas, to adapt key features of the tailored activated carbons that have been developed in bench-scale research at Penn State University [42,43].

The RSSCTs simulated a full-scale activated carbon bed that operates at a 7.6 min empty bed contact time (EBCT), per constant diffusivity similitude, where the EBCT is proportional to the square of the adsorbent particle diameter. Surface water from a full-scale drinking water utility with an influent total organic carbon (TOC) of 3 mg/L was used for these experiments. The 29 target compounds were spiked concurrently into this surface water to achieve a mixture containing 100–200 ng/L of each compound.

Table 19
Average results from full-scale MF double-pass RO (ng/L)

	MF INF	MF EFF	Single pass RO EFF	Double pass RO EFF
Acetaminophen	16	10	<1.0	<1.0
Caffeine	3460	6125	16	1.2
Carbamazepine	174	271	<1.0	<1.0
DEET	2020	3365	3.4	<1.0
Diclofenac	56	49	<1.0	<1.0
Dilantin	207	336	<1.0	<1.0
Erythromycin-H ₂ O	312	507	<1.0	<1.0
Estrone	85	63	<1.0	<1.0
Fluoxetine	12	23	<1.0	<1.0
Gemfibrozil	2885	3040	2.7	<1.0
Hydrocodone	62	104	<1.0	<1.0
Ibuprofen	354	422	<1.0	<1.0
Iopromide	1670	1810	2.3	<1.0
Meprobamate	230	341	<1.0	<1.0
Naproxen	1068	1205	2.0	<1.0
Oxybenzone	31	60	1.9	<1.0
Pentoxifylline	67	109	<1.0	<1.0
Sulfamethoxazole	341	805	2	<1.0
TCEP	300	467	1.9	1.3
Triclosan	620	424	<1.0	<1.0
Trimethoprim	248	409	<1.0	<1.0

Tests were conducted at 20–25°C. Table 21 contains results for these 29 compounds from both RSSCTs; and it depicts the improvement that the Superdarco carbon provides relative to the HYDRODARCO. On average, the Superdarco offered 3.3 times longer bed life to a given extent

Table 20
Activated carbon experiments

Carbon	Manufacturer	Feed water	Spiked
PAC	Calgon - WPM	Surface water	Yes
PAC	Norit - Hydrodarco B	Surface water	Yes
GAC	Norit - Hydrodarco	Surface water	Yes
GAC	Norit - Superdarco	Surface water	Yes
GAC	Calgon - Filtrasorb 400	Surface water	No
GAC	Not identified	Advanced primary	No

of breakthrough than did the HYDRODARCO. Figures 4 and 5 compare the breakthrough curves for 8 representative compounds (from the 29 spiked) when using the two carbons.

Two full-scale utilities using GAC were evaluated for EDC/PPCP occurrence and removal. Facility #1 is a surface water drinking water treatment plant that uses on-site regeneration to assure the GAC is capable of TOC removal. The GAC beds at Facility #1 are located downstream of coagulation/sedimentation and dual-media filtration. Facility #1 uses a down-flow configuration for the GAC beds. Facility #2 is a 13 MGD water reuse facility that does not regularly replace or regenerate the GAC. At Facility #2 GAC contactors are located after primary treatment and sand filtration. GAC absorbers at Facility #2 are configured as 30-ft diameter up-flow contactors. Unfortunately, neither Facility #1 nor

