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Evaluating occurrence of contaminants of emerging concerns in MF/RO treatment of primary effluent for water reuse – Pilot study

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ABSTRACT

This study experimented with the novel approach of using a microfiltration (MF) and reverse osmosis (RO) treatment train to treat the effluent of a primary settling tank at the Inland Empire Utility Agency in Chino, CA. The pilot used polyvinylidene fluoride hollow-fiber MF modules as pretreatment for an RO skid, which used Hydranautics ESPA2 membranes in a two-stage configuration with a feed capacity of 6 gallon per minute (gpm). In this pilot configuration, researchers monitored the removal of 38 most prevalent contaminants of emerging concerns (CECs) through the MF/RO process. To investigate how operating the RO process at two fixed recovery rates of 55% and 80% would affect the performance of the MF/RO membranes, researchers applied different fluxes (8, 10, 12 and 14 gal/d/ft^2 (gfd)) and evaluated the removal of CECs in 1-stage and 2-stage RO configurations. The occurrence of CECs in the MF influent, MF effluent, RO permeate, and RO concentrate were analyzed and studied. In the first phase (1-stage the RO process), flux of 14 gfd showed a better rejection value of inorganics (95.2%) when compared with those of other fluxes. Meanwhile, in the second phase (2-stage RO process), flux of 12 gfd showed a better rejection of inorganics (93.7%) when compared with those of other fluxes. Although concentrations of CECs slightly decreased in the RO permeate as the flux has increased, statistical analysis showed no significant differences between different fluxes in terms of CEC rejection.

Key words | contaminants of emerging concern, microfiltration, reverse osmosis, wastewater treatment, water reuse

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INTRODUCTION

The water industry is increasingly implementing recycled water projects to respond to current demands and challenges, such as water shortages, that the world faces today. To develop future water supplies that remain sustainable in dry years, water managers and their communities will heavily rely on reclamation plants and their abilities to make wastewater a viable source of potable water.

Several options exist to beneficially reuse water. Indirect potable reuse (IPR) is one method of creating high-purity product water with reduced energy inputs and economic costs (Rodriguez *et al.* 2009). In this process, municipal wastewater is treated through a conventional treatment train, including aerobic biological treatment, and processed through membrane technology, then discharged directly

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into groundwater or surface water sources, which act as an environmental buffer (Leverenz *et al.* 2011).

Another method is direct potable reuse (DPR). This process entails full advanced treatment and can directly deliver water to a potable water treatment plant's supply without any environmental buffer. With that being said, regulations on implementing DPR are still in the premature stages of development.

Today, water managers are incorporating newly developed tertiary treatment processes to their IPR or DPR treatment trains to produce higher-quality water, especially as an opportunity for water reuse. However, whatever treatment method they select, these managers still face two distinct challenges that must be addressed: (1) contaminants of emerging concerns (CECs) in wastewater, especially in the concentrate stream that is disposed of to the environment and (2) the relatively high energy consumption per volume of product water of these advanced processes.

One of the key issues related to water reuse is the occurrence of CECs (Romeyn *et al.* 2016). Some contaminants, even at low concentrations, pose a threat to public health and safety, given the potential effects of long-term exposure. Prime examples of emerging contaminants include personal care products (PCPs), endocrine disrupting compounds, and pharmaceuticals; in particular, an expanding list of pharmaceuticals are now being found ubiquitously in the environment (Focazio *et al.* 2008; Loos *et al.* 2009; Silva *et al.* 2011; González *et al.* 2012; Osorio *et al.* 2012). Effluent of wastewater treatment plants (WWTPs) contains large concentrations of CECs that are usually naturally occurring in water bodies (Zorita *et al.* 2009; Jelic *et al.* 2011; Gracia-Lor *et al.* 2012). Recent innovations in water analysis methods, primarily in gas chromatography mass spectrometry (GC-MS) and liquid chromatography (LC-MS), have allowed the industry to develop a more comprehensive understanding of contaminants. At the least, CECs have been found to present potential risks to water supplies due to their physiochemical properties, such as poor degradability and high water solubility (Knepper *et al.* 1999). These properties allow CECs to pass through most common filtration steps including some membrane treatment processes.

Membrane processes are well used in water treatment, including IPR and DPR processes, given their ability to produce stable and excellent effluent quality (Reith & Birkenhead 1998; Alonso *et al.* 2001; Qin *et al.* 2004; Ravazzini *et al.* 2005). Membrane technologies such as microfiltration (MF) and reverse osmosis (RO) separate organic compounds, total dissolved solids, and microorganisms from the aqueous phase (Hofman *et al.* 1997; Rautenbach *et al.* 2000; Lee & Lueptow 2001; Radjenović *et al.* 2008; Shivajirao 2012).

MF technologies have been found to filter out only a few emerging organic contaminants (Yoon *et al.* 2006; Kowalska 2008; Sahar *et al.* 2011). However, RO has proved highly effective at removing a wide range of emerging contaminants and its resulting treated water can be used for more exigent purposes (Snyder *et al.* 2007; Calderón-Preciado *et al.* 2011; Huang *et al.* 2011). A treatment train of MF followed by RO offers a way to bypass secondary and tertiary treatment and potentially saves some energy for the treatment process.

As of yet, no comprehensive study has evaluated the occurrence of CECs in concentration streams produced by IPR and DPR-type treatment trains. Most research pertains to the water product produced by such systems since membranes are known to effectively remove most CECs; however, concerns remain about heightened exposure to CECs in the concentrate water that is disposed to the environment.

The objectives of this study are to (a) evaluate the occurrence of CECs in MF/RO treatment of a WWTP's primary effluent and (b) demonstrate the effectiveness of MF/RO in treating primary effluent as a novel water recycling process.

MATERIALS AND METHODS

Contaminants of emerging concerns

A CEC list was created according to an exhaustive study that identified the most common CECs in the literature. The top 38 common CECs were carefully selected and categorized by type. Table 1 presents a summary of the CECs examined in this study and their properties. The list consists of chemicals with high frequencies of occurrence and health risks.

WWTP and the pilot project

The study was performed at the Carbon Canyon Water Recycling Facility (CCWRF) in Chino, CA. CCWRF provides

Table 1 | Selected and examined CECs

Type	Compound	MW g/mol	Charge pH 7.0 (mV)[a]	pKa[a]	Log K_{ow}	Hydro class[b]	Chemical formula	References
Analgesics/anti-inflammatories	Acetaminophen	151	0	9.46	0.34	HPI-N	$C_8H_9NO_2$	Yamamoto *et al.* (2009)
	Diclofenac	296	−1	4	4.5	HPO-I	$C_{14}H_{11}C_{l2}NO_2$	Carballa *et al.* (2008)
	Ibuprofen	206	−1	4.85	3.5–4.91	HPO-I	$C_{13}H_{18}O_2$	Lin *et al.* (2006)
	Naproxen	230	0	4.19	3.2	HPO-N	$C_{14}H_{14}O_3$	Carballa *et al.* (2008)
	Salicylic acid	138			2.26	HPO	$C_7H_6O_3$	Moffat *et al.* (2011)
	Primidone	218	0	11.5	0.9	HPI-N	$C_{12}H_{14}N_2O_2$	Moffat *et al.* (2011)
Antibiotic	Amoxicillin	365	−0.33	3.23	0.87	HPI-I	$C_{16}H_{19}N_3O_5S$	Jones *et al.* (2002)
	Azithromycin	749	1.8		4.02	HPO-N	$C_{38}H_{72}N_2O_{12}$	McFarland *et al.* (1997)
	Ciprofloxacin	331			0.4	HPI	$C_{17}H_{18}FN_3O_3$	Wick *et al.* (2009)
	Sulfamethoxazole	253	−1	6.16	0.89	HPI-I	$C_{10}H_{11}N_3O_3S$	Carballa *et al.* (2008)
	Trimethoprim	290	0.6	7.16	0.91	HPI-N	$C_{14}H_{18}N_4O_3$	Moffat *et al.* (2011)
Beta-blockers	Atenolol	266	1	14.08	0.16	HPI-N	$C_{14}H_{22}N_2O_3$	Vieno *et al.* (2007)
	Propranolol	259			3.48	HPO	$C_{16}H_{21}NO_2$	–
Lipid regulators	Gemfibrozil	250	0	4.42	4.77	HPO-N	$C_{15}H_{22}O_3$	–
Psychiatric drugs	Carbamazepine	236	0	15.69	2.45	HPO-N	$C_{15}H_{12}N_2O$	Carballa *et al.* (2008)
	Diazepam	285	0	2.92	2.82	HPO-N	$C_{16}H_{13}ClN_2O$	Sangster (1997)
	Fluoxetine	309	0		4.05	HPO-N	$C_{17}H_{18}F_3NO$	Moffat *et al.* (2011)
Hormones	Estrone	270	0	10.3	4.1	HPO-N	$C_{18}H_{22}O_2$	Carballa *et al.* (2008)
	Testosterone	288	0		3.32	HPO-N	$C_{19}H_{28}O_2$	Hansch *et al.* (1995)
	17-β-Estradiol	604	0		3.9–4.0	HPO-N	$C_{40}H_{60}O_4$	Carballa *et al.* (2008)
	Progesterone	314	0		3.87	HPO-N	$C_{21}H_{30}O_2$	Hansch *et al.* (1995)
Antiseptics	Triclosan	290	−0.14	7.68	4.8	HPO-I	$C_{12}H_7Cl_3O_2$	Moffat *et al.* (2011)
Contrast media	Iopromide	791	0	11.1	−2.33	HPI-N	$C_{18}H_{24}I_3N_3O_8$	–
Psychostimulants	Caffeine	194	0		−0.07	HPI-N	$C_8H_{10}N_4O_2$	Hansch *et al.* (1995)
Component of plastics	Bisphenol A	228	0	9.78	3.32	HPO-N	$C_{15}H_{16}O_2$	–
Drugs of abuse	Cotinine	176	0		0.07	HPI-N	$C_{10}H_{12}N_2O$	Li *et al.* (1992)
Pesticides	Diethyl toluamide (DEET)	191	0		2.2	HPO-N	$C_{12}H_{17}NO$	Moffat *et al.* (2011)
Industrial compound	1,4 Dioxane	88			−0.27	HPI	$C_4H_8O_2$	Hansch *et al.* (1995)
By-products (BPs)	N-Nitrosodimethylamine (NDMA)	74			−0.57	HPI	$C_2H_6N_2O$	Hansch *et al.* (1995)
	N-Nitrosodiethylamine	102			0.48	HPI	$C_4H_{10}N_2O$	Hansch *et al.* (1995)
	N-Nitrosomorpholine	116			−0.44	HPI	$C_4H_8N_2O_2$	Hansch *et al.* (1995)
Antianxiety	Meprobamate	218	0		0.7	HPI-N	$C_9H_{18}N_2O_4$	Hansch *et al.* (1995)
Flame retardant	TCEP	285	0		2.11	HPO-N	$C_6H_{12}C_{13}O_4P$	–
	TCPP	327	0		2.59	HPO-N	$C_9H_{18}Cl_3O_4P$	Miti (1992)
	TDCPP	430	0		3.65	HPO-N	$C_9H_{15}Cl_6O_4P$	Miti (1992)
Statins	Atorvastatin	558			6.36	HPO	$C_{33}H_{35}FN_2O_5$	Moffat *et al.* (2011)
Opioid	Methadone	309			3.93	HPO	$C_{21}H_{27}NO$	Hansch *et al.* (1995)
Perfluorinated organic compounds	Perfluorooctane sulfonic acid (PFOS)	500			−1.08	HPI	$C_8HF_{17}O_3S$	Krop & Voogt (2008)