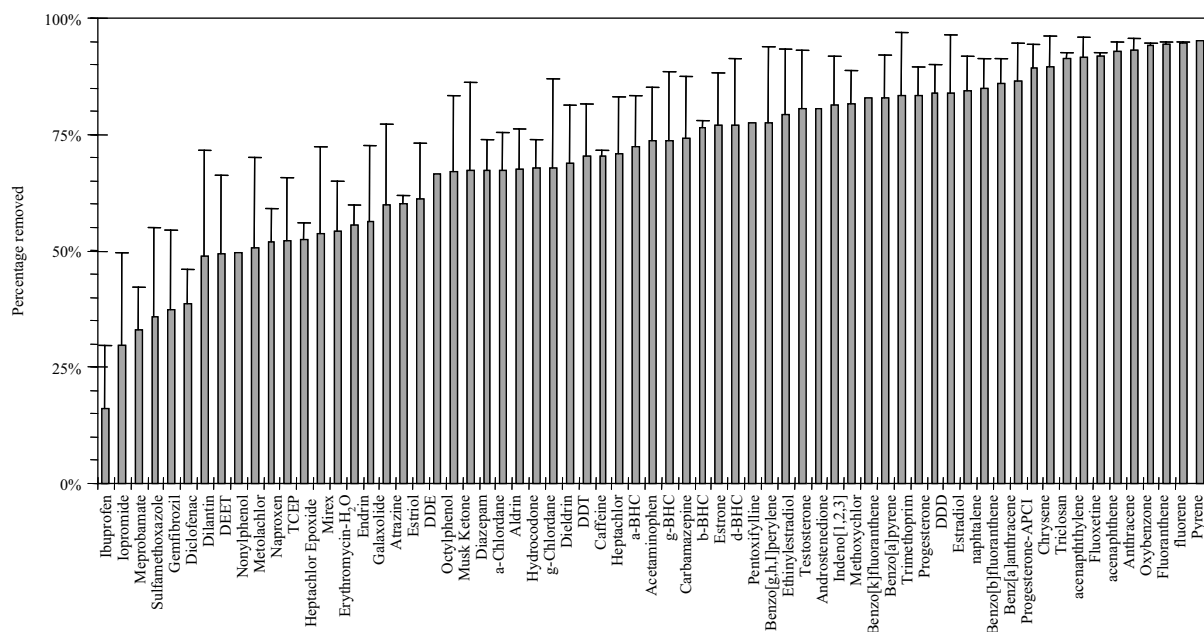


Fig. 2. Average removal of EDCs/PPCPs using 5 mg/L WPM PAC.

Facility #2 provided specifics on the manufacturer or type of GAC used in the treatment plants. Results for Facilities #1 and #2 are shown in Tables 22 and 23, respectively. These results indicate that Facility #1, which provides regular regeneration, is quite efficient for organic contaminant removal while Facility #2 shows essentially no removal of any organic contaminant.

5. Results and discussion

Membranes are an effective means to reduce the concentration of a diverse set of EDC and PPCP contaminants during both drinking water and wastewater treatment. The degree of removal is directly related to membrane characteristics, and to some extent the molecular properties of the particular contaminant. The experiments shown here demonstrate that MF and UF membranes have little value for the removal of the vast majority of organic contaminants. However, this limited data set indicates a potential for the removal of steroids using MF/UF membranes,

especially when operated as an MBR. While additional studies are needed to validate this observation at additional full-scale utilities, the removal of steroids is valuable since these compounds have been shown to induce biological effects at even minute concentrations (i.e., ng/L) [10,55–57]. In contrast, RO membranes are capable of removing nearly all compounds investigated to levels less than method reporting limits. However, trace levels of some contaminants were still detectable in RO permeates. The compounds that breached RO membranes were not consistent, and no clear relationship between molecular structure and membrane breaching could be established. Initially, it appeared that the flame-retardant TCEP and the stimulant caffeine had breached all RO membranes evaluated; however, closer examination of the data demonstrated that both of these compounds were ubiquitous in field and laboratory blanks. Therefore, the MRL for caffeine and TCEP were adjusted to approximately twice the average concentration detected in blanks. Once the MRL

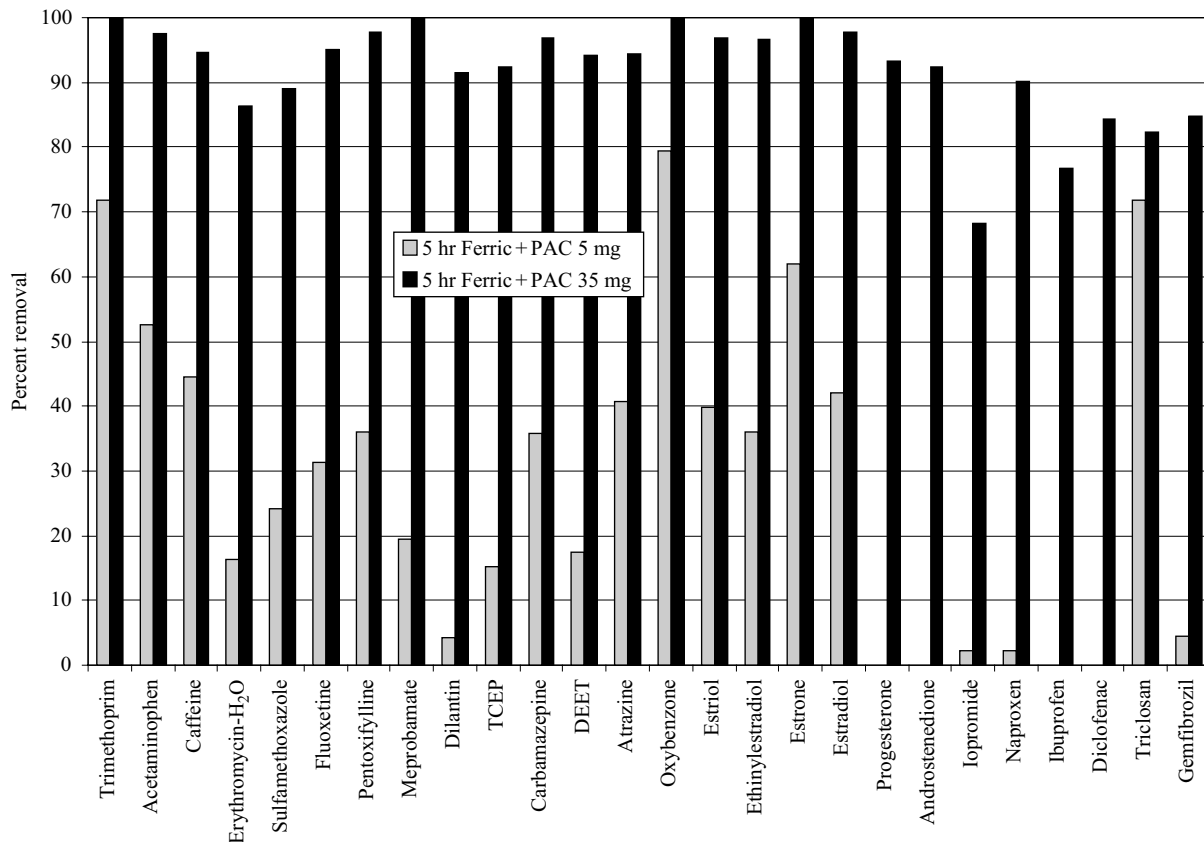


Fig. 3. Pilot-scale removal of EDC/PPCPs by PAC.

was raised to compensate for contamination, no significant break-through could be observed. Breaching of the RO membrane could be the result of diffusion into and through the membrane, short-circuiting of the membrane or support media failure (i.e., adhesive failure). The full-scale double-pass RO system showed that the second pass was able to remove compounds that were not entirely removed during the first pass. Without question, a multi-barrier approach is most successful in the removal of trace contaminants.

Activated carbon can be extremely effective for the removal of emerging contaminants. In the study described here, both PAC and GAC were capable of removing nearly all compounds evaluated by greater than 90%. However, activated

carbon efficacy is greatly reduced by the presence of natural organic matter which competes for binding sites and can block pores within the activated carbon structure. PAC offers the advantage of providing fresh carbon continuously since it is fed as a new product and is not recycled through the treatment process. Since PAC is added to the plant dynamically as a feed “chemical”, it can be used seasonally when risk of trace organics may be greater (e.g., low-flow events). The ability of PAC to remove organic contaminants depends upon PAC dose and contact time, as well as the molecular structure and behavior of the contaminant of interest. GAC also was found to be highly-effective; however, water soluble contaminants can breakthrough the GAC much more rapidly than strongly bound