[a]ACS 2015, ChemAxon 2015.
[b]Hydrophobicity class: HPI, hydrophilic; HPO, hydrophobic; *N*, neutral; I, ionic charged.

primary treatment by preliminary screening and grit removal, primary clarification, secondary treatment by aeration basins and clarification, tertiary treatment by filtration and disinfection using chlorine, and finally dechlorination. The plant is designed to treat an annual average flowrate of 11.4 million gallon per day (mgd) (Inland Empire Utilities Agency 2014).

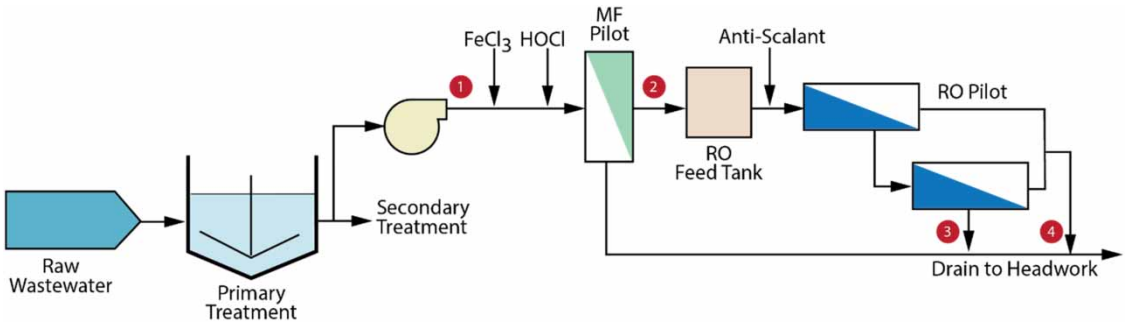

Figure 1 | Pilot system with sampling points, 1 (Primary effluent), 2 (MF permeate), 3 (RO concentrate) and 4 (RO permeate).

In collaboration with the Inland Empire Utility Agency (IEUA), this pilot project researched the effects of sending primary treated effluent directly to MF followed by RO, thus bypassing secondary and tertiary treatment. Figure 1 shows the schematic of the treatment train used in this study as well as the locations of sampling points for CECs.

The scope of the project involved demonstrating the feasibility of this innovative treatment train, especially in removing CECs, and displaying a mass balance of CECs between the feed, product, and concentrate streams. A future benefit of this treatment train would be decreased energy consumption for overall treatment, given that the most energy-intensive component of a conventional treatment train is associated with the secondary biological treatment processes (Raucher & Tchobanoglous 2014).

Raw wastewater

The pilot project used primary effluent wastewater from the CCWRF as feed to the MF and RO system. Table 2 shows the wastewater characteristics that the IEUA reported in 2012.

MF system

The MF pilot system was a fully automated membrane system designed and maintained by PALL Corporation. Its operational parameters were measured continuously at ten-minute intervals and automatically recorded. Total feed flow rate into the MF unit was 25 gpm. Average flux during the course of experiments was 13 gfd.

The pilot unit included a hot water heater and chemical pumps for automatic enhanced flux maintenance cleans that were carried out every 24 hours. The system was equipped with two new UNA-620A hollow-fiber MF modules, each

Table 2 | Influent wastewater characteristics at carbon canyon water recycling facility

Constituent	Unit	Minimum	Average	Maximum
Specific conductance	µm/cm	903	1,048	1,184
pH	units	6.9	7.1	7.2
Total organic carbon (TOC)	mg/L	166	246	334
Biochemical oxygen demand (BOD)	mg/L	308	451	627
Total suspended solids (TSS)	mg/L	228	390	730
Total dissolved solids (TDS)	mg/L	509	538	559
Ammonia-nitrogen (NH3-N)	mg/L	29.2	34.1	45.8
Total inorganic nitrogen (TIN)	mg/L	29.7	31.7	33.1
Total nitrogen (TN)	mg/L	46.0	53.3	59.6
Boron	mg/L	0.2	0.3	0.3
Chloride	mg/L	100	116	132
Fluoride	mg/L	0.2	0.2	0.3
Sulfate	mg/L	35	45	53
Total hardness, as $CaCO_3$	mg/L	169	198	250
Arsenic, total recoverable	µg/L	<10	<10	<10
Cadmium, total recoverable	µg/L	<10	<10	<10
Chromium, total recoverable	µg/L	<10	<10	<10
Copper, total recoverable	µg/L	40	63	80
Lead, total recoverable	µg/L	<20	<20	<20
Mercury, total recoverable	µg/L	<0.5	<0.5	<0.5
Nickel, total recoverable	µg/L	<10	<10	<10
Selenium, total recoverable	µg/L	<20	<20	<20
Silver, total recoverable	µg/L	<10	<10	<10
Zinc, total recoverable	µg/L	120	195	280
Free cyanide (Aquatic)	µg/L	<2	<3	4
Bis (2-ethylhexyl) phthalate	µg/L	12	12	13

Source: IEUA, 2011–12, from 2012 data (IEUA, 2011–12 and IEUA, 2014).

of which contained 538 sq ft of active membrane surface area and operated in outside-to-inside filtration mode. The membrane was a polyvinylidene fluoride (PVDF) hollow-fiber type with a nominal pore size of 0.1 μm. PVDF fibers are known for having high mechanical and chemical resistance.

Ferric chloride and chlorine (bleach) were injected directly into the feed stream (i.e., the WWTP's primary effluent), which then fed the MF pilot skid at a target concentration of 20 ppm and 1.5 ppm, respectively. Bleach was added to create a chloramine residual to reduce microbial growth on the membranes. While further testing would be valuable to find the optimum dosage for the coagulant, the present configuration was adequate for demonstrating the benefit of adding ferric chloride to the process. The two membranes were operated in parallel to provide a suitable flow rate to the downstream RO pilot.

RO system

The RO pilot system was the Membrane Evaluation Research Unit 5 (MERU5) skid owned by the US Bureau of Reclamation. MERU5 has up to three stages; however, for this study, only 1-stage and 2-stage were used. 1-stage consisted of two 4-inch pressure vessels, each containing three RO ESPA2-4040 elements, while 2-stage consisted of two 2.5-inch pressure vessels, each containing three RO ESPA2-2540 elements.

The effluent from MF was used as feed water to the RO and contained inorganics, dissolved organics constituents, and a trace level of suspended materials that could potentially precipitate on the membrane surface. A 34-mm-thick feed spacer in the ESPA2 membrane was used to prevent colloidal fouling and increase the effectiveness of membrane cleaning. Furthermore, by using these membranes, precipitation and the costs of additional cleaning were minimized.

An antiscalant, Vitec 1400, was dosed into the RO feed stream at a concentration of approximately 3 mg/L to prevent inorganic scale from forming on the membrane's surface.

Mass balance

The mass balance was calculated following the method used by Gao *et al.* (2012). The average mass flow of each compound was calculated by multiplying the sum of the CEC concentrations in the permeate and concentrate with corresponding average flows in the influent. The equations involved are as follows

$$M_f = Q_f \cdot C_f \tag{1}$$

$$M_c = Q_c \cdot C_c \tag{2}$$

$$M_p = Q_p \cdot C_p \tag{3}$$

M_f, M_p and M_c (ng/min) are the mass flux of CECs calculated in the influent, permeate and concentrate streams, respectively. Q_f, Q_p and Q_c (L/min) represent feed, product and concentrate flows, respectively. C_f, C_p and C_c (ng/L) are the average concentrations of CECs measured in the feed, permeate and concentrate flows, respectively.

The discrepancy in the mass balance of CECs compounds can be calculated and presented as $M_{\text{discripancy}}$. To estimate the mass of CECs that is lost due to the membranes' capabilities, the following equation is used

$$M_{\text{disc}} = M_f - M_p - M_c \tag{4}$$

The mass balance discrepancy, in percentage, is calculated as follows

$$R_{\text{disc}} = \frac{M_{\text{disc}}}{M_f} \times 100 \tag{5}$$

Experimental procedure

The RO feed tank (500 gallons) was filled with MF permeate at a constant flow rate of 10 gpm. To start the RO process, the pressure of the feed water was gradually increased along with the pump speed. After the target pressure (i.e., 300 kPa) was achieved, the RO feed valve was gradually opened. At the same time, the concentrate valve and permeate valves were fully opened and initiated. By increasing and decreasing the pump rate and controlling the flow rate of the concentrate valve, the target flow rate in the permeate can be achieved. To achieve the target flux and recovery rate, permeate and concentrate flow rates were calculated and

set in the RO unit by changing the set points of the feed valve, concentrate valve and the feed's pump rate.