Table 21
Results of RSSCT GAC tests with representative EDCs/pharmaceuticals

% Breakthrough	Bed volumes treated						Improvement factor*	Avg. influent conc. (ng/L)
	HD4000		SUPER		HD4000			
	5%	5%	10%	10%	20%	20%		
Acetaminophen	19,500	36,000	28,100	45,100	40,400	57,300	1.6	148
Androstenedione	37,200	89,600	58,000	>90,000	>55,000	>90,000	2.4	209
Atrazine	13,000	41,600	18,400	49,600	29,300	66,300	2.7	227
Caffeine	19,700	50,900	23,600	56,800	34,200	62,900	2.3	234
Carbamazepine	16,400	54,100	23,700	67,100	34,000	78,600	2.8	181
DEET	10,900	36,800	14,300	40,600	23,200	51,000	2.8	210
Diazepam	11,700	65,300	26,100	73,000	36,000	88,400	3.6	153
Diclofenac	9810	37,900	12,800	47,800	18,100	63,400	3.7	146
Dilantin	7900	32,800	11,300	38,900	17,100	54,200	3.6	170
Erythromycin-H ₂ O	18,000	141,000	32,100	>90,000	38,500	>90,000	7.8	14
Estradiol	41,900	82,800	51,200	101,000	>55,000	>90,000	2	200
Estriol	32,000	66,100	38,200	73,800	48,200	89,300	2	227
Estrone	36,900	70,900	58,000	85,200	>55,000	>90,000	1.9	228
Ethinylestradiol	31,800	69,600	44,000	83,000	65,500	107,000	1.9	209
Fluoxetine	37,700	94,300	>55,000	>90,000	>55,000	>90,000	2.5	117
Gemfibrozil	10,200	40,300	13,200	49,300	18,400	63,500	3.7	186
Hydrocodone	19,100	57,900	27,500	69,500	39,700	82,100	2.5	204
Ibuprofen	4280	28,900	6880	30,400	10,100	33,200	4.8	179
Iopromide	2290	28,600	4580	29,600	8260	31,700	7.6	215
Meprobamate	5960	28,600	8070	29,800	12,000	32,100	3.7	198
Naproxen	11,500	42,200	14,800	52,100	18,400	68,200	3.6	173
Oxybenzone	>55,000	>90,000	>55,000	>90,000	>55,000	>90,000	–	6
Pentoxifylline	18,100	59,100	26,300	70,100	36,800	84,300	2.7	177
Progesterone	>55,000	>90,000	>55,000	>90,000	>55,000	>90,000	–	179
Sulfamethoxazole	3090	28,300	6030	29,100	9370	30,700	5.8	164
TCEP	11,900	37,100	13,000	39,300	15,200	43,600	3.0	178
Testosterone	35,100	87,700	51,400	110,000	>55,000	>90,000	2.5	201
Triclosan	>55,000	93,100	>55,000	>90,000	>55,000	>90,000	–	95
Trimethoprim	23,300	65,200	31,600	72,700	47,400	87,600	2.3	199

*Improvement factor = (ratio of 5% breakthrough + ratio of 10% BT + ratio of 20% BT)/3.

hydrophobic contaminants. The data shown here also demonstrate that a steam-treated GAC has significantly greater absorption capacity as shown by the great increase in bed volumes passed prior to contaminant breakthrough. In two full-scale GAC applications evaluated, vastly different results were observed. At a drinking

water facility with on-site and regular regeneration, removal of trace organics occurring in source water was efficiently improved. In contrast, a facility with relatively high levels of TOC using GAC without regular replacement/regeneration provided very little removal. These data collectively show that activated carbon in