The experiments in this study were performed in two phases. In the first phase, only 1-stage RO was operated using 4-inch elements with a fixed recovery rate of 55%. This recovery rate was selected to evaluate whether recovery has any significant effect on the membranes' ability to reject CECs. The total membrane surface area used in this phase was 510 ft^2. Four different fluxes of 8, 10, 12, and 14 gfd were selected and targeted under the constant recovery rate of 55%.

In the second phase of the study, 1-stage and 2-stage RO membranes were operated. Again, 1-stage RO used 4-inch elements, while 2-stage used 2.5-inch elements to achieve a recovery rate of 80%. Four different fluxes of 8, 10, 12, and 14 gfd were selected and targeted under the constant recovery rate of 80%. The total membrane surface area used in this set of experiments was 660 ft^2.

Antiscalant with a concentration of 3 mg/l was added to the RO feed stream before the high-pressure pumps. Ferric chloride ($FeCl_3$) and chlorine (HOCl) were injected directly into the primary effluent stream that fed the MF pilot skid at a target concentration of 20 ppm and 7 ppm, respectively.

Permeate and concentrate from the RO unit were collected for sampling, and the streams were blended and sent to the common drain line to the WWTP's headworks. The duration for each flux test ranged from three to five hours. After each test condition, the RO pilot was flushed with RO permeate and each test was done in a different day. Permeate and concentrate samples for each test run were collected no sooner than three hours after the start of testing to allow the RO system to stabilize. RO samples were taken when permeate and concentrate conductivity were constant for at least for an hour with no feed temperature variations.

The sample volume was 8 L for organic compounds analysis and 2.5 L for inorganic compounds analysis. Prepared amber glass (for organic compounds) and poly-nutrients and poly-metals (for inorganic compounds) bottles were used for sampling. Bottles contained sodium thiosulfate and ascorbic acid (for organic analysis) and phosphoric acid, sulfuric acid and nitric acid (for inorganic analysis) as preservatives. Samples were chilled to below 4 °C on ice or frozen gel packs and delivered to the local, certified laboratory on the same day. All CEC and inorganic analyses were performed at this location.

Due to limited resources, the MF feed (i.e., primary effluent) and MF product (i.e., RO feed) were sampled and analyzed for CECs only once during the study. According to CCWRF, water chemistry of raw sewage to the plant does not have significant variations over extended periods of time. However, a municipal WWTP can experience daily variations in its feed water's water chemistry.

Analytical method

The collected samples were then shipped in the same day to the Weck Laboratories, Inc. in City of Industry, California. Methods 8270, 1694, and 1625 provided quantitative data on the suite of 38 CECs being investigated for this research. These methods involved online pre-concentration followed by liquid chromatograph separation and series mass spectrometry (LS-MS-MS) with electrospray ionization in positive and negative modes. Samples were pre-concentrated using a previously developed direct online extraction/analysis method (Haghani *et al.* 2009) to achieve low-ng/L method reporting limits (MRL). The utilized test methods MRL for the subject 38 CECs ranged from 1 to 2,500 ng/L.

RESULTS AND DISCUSSION

Occurrence and removal of inorganics in the MF

CECs originate from industrial and domestic products such as pesticides, PCPs, preservatives, surfactants, flame retardants and perfluorochemicals. These contaminants are also excreted by humans in the form of human waste that contains pharmaceutical residues or steroidal hormones. CECs also surface as chemicals formed during wastewater and drinking water treatment, known as disinfection by-products (DBPs).

Table 3 shows an analysis of the primary effluent (i.e., MF feed) and MF permeate (i.e., MF effluent) for inorganics compounds. The data in the 'MF feed' column was obtained from the reports provided by CCWRF (Inland Empire Utilities Agency 2014). As expected, the MF process does not remove dissolved inorganic constituents; however, it

Table 3 | Characteristics of primary effluent and MF permeate

Compound	Unit	MF feed	MF permeate
Chloride	mg/L	116	120
Sulfate as (SO_4)	mg/L	45	45
Ammonia as N	mg/L	34.1	53
Phosphorus as (PO_4)	mg/L	NA	11
Barium	mg/L	NA	0.0090
Calcium	mg/L	NA	42.8
Magnesium	mg/L	NA	10.2
Silica as (SiO_2)	mg/L	NA	18
Sodium	mg/L	NA	80
Bicarbonate alkalinity as HCO_3	mg/L	NA	380
Alkalinity as $CaCO_5$	mg/L	250	320
Total dissolved solids (TDS)	mg/L	538	510
Total suspended solids (TSS)	mg/L	390	ND
Total organic carbon (TOC)	mg/L	246	74
Biochemical oxygen demand (BOD)	mg/L	451	140
Specific conductance (EC)	μm/cm	1,048	1,097
pH		7.1	6.8

NA, not analyzed; ND, not detected.

is excellent at removing suspended materials, which reduces the concentration of certain organic compounds represented by BOD and TOC.

Considering the CECs' molecular weights (MWs) listed in Table 1, the MF process is unlikely to significantly or meaningfully remove CEC micropollutants from the primary effluent. After all, MF is generally used as pretreatment for particulate matter reduction and water stabilization and to avoid fouling of the RO membranes, which creates optimal operating conditions for the RO process.

Acetaminophen was the most abundant compound with a concentration of 130 μg/L in primary effluent (e.g. MF feed). Acetaminophen was followed by other analgesics, anti-inflammatories, lipid regulators gemfibrozil and bezafibrate, and the betablocker atenolol. High concentrations of acetaminophen and caffeine have also has been reported in similar studies: Yang *et al.* (2011) reported acetaminophen and caffeine concentrations of about 100 μg/L in an advanced wastewater reclamation plant located in Gwinnett County, Georgia, USA. They found a high ibuprofen concentration of approximately 10 μg/L and carbamazepine concentration of approximately 1 μg/L, which are similar to the numbers that were observed in this study's MF feed analysis.

The presence of by-products (BPs), such as NDMA, is particularly important in places where a treatment plant's effluent is used for IPR. Chlorinating wastewater leads to relatively high concentrations of BPs. In fact, NDMA formation can exceed 100 ng/L during the chlorination of secondary wastewater effluent (Najm & Trussell 2017), whereas chlorination of surface waters typically results in the formation of less than 10 ng/L of NDMA (Najm & Trussell 2017).

NDMA results from chlorination due to the slow reaction of monochloramine with dimethylamine, which ultimately forms an unsymmetrical dimethylhydrazine intermediate (Choi & Valentine 2002; Mitch & Sedlak 2002). There were no N-nitroso compounds found in the primary effluent. However, the MF process uses chloramines as a disinfectant, which is formed by adding chlorine bleach to naturally occurring ammonia in the primary effluent. Therefore, after the MF process, N-nitroso compounds were detected in the laboratory analysis. Other studies have shown that chlorination using hypochlorite results in approximately an order of magnitude less NDMA than what is formed through chlorination using monochloramine (Mitch & Sedlak 2002).

As for perfluorooctane sulfonate (PFOS), the compound was not detected in the MF feed but was found in the MF permeate. This result could be due to an inaccuracy in the laboratory analysis or a possible transformation of fluorosulfonamides, such as FOSE and FOSA, to PFOS. This observation has been reported in other studies as well (Schultz *et al.* 2006; Sinclair & Kannan 2006; Loganathan *et al.* 2007). However, in prior studies, the average PFOS concentration formed was 4 ng/L; in this study, the PFOS concentration was 270 ng/L.

In general, conventional wastewater treatment techniques, such as trickling filtration, activated sludge, anaerobic digestion, and chlorination, have been reported to have little effect on PFOS removal (Schultz *et al.* 2006; Sinclair & Kannan 2006), given that microbial communities cannot metabolize PFOS (Key *et al.* 1998; Hollingsworth *et al.* 2005). In some cases, PFOS concentrations were greater in the WWTP effluent as compared with those in the influent (Schultz *et al.* 2006; Sinclair & Kannan 2006). This suggests microbial transformation (Schultz *et al.* 2006;

Sinclair & Kannan 2006; Loganathanet al. 2007) of fluorosulfonamides (e.g. FOSE and FOSA) to PFOS (Tomy *et al.* 2004; Xu *et al.* 2004), the transformation of fluorotelomer alcohols to PFOA, or the release of residual PFOX from the solid phase. The RO process has been reported to be effective in removing PFOSs.

RO pilot operation data

As mentioned before, this study consisted of two phases: the first phase was an MF process followed by a 1-stage RO process using 4-inch ESPA2-4040 elements with a target recovery rate of 55%. The second phase was an MF process followed by a 2-stage RO process using 4-inch ESPA2-4040 and 2.5-inch ESPA-2540 elements with a recovery rate of 80%. For both phases, four different fluxes of 8, 10, 12 and 14 gfd were selected and targeted.

The RO pilot unit had a capacity of 19.5 L/min–33.6 L/min of feed from the RO feed tank, and the pressure was variable between 470 kPa and 1,000 kPa to obtain the mentioned fluxes with 55% and 80% recoveries for phase one and phase two, respectively. Antiscalant with a concentration of 3.02 mg/L was added to the RO feed stream before the high-pressure pumps. Permeate and concentrate from the RO unit were collected for sampling, and the remainder of the streams was blended with the RO concentrate and directed to the common drain line to the plant's headworks.

Recovery of the membranes was derived from the following equation

$$\text{Recovery } (\%) = \frac{\text{volume of the permeate}}{\text{volume of the feed}} \times 100 \quad (6)$$

Flux (J) is the volume of permeate (V) collected per unit membrane area (A) per time (t)

$$J = \frac{V}{At} \quad (7)$$

Removal of inorganics through the RO process

The RO system's performance was evaluated in terms of the permeate's pollutant concentrations and the membrane rejection. The rejection of the RO membrane was calculated as follows

$$\text{Rejection} \quad (\%) = \left(\frac{C_f - C_p}{C_f}\right) \times 100 \quad (8)$$

where C_f, mg/L, is the feed concentrations and C_p, mg/L, is the permeate concentration.

Tables 4 and 5 show all removal rates at the different fluxes tested. For the first phase of this study, conductivity rejection was found to be 92.8%, 90.0%, 93.3% and 93.5% for fluxes of 8, 10, 12 and 14 gfd, respectively. For the second phase, conductivity rejection was 85.5%, 89.1%, 91% and 91.5% for fluxes of 8, 10, 12 and 14 gfd, respectively.

These findings matched expectations: increasing flux slightly decreases the salt concentration in the permeate. This is because the salt leakage across the membrane remains fairly constant. At higher flux rates, the mass of salt passing across the membrane is blended with more permeate than at lower flux rates, resulting in a lower conductivity product stream. The only exception to this condition was when applying flux of 8 gfd in the first phase. With that being said, this relatively high salt-removal rate could simply be an error since this was the first data point collected in this pilot study and the experiment was not mature enough for data collection.

For the first phase of this study, 94.1%, 90.0%, 93.4% and 93.5% of chloride rejections were achieved with fluxes of 8, 10, 12 and 14 gfd, respectively. For the second phase, 85.8%, 90.8%, 92.1% and 92.9% of chloride rejections were achieved with fluxes of 8, 10, 12 and 14 gfd, respectively. These results align with what was explained earlier about conductivity removal.

More than 98.2% of sulfate rejection was obtained with all fluxes in both phases. In addition, calcium removal was 97.7% with all fluxes for both phases, while average sodium removal was 89.4% for the first phase and 86.9% for the second phase with all fluxes.

Higher rejection of di- and multivalent ions could be explained by the size of multivalent ions, which is larger than monovalent ones, and by their charge effect, which is consistent with results reported in past literature. An increase in an anion charge leads to an increase of electrostatic interactions with membranes.

Table 4 | Occurrence of the target CECs through the process with different fluxes in phase one with one stage RO

				Flux 8			Flux 10			Flux 12			Flux 14		
Compound	**Unit**	**Primary effluent**	**MF permeate**	**Concentrate Conc.**	**Permeate Conc.**	**Removal %**	**Concentrate Conc.**	**Permeate Conc.**	**Removal %**	**Concentrate Conc.**	**Permeate Conc.**	**Removal %**	**Concentrate Conc.**	**Permeate Conc.**	**Removal %**
1,4-Dioxane	µg/L	ND	0.7	1.9	ND	100	2	ND	100	2.2	ND	100	2.1	ND	100
N-Nitrosodiethylamine	ng/L	ND	6	4	ND	100	ND	ND	100	23	ND	100	2.7	ND	100
N-Nitrosodimethylamine (NDMA)	ng/L	ND	8.1	15	7.6	6.2	42	28	0	18	11	0	20	10	0
N-Nitrosomorpholine	ng/L	ND	12	45	ND	100	47	6.7	44.2	14	2.1	82.5	44	2.6	78.3
Propranolol	ng/L	0.013	0.058	ND	0.0028	95.2	73[a]	4.4	0	2.6[b]	2.7	0	130[c]	3.8	0
Perfluorooctane sulfonate (PFOS)	ng/L	ND	270	300	7.8	97.1	590	26	90.4	580	20	92.6	ND	13	95.2
17-b-Estradiol	ng/L	43	51	80	ND	100	32	1.5	97.1	11	ND	100	46	ND	100
Estrone	ng/L	33	160[a]	180[a]	ND	100	78	ND	100	110[a]	ND	100	57	ND	100
Progesterone	ng/L	5.2	26	28	ND	100	93	ND	100	49	ND	100	73	1.1	95.8
Testosterone	ng/L	4.2	110	230[a]	ND	100	260[a]	4.1	96.3	180[a]	3.7	96.6	260[a]	3.6	96.7
Bisphenol A	ng/L	310	170	360[a]	39	77.1	820	21[d]	87.6	520[a,c]	16[d]	90.6	470[a,c]	35	79.4
Diclofenac	ng/L	200	160[a]	220[a]	12	92.5	540	48	70	580[a]	39	75.6	600	46	71.3
Gemfibrozil	ng/L	4,200[a]	3,900	12,000[a]	82	97.9	6,100[a]	90	97.7	5,500[a,c]	74	98.1	6,000[a]	70	98.2
Ibuprofen	ng/L	15,000[a]	12,000[a]	13,000[a]	690[a]	94.3	34,000[a]	2,300[a]	80.8	33,000[a]	1,800[a]	85	43,000[a]	2,500[a]	79.2
Iopromide	ng/L	1,700[a]	1,300	3,600[a]	ND	100	ND	ND	100	6.1	ND	100	25	16	98.8
Naproxen	ng/L	19,000[a]	8,900[a]	8,800[a]	580[a]	93.5	12,000[a]	1,900[a]	78.7	12,000[a]	1,300	85.4	14,000[a]	1,500[a]	83.1
Salicylic acid	ng/L	95,000[a]	54,000	880	8,400[a,c]	84.4	240	100	99.8	260	61[a]	99.9	950	1,900	96.5
Triclosan	ng/L	1,600[a]	120	280[a]	5.3	95.6	180[a,c]	4.1	96.6	310[a,c]	8	93.3	220[a,c]	8.7	92.8
Acetaminophen	ng/L	130,000[a]	27,000[a,c]	67,000[c]	22,000[a]	18.5	18,000[a]	22,000[a]	18.5	6,000[a]	10,000[a]	63	10,000[a]	11,000[a]	59.3
Amoxicillin	ng/L	6,400	2,400[c]	25[c]	41	98.3	ND	ND	100	ND	ND	100	980[c]	51	97.9
Atenolol	ng/L	3,500[a]	2,500[a]	4,600[a]	210[a]	91.6	4,400[a]	260[a]	89.6	3,300[a]	160[a]	93.6	4,200[a]	210[a]	91.6
Atorvastatin	ng/L	280	470[a]	1,500[a,c]	14	97	820[a]	17	96.4	1,100[a,c]	16	96.6	640[a]	18	96.2
Azithromycin	ng/L	1,400	780	210	ND	100	ND	ND	100	ND	ND	100	37[a,d]	ND	100
Caffeine	ng/L	84,000[a]	26,000[a,c]	32,000[a,c]	4,500[a]	82.7	130,000[a,c]	5,300[a]	79.6	30,000[a,c]	4,400[a]	83.1	31,000[a]	3,800[a]	85.4
Carbamazepine	ng/L	170	200[a,c]	43[c]	5.9	97.1	260[a]	12	94	76	8.6	95.7	220[a,c]	8.6	95.7
Ciprofloxacin	ng/L	1,500	570[c]	15[c]	43	92.5	790[a,d]	32[d]	94.4	860[a,c,d]	70[d]	87.7	ND	65[d]	88.6
Cotinine	ng/L	1,700[a]	1,300[a]	2,900[a,c]	51	96.1	340[a,d]	130[d]	90	1,700[a]	61[d]	95.3	2,400[a]	79[d]	93.9
DEET	ng/L	2,100[a]	1,800[a]	6,300[a,c]	150[a]	91.7	3,800[a]	120	93.3	3,900[a]	100	94.4	4,500[a]	110	93.9
Diazepam	ng/L	ND	6.4	12[c]	ND	100	10	ND	100	13	ND	100	16	ND	100
Fluoxetine	ng/L	62	8.6	ND	1	88.4	52[a]	ND	100	18	1	88.4	16[b]	1.1	87.2
Meprobamate	ng/L	72	19	47[c]	3.2	83.2	20	13	31.6	24	7.2	62.1	370[a]	16	15.8
Methadone	ng/L	27	30	3.7[c]	ND	100	ND	ND	100	ND	ND	100	ND	ND	100

(*continued*)

Table 4 | continued

Compound	Unit	Primary effluent	MF permeate	Flux 8			Flux 10			Flux 12			Flux 14		
				Concentrate Conc.	Permeate Conc.	Removal %	Concentrate Conc.	Permeate Conc.	Removal %	Concentrate Conc.	Permeate Conc.	Removal %	Concentrate Conc.	Permeate Conc.	Removal %
Primidone	ng/L	200[c]	38[c]	6.4[c]	6	84.2	18	ND	100	ND	ND	100	ND	ND	100
Sulfamethoxazole	ng/L	1,800[a]	920[a]	3,000[a,c]	37	96	2,600[a]	43	95.3	3,600[a]	34	96.3	1,200[a]	38	95.9
TCEP	ng/L	290	280[a]	230[c]	15[d]	94.6	710[a]	25	91.1	810[a]	23	91.8	460[a]	20	92.9
TCPP	ng/L	920[a]	760[a]	1,200[a,c]	46[d]	93.9	2,800[a]	86[d]	88.7	1,700[a]	110[d]	85.5	3,000[a]	71[d]	90.7
TDCPP	ng/L	370	190[a]	1,600[a,c]	14	92.6	1,700[a]	15[d]	92.1	2,800[a]	18[d]	90.5	1,100[a]	20[d]	89.5
Trimethoprim	ng/L	680[a]	590[a]	1,200[a,c]	35	94.1	1,000[a]	59	90	1,000[a]	53	91	1,100[a]	35	94.1

ND, not detected.
[a]The concentration indicated for this analyte is an estimated value above the calibration range.
[b]The original extraction and/or analysis of this sample yielded QC recoveries outside acceptance criteria. It was re-extracted/re-analyzed after the recommended maximum hold time.
[c]Low internal standard recovery possibly due to matrix interference. The result is suspect.
[d]Blank contamination. The analyte was found in the associated blank as well as in the sample.

Phosphate rejection was more than 99.2% for all conditions in the first phase; but, in the second phase, phosphate was not efficiently rejected. This result cannot be explained when the removal is compared with other ions.

Overall, in the first phase (i.e. 1-stage RO), the flux of 14 gfd showed better rejection values for most inorganic compounds compared with those of other fluxes. Similar results were found for the second phase, which ultimately means that increasing flux improves the permeate quality.

However, results show that 1-stage RO with a 55% recovery rate had a better removal rate of CECs when compared with 2-stage RO with an 80% recovery rate. These results align with those of other studies. As the concentration gradient of contaminants increases across the membrane at higher recovery rates, the overall removal efficiency for various compounds decreases.