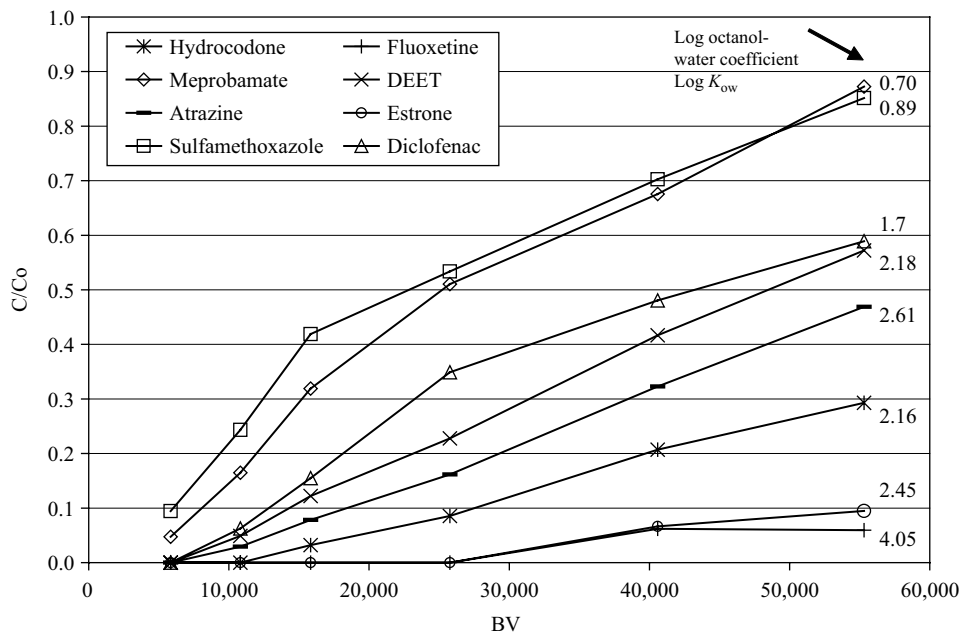


Fig. 4. Selected RSSCT results for HD4000 shown with $\text{Log } K_{ow}$.