Removal of CECs through the RO process

CECs were studied in the permeate and concentrate streams at fluxes of 8, 10, 12 and 14 gfd, with recovery rates of 55% and 80%. Pressure-driven separation membranes are effective barriers in rejecting these pollutants (Gur-Reznik *et al.* 2011). In particular, studies have shown that RO is effective in removing compounds that have MWs of greater than approximately 200 g/mol (Sedlak & Pinkston 2011). The majority of the target CECs have MWs between 100 and 560 g/mol, except a few such as iopromide, azithromycin, NDMA and 1,4 dioxane, which have MWs of 791, 749, 74 and 88 g/mol, respectively. Compounds with lower MWs exhibited much lower removal by RO.

Figure 2 shows the effects of CECs' MW on their removal in the first and second phases of this study, as well as expected high removal rates.

Figure 2 shows that both phases experienced sharp drop-offs in removal efficiency for compounds with MWs of 300 g/mol or less.

Tables 4 and 5 shows the concentrations of CECs in the RO feed, permeate and concentrate for the first and second phases of this study, respectively. Correspondingly, Figure 3 presents average concentrations of different CECs in the RO permeate for all three of the mentioned analyses.

The data demonstrates the effectiveness of RO treatment in eliminating CECs in the RO permeate while operating at

Table 5 | Occurrence of the target CECs along the process with different fluxes in phase two with two stages RO

				Flux 8			Flux 10			Flux 12			Flux 14		
Compound	**Unit**	**Primary Eff.**	**MF Perm.**	**Permeate Conc.**	**Concentrate Conc.**	**Removal %**	**Permeate Conc.**	**Concentrate Conc.**	**Removal %**	**Permeate Conc.**	**Concentrate Conc.**	**Removal %**	**Permeate Conc.**	**Concentrate Conc.**	**Removal %**
1,4-Dioxane	μg/L	ND	0.7	ND	2.3	100.0	ND	4.4	100.0	ND	4.9	100.0	ND	4.5	100.0
N-Nitrosodiethylamine	ng/L	ND	6	3.1	12	48.3	ND	ND	100.0	ND	20[b]	100.0	ND	11[b]	100.0
N-Nitrosodimethylamine (NDMA)	ng/L	ND	8.1	17	56	0.0	17	75	0.0	21	66	0.0	16	68	0.0
N-Nitrosomorpholine	ng/L	ND	12	2.8	24	76.7	3.8	74	68.3	3	13	75.0	2.4	20	80.0
Propranolol	ng/L	0.013	0.058	5.5	6.1[a]	0.0	ND	ND	100.0	6.2	ND	0.0	1.9	ND	0.0
Perfluorooctane sulfonate (PFOS)	ng/L	ND	270	ND	ND	100.0	9.2	ND	96.6	7.9	ND	97.1	7.7	ND	97.1
17-b-Estradiol	ng/L	43	51	ND	ND	100.0	ND	ND	100.0	ND	ND	100.0	ND	ND	100.0
Estrone	ng/L	33	160[a]	ND	2.9	100.0	ND	4.4	100.0	ND	2.2	100.0	ND	2.3	100.0
Progesterone	ng/L	5.2	26	ND	2.3	100.0	ND	3.8	100.0	ND	2.7	100.0	ND	2.9	100.0
Testosterone	ng/L	4.2	110	2.8	5.7	97.5	2	10	98.2	1.4	5.7	98.7	1.6	6.3	98.5
Bisphenol A	ng/L	310	170	43[c]	1,100[a,b]	74.7	27[c]	1,100[a,b]	84.1	19[c]	1,200[a,b]	88.8	13	660[a,b]	92.4
Diclofenac	ng/L	200	160[a]	8.8	1,100[a,b]	94.5	10	1,800[a,b]	93.8	6.3	1,300[a,b]	96.1	5.3	1,300[a,b]	96.7
Gemfibrozil	ng/L	4,200[a]	3,900	100	12,000[a]	97.4	56	13,000[a,b]	98.6	42	11,000[a,b]	98.9	43	14,000[a,b]	98.9
Ibuprofen	ng/L	15,000[a]	12,000[a]	1,000[a]	130,000[a,b]	91.7	460[a]	100,000[a,b]	96.2	260[a]	60,000[a,b]	97.8	300	81,000[a,b]	97.5
Iopromide	ng/L	1,700[a]	1,300	34	480[b]	97.4	93	640[a,b]	92.8	14	280[b]	98.9	29	520[b]	97.8
Naproxen	ng/L	19,000[a]	8,900[a]	800[a]	63,000[a,b]	91.0	440[a]	70,000[a,b]	95.1	280[a]	40,000[a,b]	96.9	250	48,000[a,b]	97.2
Salicylic acid	ng/L	95,000[a]	54,000	3,000[a]	190,000[a,b]	94.4	2,200[a]	11,000[a,b]	95.9	1,600[a]	21,000[a,b]	97.0	1,400	20,000[a,b]	97.4
Triclosan	ng/L	1,600[a]	120	200[a]	710[a]	0.0	260[a]	610[a]	0.0	340[a]	660[a]	0.0	440	560[a]	0.0
Acetaminophen	ng/L	130,000[a]	27,000[a,b]	15,000[a]	86,000[a,b]	44.4	16,000[a]	42,000[a,b]	40.7	14,000[a]	140,000[a,b]	48.1	14,000	420,000[a,b]	48.1
Amoxicillin	ng/L	6,400	2,400[b]	43	ND	98.2	31	ND	98.7	13	ND	99.5	14	ND	99.4
Atenolol	ng/L	3,500[a]	2,500[a]	270[a]	7,000[a]	89.2	150[a]	6,100[a]	94.0	200[a]	8,000[a,b]	92.0	130	12,000[a]	94.8
Atorvastatin	ng/L	280	470[a]	1.6	2,100[a]	99.7	3.5	9,300[a]	99.3	1.6	2,600[a]	99.7	2.3	4,400[a]	99.5
Azithromycin	ng/L	1,400	780	180[b]	ND	76.9	ND	ND	100.0	180[b]	ND	76.9	ND	ND	100.0
Caffeine	ng/L	84,000[a]	26,000[a,b]	3,200[a]	9,400[a]	87.7	2,600[a]	15,000[a]	90.0	2,600[a]	11,000[a]	90.0	19,000	14,000[a]	26.9
Carbamazepine	ng/L	170	200[a,b]	12	250[a,b]	94.0	7.6	80[b]	96.2	6.7	120[b]	96.7	6.3	92[b]	96.9
Ciprofloxacin	ng/L	1,500	570[b]	57[c]	76	90.0	16[c]	180	97.2	210	140	63.2	8.8	120	98.5
Cotinine	ng/L	1,700[a]	1,300[a]	42	2,900[a]	96.8	47	1,500[a]	96.4	31	1,200[a,b]	97.6	34	3,200[a,b]	97.4
DEET	ng/L	2,100[a]	1,800[a]	120	4,500[a]	93.3	81[c]	5,100[a]	95.5	68[c]	4,400[a]	96.2	32	3,000[a]	98.2
Diazepam	ng/L	ND	6.4	ND	8.1	100.0	ND	9.3	100.0	ND	13	100.0	ND	13	100.0
Fluoxetine	ng/L	62	8.6	1.5	ND	82.6	ND	ND	100.0	ND	ND	100.0	ND	9.8[b]	100.0
Meprobamate	ng/L	72	19	120	3,800[a]	0.0	ND	18	100.0	150[a]	3,000[a]	0.0	7.5	100	60.5
Methadone	ng/L	27	30	1.9	ND	93.7	ND	ND	100.0	ND	ND	100.0	ND	ND	100.0

(*continued*)

Table 5 | continued

Compound	Unit	Primary Eff.	MF Perm.	Flux 8			Flux 10			Flux 12			Flux 14		
				Permeate Conc.	Concentrate Conc.	Removal %	Permeate Conc.	Concentrate Conc.	Removal %	Permeate Conc.	Concentrate Conc.	Removal %	Permeate Conc.	Concentrate Conc.	Removal %
Primidone	ng/L	200[b]	38[b]	5.1	67[b]	86.6	2.5	11[b]	93.4	2.8[b]	40	92.6	3	23[b]	92.1
Sulfamethoxazole	ng/L	1,800[a]	920[a]	65	4,800[a]	92.9	37	5,000[a]	96.0	20	4,000[a]	97.8	22	5,500[a]	97.6
TCEP	ng/L	290	280[a]	670[a]	880[a]	0.0	ND	2,300[a]	100.0	4,800[a]	4,400[a]	0.0	1,100	6,500[a]	0.0
TCPP	ng/L	920[a]	760[a]	72[e]	1,100[a,e]	90.5	68[e]	1,800[a,e]	91.1	80[e]	4,300[a,e]	89.5	41	2,800[a,e]	94.6
TDCPP	ng/L	370	190[a]	13	810[a]	93.2	14	800[a]	92.6	15	1,600[a]	92.1	8.4	890[a]	95.6
Trimethoprim	ng/L	680[a]	590[a]	57	1,900[a]	90.3	1.1	1,900[a,b]	99.8	92	1,500[a]	84.4	6.1	1,800[a]	99.0

ND, not detected.
[a]The concentration indicated for this analyte is an estimated value above the calibration range.
[b]Low internal standard recovery possibly due to matrix interference. The result is suspect.
[c]Blank contamination. The analyte was found in the associated blank as well as in the sample.
[d]The original extraction and/or analysis of this sample yielded QC recoveries outside acceptance criteria. It was re-extracted/re-analyzed after the recommended maximum hold time.
[e]The recovery of this analyte in the CCV's was over the control limit. Sample result is suspect.
[f]The sample was originally analyzed within holding time. However, it required a dilution and the re-analysis was performed after the recommended holding time had expired.

different flux rates. For the first phase, the average removal rates for the analyzed CECs with fluxes of 8, 10, 12 and 14 gfd were 90.2%, 83.8%, 87.2% and 85.1%, respectively. For the second phase, the average removal rates at the same fluxes were 78%, 89.5%, 80.6% and 83%, respectively.

1-stage RO with a 55% recovery rate had an overall better removal rate of CECs when compared with 2-stage RO with an 80% recovery rate. This result aligns with those of past studies (Chellam & Taylor 2001). As mentioned earlier, when the concentration gradient of contaminants increases across the membrane at higher recovery rates, the overall removal effectiveness for various compounds decreases.