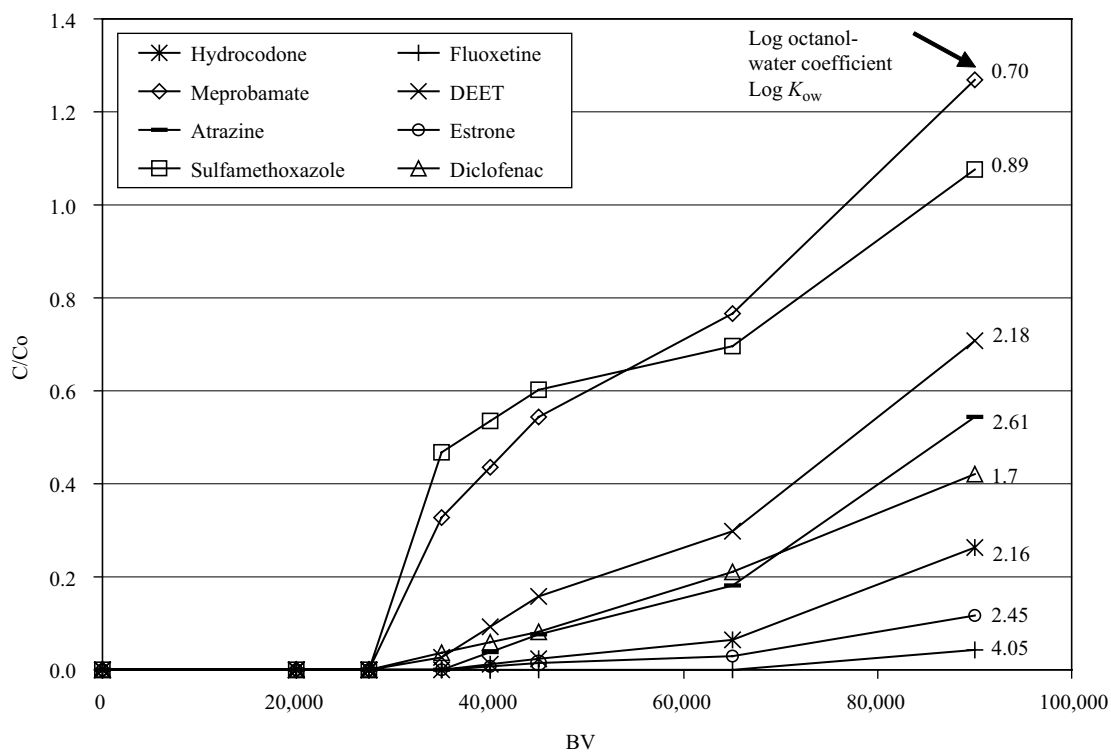


Fig. 5. Selected RSSCT results for Superdarco carbon shown with $\text{Log } K_{ow}$.

Table 22
Results of full-scale GAC testing at Facility #1 (ng/L)

	GAC INF	GAC EFF
Atrazine	650	6.1
Caffeine	17	<10.0
Carbamazepine	2.2	<1.0
DEET	1.8	<1.0
Dilantin	1.8	<1.0
Erythromycin-H ₂ O	1.8	<1.0
Gemfibrozil	1.2	<1.0
Ibuprofen	1.1	<1.0
Iopromide	3.3	<1.0
Meprobamate	1.2	<1.0
Metolachlor	122	<10
Oxybenzone	1.0	<1.0
Sulfamethoxazole	6.0	<1.0

both powdered and granular forms has great potential for the removal of trace organic contaminants; however, PAC dose and GAC regeneration/replacement will be critical for excellent removal.

While certain membrane and activated carbon processes can greatly reduce the concentrations of many trace organic contaminants, meaningful treatment goals cannot yet be deduced since toxicological relevance of these compounds has not been established. Ultimately, the application of advanced water treatment technologies will yield significant benefits for both wastewater and drinking water qualities. For instance, the use of membranes and/or activated carbon will greatly reduce the concentrations of disinfection byproduct precursors, which otherwise could form known toxic and regulated water contaminants. The removal of EDCs and PPCPs is an ancillary benefit when applying these technologies for general water quality improvement. It is also important to consider brine disposal and carbon regeneration/disposal issues associated with RO/NF membranes and GAC/PAC, respectively. While RO and tight NF membranes can remove nearly all organic and inorganic contaminants, these rejected compounds are merely concentrated

Table 23
Results of full-scale GAC testing at Facility #2 (ng/L)

	AVE GAC INF	AVE GAC EFF
Acetaminophen	10,650	47
Androstenedione	182.5	72
Atrazine	33	32
Caffeine	42,650	35,700
Carbamazepine	199	168
DEET	701	256
Diclofenac	3.2	<1.0
Dilantin	110	85
Erythromycin	139	128
Estriol	8.3	28
Gemfibrozil	3710	3405
Hydrocodone	57	<25
Ibuprofen	8760	7325
Iopromide	5.0	1.4
Meprobamate	226	196
Naproxen	3545	3320
Pentoxifylline	34	<25
Sulfamethoxazole	426	69
Testosterone	150.5	39
Triclosan	3.8	4.2
Trimethoprim	135	48

in brine streams which must be disposed of properly. The brine from an RO/NF process would be expected to have much greater toxicity than the influent water; therefore, disposal to natural waters would not achieve a net increase in safety. Likewise, used PAC must be disposed through land filling or other solids handling while spent GAC must also be disposed or regenerated. The relatively high-pressures required for NF/RO processes and the thermal regeneration of GAC require significant amounts of energy, which may lead indirectly to greater environmental risks than the presence of minute concentrations of organic contaminants. Thus careful consideration must be given to the actual costs and benefits of these processes simply for the removal of trace contaminants.

Future research efforts should focus on mechanistic evaluations of various membrane

and carbon treatment processes for contaminant removal. Additionally, animal studies are required to determine the toxicologically relevant levels of these emerging contaminants and to establish meaningful treatment goals.

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