As can be seen in Figure 3, CECs with the lowest rejections were meprobamate, beta-blockers and BPs, which had 48.2%, 57.7% and 59.3% removal, respectively. CECs that were completely rejected were 1,4-dioxane and methadone. Similarly, more than 98% of hormones and gemfibrozil were rejected. Other CECs with high rejection rates were iopromide with 99.5% rejection and atorvastatin with 95.6% rejection. High rejection rates also occurred for some antibiotics such as amoxicillin, azithromycin, ciprofloxacin, sulfamethoxazole and trimethoprim. In addition, high removal efficiencies of 93% were observed for compounds such as caffeine, cotinine and DEET.

As mentioned before, NDMA was poorly removed in RO because of its low MW.

The concentration of 1,4 dioxane in the RO feed was lower than the notification level of 1 μg/L. And while 1,4 dioxane was not observed in the RO permeate, its concentration was higher than the notification level in the concentrate stream.

As expected, the compounds rejected during the RO treatment were concentrated to different degrees in the RO concentrate stream. In this study, the highest concentration in the concentrate was of acetaminophen at 130 μg/L at a flux of 8 gfd, and the lowest concentration was of NDMA at 2.7 ng/L at a flux of 14 gfd.

The concentration of each compound in the concentrate stream was found for every test condition in phase one (i.e., with 55% recovery), and the results were compared against one another. The highest concentrations of CECs were found at a flux of 8 gfd and 55% recovery. CECs with the highest concentrations were as follows: 1,4-dioxane,

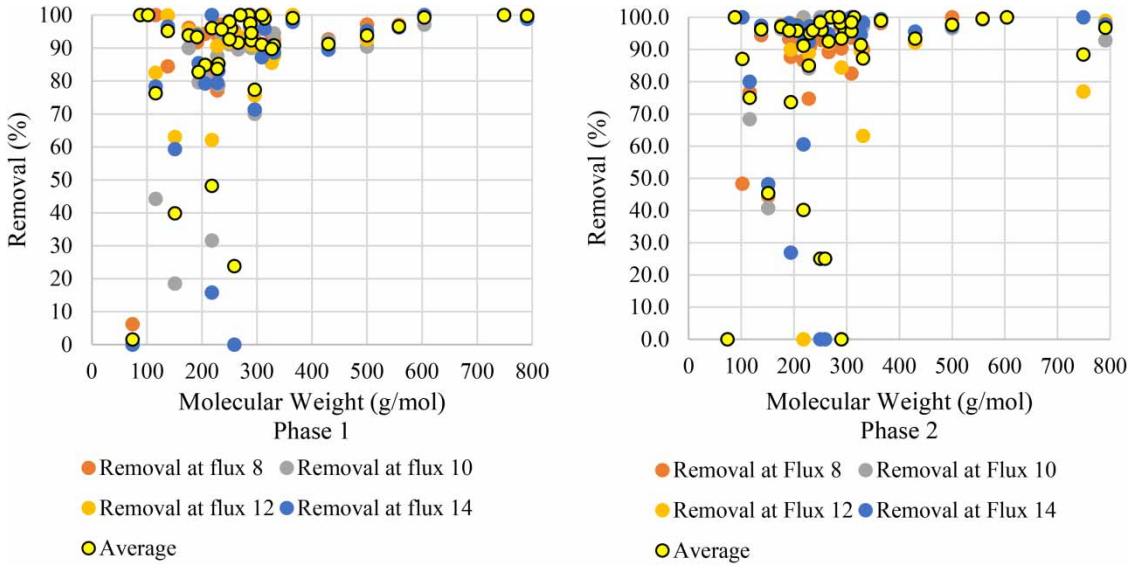

Figure 2 | Effect of MW on the removal of CECs for phase one and phase two.

17-b-estradiol, estrone, gemfibrozil, iopromide, acetaminophen, atenolol, atorvastatin, azithromycin, cotinine, deet and trimethoprim. The reason for this could be the lower concentration gradient across the membrane in the low flux.

The main drawbacks of using RO membrane processes are the costly disposal or treatment of the resulting RO concentrate and the potential environmental risks to aquatic ecosystems that receive the said concentrate (Perez-Gonzalez *et al.* 2012). Acceptable methods of waste disposal typically include discharge to waste treatment facilities, natural waters or an evaporation pond. Other methods to reduce the organic pollutant load of RO concentrate include advanced oxidation processes such as ozonation, fenton processes, photocatalysis and photooxidation, sonolysis and electrochemical oxidation. However, the high cost of some of these technologies may limit their application (Perez-Gonzalez *et al.* 2012).

CECs and their associated degradates represent a challenge for regulators to establish human health-based criterion due to the limited scientific knowledge regarding acute and chronic health effects (Tchobanoglous *et al.* 2015). In recognition of the lack of human health based criterion related to reuse water supply, the National Water Research Institute (NWRI) convened an independent advisory panel (IAP) to develop a list of recommended CECs, based on collective knowledge, to be considered as performance monitoring protocol for DPR systems (NWRI 2013). The IAP suggested risk-based human health criterion for the control of 13 CECs in DPR applications and the maximum concentration of those 13 CECs in the RO permeate for two phases of testing in this study is provided in Table 6.

In the electrostatic repulsion mechanism, rejection relies on relative charge interactions and not just on molecule size. Rejection of organics, colloids and large molecules depends on the sieving parameter, solute and pore size; meanwhile, ionic components and lower MW organics are rejected due to charge interactions between membrane surfaces (Hilal *et al.* 2004).

Accordingly, CEC retention could be the result of both size exclusion and the charge repulsion mechanism. Specifically, negatively charged compounds studied by Verliefde *et al.* (2007a, 2007b) were rejected more effectively than neutral and positive compounds. Berg *et al.* (1997) obtained similar results: charged organics were rejected at higher rates than noncharged organics of the same MW. Kimura *et al.* (2003) investigated the rejection of organic CECs categorized as DBPs and pharmaceuticals using polyamide NF/RO membranes in bench-scale filtration experiments.

This study found that charged compounds could be rejected by more than 90%, regardless of other physicochemical properties. Although the charge of the CEC compounds was not analyzed in this study, CECs such as

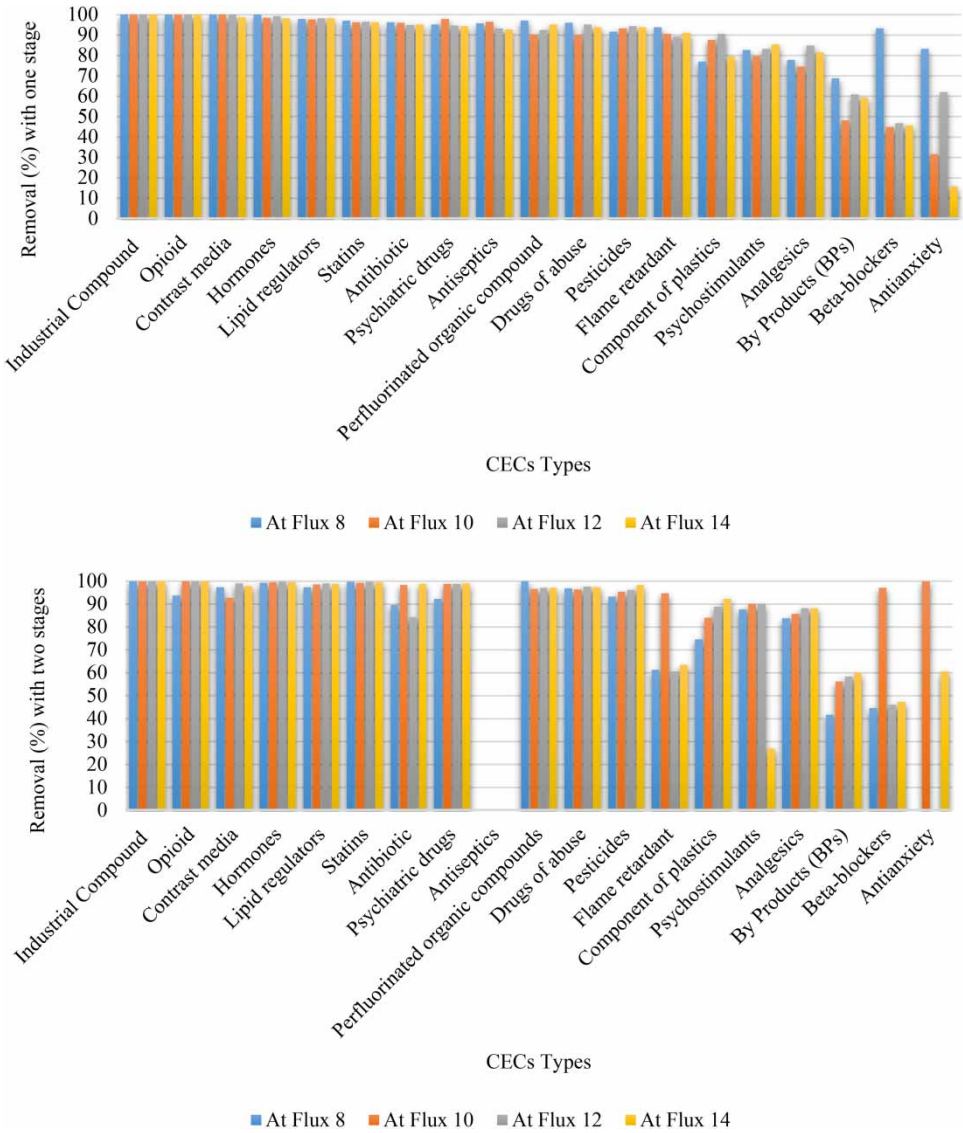

Figure 3 | Removal of CECs with different fluxes for phase one and phase two.

diclofenac, ibuprofen, sulfamethoxazole and triclosan, which are negatively charged, were rejected by more than 90% in both phases. In contrast, the rejection of noncharged compounds such as acetaminophen was found to be influenced mainly by their size. To assess the percent rejection of charged/ionic CECs, frequency distributions were plotted for observed RO rejection. Figure 4 shows the frequency of observed rejection for neutral and ionic/charged CECs. With few exceptions, charged/ionic CECs were rejected (<90%) by the RO membrane.

A membrane surface gains negatively charged properties usually due to the presence of sulfonic and/or carboxylic acid groups, which are deprotonated at neutral pH (Bellona *et al.* 2004; Verliefde *et al.* 2007a). Different pH conditions will substantially change the membrane surface charge. Studies have revealed that increasing pH can also increase the negative surface charge of membranes; thus, higher rejections, especially for negatively charged compounds, can be expected (Childress & Elimelech 2000; Tanninen & Nyström 2002).

Table 6 | DWQ SWRCB and NWRI risk-based human health criterion

		Phase one, RO permeate				Phase two, RO permeate			
CEC	**Criterion[a] (ng/L)**	**at Flux 8**	**at Flux 10**	**at Flux 12**	**at Flux 14**	**at Flux 8**	**at Flux 10**	**at Flux 12**	**at Flux 14**
17-β-estradiol	MRL: 5	ND	1.5	ND	ND	ND	ND	ND	ND
Estrone	320	ND	ND	ND	ND	ND	ND	ND	ND
Cotinine	1,000	51	130	61	79	42	47	31	34
Primidone	10,000	6	ND	ND	ND	5.1	2.5	2.8	3
Meprobamate	200,000	3.2	13	7.2	16	120	ND	150	7.5
Atenolol	4,000	210	260	160	210	270	150	200	130
Carbamazepine	10,000	5.9	12	8.6	8.6	12	7.6	6.7	6.3
TCEP	5,000	15	25	23	20	670	ND	4,800	1,100
DEET	200,000	150	120	100	110	120	81	68	32
Triclosan	50,000	5.3	4.1	8	8.7	200	260	340	440
PFOS	70[b]	7.8	26	20	13	ND	9.2	7.9	7.7

[a]NWRI (2013).
[b]DWQ (2017).

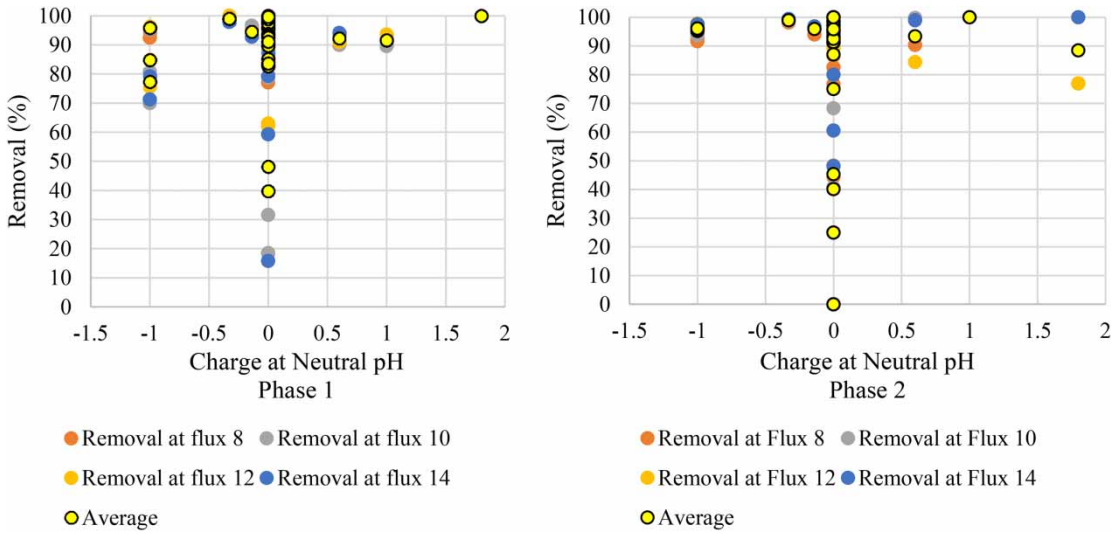

Figure 4 | Effect of surface charge on the removal of CECs for phase one and phase two.

Mass balance of CECs in the RO process

Tables 7 and 8 show the summary of the mass balance analysis using Equations (4) and (5). In an ideal situation with zero lab-analysis error, all M_{disc} values would be zero. With that being said, when calculating the mass of discrepancy using mass balance analysis via Equations (4) and (5), a positive M_{disc} value equates to a possibility of CECs accumulating within the system and being adsorbed to the solid phase.

Positive and negative results for M_{disc} (e.g. azithromycin and estrone for positive and NDMA and propranolol for negative) occurred for the following potential reasons. First, variations may have existed in the feed quality (i.e. CEC concentration in feed). Because this study had limited resources to analyze CECs in the feed sample, it assumed

Table 7 | Mass loss of CECs (M_{disc}) and percent of elimination due to sorption (R_{disc}) with 1-stage RO

	Flux 8		Flux 10		Flux 12		Flux 14	
Compound	M_{disc} (mg/d)	R_{disc} (%)	M_{disc} (mg/d)	R_{disc} (%)	M_{disc} (mg/d)	R_{disc} (%)	M_{disc} (mg/d)	R_{disc} (%)
Methadone	0.8	94.6	1.1	100.0	1.2	100.0	1.5	100.0
Primidone	0.9	83.8	1.1	78.8	1.6	100.0	1.8	100.0
Iopromide	−7.5	−20.5	45.7	100.0	53.8	99.8	62.0	98.5
Azithromycin	19.5	88.3	27.4	100.0	32.3	100.0	36.9	97.8
Perfluorooctane sulfonate (PFOS)	3.8	50.0	−0.3	−2.9	0.1	0.7	12.7	97.4
Salicylic acid	1,380.8	90.5	1,891.6	99.7	2,231.8	99.7	2,543.2	97.3
Ciprofloxacin	15.2	94.6	7.0	35.0	6.2	26.3	25.9	93.8
Estrone	2.3	51.0	4.4	78.2	4.6	69.5	6.5	83.8
Amoxicillin	66.8	98.6	84.3	100.0	99.5	100.0	93.3	80.3
N-Nitrosodiethylamine	0.1	71.0	0.2	100.0	−0.2	−69.8	0.2	79.6
Acetaminophen	−412.1	−54.0	241.6	25.5	778.0	69.5	796.6	60.9
17-b-Estradiol	0.5	31.7	1.3	70.4	1.9	90.4	1.5	59.0
Carbamazepine	5.0	89.0	2.7	38.6	6.7	80.8	4.6	47.7
Sulfamethoxazole	−11.5	−44.2	−9.3	−28.8	−28.8	−75.4	17.1	38.5
Caffeine	269.3	36.7	−1,229.2	−134.6	425.2	39.5	476.7	37.9
Atorvastatin	−5.4	−40.6	3.3	20.1	−1.1	−5.6	8.2	36.1
Gemfibrozil	−38.7	−35.1	39.5	28.9	58.9	36.5	55.0	29.1
TCEP	4.8	61.2	−1.8	−18.2	−3.8	−32.7	2.9	21.5
Naproxen	134.0	53.3	87.7	28.0	118.5	32.1	83.4	19.4
Atenolol	10.7	15.2	13.8	15.7	39.3	38.0	23.1	19.1
Cotinine	0.3	0.7	37.8	82.8	21.3	39.5	8.1	12.8
Triclosan	−0.1	−4.1	1.3	31.1	−0.9	−18.2	0.7	12.8
Trimethoprim	1.4	8.1	3.9	18.8	4.9	19.9	3.5	12.1
Fluoxetine	0.2	93.4	−0.5	−170.1	0.0	0.8	0.0	8.5
Testosterone	0.3	9.0	−0.3	−7.6	1.2	25.6	−0.5	−9.1
Diazepam	0.0	18.4	0.1	30.2	0.0	10.0	0.0	−13.5
DEET	−29.0	−57.1	1.3	2.0	0.7	0.9	−14.7	−16.9
Progesterone	0.4	53.1	−0.5	−59.8	0.2	16.5	−0.4	−29.8
1,4-Dioxane	−3.6	−18.1	−6.8	−27.6	−11.4	−39.2	−12.3	−36.3
Bisphenol A	−0.2	−5.1	−7.3	−122.3	−2.9	−40.8	−3.0	−36.8
Ibuprofen	168.2	49.6	−156.4	−37.1	−150.1	−30.2	−430.6	−74.1
N-Nitrosomorpholine	−0.2	−63.2	−0.4	−105.6	0.2	38.6	−0.5	−78.4
N-Nitrosodimethylamine (NDMA)	−0.1	−33.6	−0.9	−321.5	−0.2	−74.1	−0.3	−79.5
TCPP	6.0	27.9	−18.9	−70.8	−2.3	−7.2	−31.0	−84.4
Diclofenac	1.6	35.9	−3.8	−67.2	−4.9	−74.2	−6.7	−86.0
TDCPP	−14.5	−270.7	−20.3	−304.0	−43.9	−558.1	−15.5	−168.7
Meprobamate	−0.1	−17.2	0.1	15.4	0.2	22.9	−7.6	−830.4
Propranolol	0.0	97.3	−1.2	−60,291.5	−0.1	−4,478.8	−3.0	−105,278.1

Table 8 | Mass loss of CECs (M_{disc}) and percent of elimination due to the sorption (R_{disc}) with 2-stage RO

	Flux 8		Flux 10		Flux 12		Flux 14	
Compound	M_{disc} (mg/d)	R_{disc} (%)	M_{disc} (mg/d)	R_{disc} (%)	M_{disc} (mg/d)	R_{disc} (%)	M_{disc} (mg/d)	R_{disc} (%)
17-b-Estradiol	1.2	100.0	1.6	100.0	1.9	100.0	2.2	100.0
Azithromycin	15.2	81.3	24.3	100.0	23.9	81.6	34.4	100.0
Methadone	0.7	94.9	0.9	100.0	1.1	100.0	1.3	100.0
Estrone	3.8	99.7	5.0	99.4	6.0	99.7	7.0	99.7
Amoxicillin	56.6	98.5	74.1	99.0	89.7	99.6	105.1	99.4
Progesterone	0.6	98.3	0.8	97.1	1.0	97.9	1.1	97.8
Testosterone	2.6	97.0	3.3	96.7	4.0	97.9	4.7	97.4
Perfluorooctane sulfonate (PFOS)	6.5	100.0	8.2	97.3	9.9	97.7	11.6	97.1
Ciprofloxacin	12.2	89.4	16.2	91.4	14.0	65.7	23.7	94.3
Salicylic acid	372.3	28.8	1,559.8	92.7	1,818.3	89.7	2,145.0	90.1
Iopromide	28.3	90.9	34.2	84.4	46.2	94.8	51.5	89.9
Carbamazepine	3.4	71.4	5.5	88.9	6.4	85.1	7.7	87.8
Primidone	0.5	55.7	1.1	88.9	1.0	72.7	1.3	80.2
Fluoxetine	0.2	85.9	0.3	100.0	0.3	100.0	0.3	77.7
DEET	20.3	47.2	22.2	39.5	31.9	47.3	52.0	65.5
N-Nitrosodiethylamine	0.0	20.2	0.2	100.0	0.1	32.2	0.2	64.1
Diazepam	0.1	76.0	0.1	70.8	0.1	58.7	0.2	60.2
Cotinine	17.1	55.1	30.0	73.9	38.7	79.3	28.1	49.1
N-Nitrosomorpholine	0.1	43.2	−0.2	−49.2	0.3	58.1	0.3	47.3
Trimethoprim	4.4	31.1	6.5	35.1	7.9	35.9	10.2	39.1
Gemfibrozil	37.0	39.6	38.8	31.9	61.1	41.8	49.0	28.5
TCPP	11.8	64.9	10.7	45.3	−6.7	−23.5	7.5	22.4
Caffeine	517.5	83.2	651.8	80.4	814.0	83.4	187.5	16.4
Bisphenol A	−1.8	−43.1	−2.3	−42.7	−3.3	−52.5	1.2	16.2
TDCPP	0.6	13.7	0.6	9.5	−5.5	−77.6	0.3	3.7
Atenolol	22.8	38.2	36.0	46.2	26.8	28.5	0.8	0.7
Naproxen	−88.3	−41.4	−172.0	−62.0	20.3	6.1	−33.6	−8.6
Sulfamethoxazole	−1.0	−4.6	−3.6	–12.4	3.4	9.8	−8.0	−19.6
1,4-Dioxane	6.3	37.7	−5.7	−26.3	−11.1	−42.4	−8.0	−26.1
Ibuprofen	−321.9	−112.1	−263.7	−70.5	−15.4	−3.4	−184.3	−34.9
Meprobamate	−19.1	−4,202.5	0.5	81.0	−26.7	−3,740.1	−0.4	−42.7
Diclofenac	−1.3	−34.8	−6.5	−131.0	−4.1	−68.4	−4.4	−62.6
Atorvastatin	1.7	15.0	−43.7	−298.2	−2.3	−12.8	−17.4	−84.1
Acetaminophen	−34.9	−5.4	180.1	21.4	−473.8	−46.8	−3,056.0	−256.9
N-Nitrosodimethylamine (NDMA)	−0.4	−201.1	−0.6	−253.7	−0.8	−272.2	−0.9	−262.1
Triclosan	−4.2	−147.2	−6.6	−175.3	−10.7	−237.6	−18.9	−358.2
TCEP	−10.3	−153.5	−5.7	−65.0	−166.6	−1,585.2	−92.3	−748.0
Propranolol	−0.1	−9,578.8	0.0	100.0	−0.2	−8,415.6	−0.1	−3,175.9

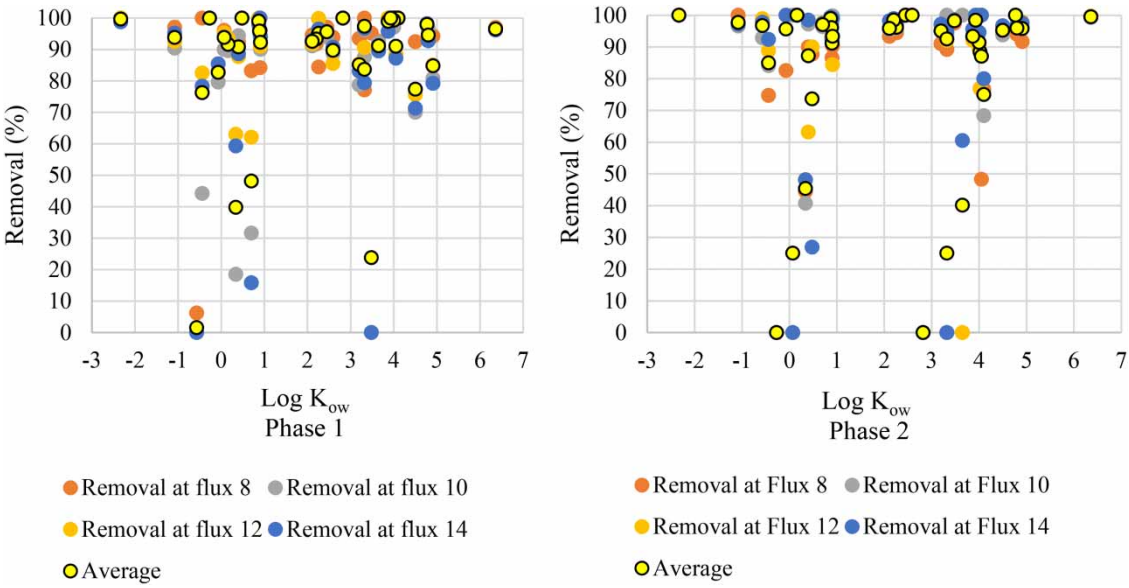

Figure 5 | Effect of Log K_{ow} on the removal of CECs for phase one and phase two.

that there were no feed chemistry variations and then analyzed one sample of primary effluent (i.e. MF feed) and one sample of MF permeate (i.e. RO feed), both of which were collected on the same day at the same time.

Another reason could be adsorption or desorption of CECs from the dissolved (i.e. aqueous) phase to the solid phase in the process. The solid phase in this study included the surface of the RO membrane, the concentrate and permeate stream piping, and, most importantly, suspended and deposited micro-particles on the concentrate side of the membrane. A negative value of M_{disc} in Tables 7 and 8 represents desorption, and a positive value of M_{disc} represents adsorption.

Furthermore, positive and negative M_{disc} values could be attributed to lab measurement errors. Tables 7 and 8 note varying laboratory procures such as 'The concentration indicated for this analyte is an estimated value above the calibration range.' Therefore, some level of error may have been introduced to the lab results. Measuring chemicals in the level of nanograms per liter can be a sensitive process that always comes with some uncertainties about quality control (i.e. result replicates).

Understanding the removal mechanism and relationships between controlling parameters in the RO system is key to optimizing CEC rejection. At the early stage of filtration in RO when the membrane is not ripe, the dominant mechanism for removal is the adsorption of nano-amounts of CECs into the membrane surface (Nghiem *et al.* 2004a, 2004b), until it reaches equilibrium. Preliminary removal could yield false results (Nghiem & Schäfer 2002). A cake develops on the surface of the membrane that decreases its pore size to below the nominal rating, thus improving removal (Nghiem et al. 2004a, 2004b; Xu *et al.* 2014), but later develops fouling. In addition to the pore size decreasing, this improvement in removal could also be due to the enhanced adoption capacity of the solid phase (e.g. fouling biofilm).

The adsorption mechanism correlates with solute–solid hydrophobic interactions (Nghiem & Schäfer 2002; Nghiem *et al.* 2002). Hydrophobic interaction between the solid phase, particularly the RO membrane, and solutes is one of RO's important rejection mechanisms. A membrane's hydrophobicity is typically characterized by its contact angle, whereas hydrophobicity of solutes can be correlated and quantified using the logarithm of the octanol-water partition (log K_{ow}). Molecules with log K_{ow} greater than 2 are referred to as hydrophobic. Octanol and water partition coefficient values are determined as logs, the ratio of the concentration in the octanol phase against the concentration in the aqueous phase at adjusted pH, such that the predominant form of the compound is unionized. Figure 5 shows the effect of Log K_{ow} on the removal examined CECs for phases of the test.

Hydrophobic properties have an influence on the sorption mechanisms. For instance, strong hydrophobic compounds such as aromatic pesticides, non-phenylic pesticides and alkyl-phthalates were highly rejected even by the lowest desalting membrane (Kiso *et al.* 2001). However, the retention decreases as the membrane is saturated and its ability for sorption is reduced. As studied by Braeken *et al.* (2005), hydrophobic molecules are rejected better than hydrophilic molecules after long-term operation.

In this study, hormones such as estrone and 17-β-estradiol, azithromycin and methadone, which have values of log K_{ow} >2, adsorbed to the solid phase and potentially followed this pattern. See the mass balance calculation and the results in Tables 7 and 8.

CONCLUSION

The effect of CECs on the public health and the environment has urged water managers to more actively implement strategies that remove these compounds not only from drinking water but also from the wastewater treatment process. Primary treatment is currently unable to eliminate all substances; therefore, it is usually followed by secondary treatment.

However, the innovative MF/RO treatment train generates a water source without secondary treatment and can still remove many CECs. By analyzing the RO concentrate stream, this study showed the viability of eliminating secondary treatment and efficiently preparing wastewater for reuse through this novel treatment train.

This study investigated the removal of 38 different CECs in the pilot scale with different applied fluxes. In the first phase (1-stage RO), the flux of 14 gfd showed a better rejection value of 95.2% when compared with those of other fluxes. In the second phase (2-stage RO), the flux of 12 gfd showed a better rejection value of 93.7% when compared with those of other fluxes. Statistical analysis revealed that there is no significant difference between different fluxes.

The results showed that 1-stage RO with a 55% recovery rate had a better removal rate of CECs when compared with 2-stage RO with a 80% recovery rate. As the concentration gradient of contaminants increased across the membrane at the higher recovery rate, the overall removal rate decreased for various compounds.

Azithromycin, hormones, carbamazepine, diazepam, gemfibrozil, atorvastatin, methadone and iopromide were removed the most effectively by RO in both phases. All these compounds have MW >200 g/mol and are also based on the log K_{ow}. All those CECs also have hydrophobic characteristics; therefore, the RO process was able to remove them efficiently. In contrast, NDMA, propranolol, acetaminophen and meprobamate were the least effectively removed, given their low MW (less than 200 g/mol).

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