EVALUATING MANAGEMENT AND DISPOSAL OF CECs IN WATER REUSE PROJECTS

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Abstract

Recycled water projects that include some form of potable reuse are becoming more common in the water industry. They are being built to help alleviate water shortages throughout the world by allowing the reuse of available water. Many of these systems utilize membrane processes to remove soluble and insoluble contaminants to produce high quality product streams for reuse. Despite the effectiveness of these systems, for those systems that employ reverse osmosis (RO), the generation of a concentrate stream is a major drawback that is a particular problem for inland facilities that cannot easily discharge this waste to the ocean. The presence of chemicals of emerging concern (CECs) in the concentrate could also be a significant underlying health consideration for final disposal of concentrate to the environment, be it to the ocean or inland disposal. This project focuses on understanding the best way to manage and dispose of concentrate streams containing high levels of emerging contaminants, and doing so in a manner that results in the least impact to the environment. The pilot work, just getting underway, will focus on producing RO concentrate from an MF system operating on primary effluent. This provides an opportunity to capture higher concentrations of CECs from a stream that has not undergone aerobic biological treatment and explore the removal efficiencies of RO under these more challenging conditions. Until now, the focus of direct/indirect potable reuse projects has been on the quality of the recycled water. This study begins to look at how CECs captured by the treatment process may be treated in some way before being released to the environment.

Introduction

The California drought has affected the available sources of water in one of the largest states in the United States with 37 million residents and over 400,000 km² of land area. The geography and climate are equally diverse, with central and northern coastal regions of the state receiving abundant rainfall (e.g., nearly 1700 mm/y) compared with the largely arid southern California region, averaging 250 mm of rainfall per annum, and where a large percentage of the population live. Because of the conditions in the arid areas, other sources of water must be developed and recycled water continues to be the biggest source of "new" water for the State. California has lead the nation in recycled water use for decades and the State set a goal of increasing the use of recycled water over 2002 levels by at least one million acre-feet per year (AFY) by 2020 and by at least two million AFY by 2030 (SWRCB, 2009). In 2009 the total volume of water reused was
669,000 AF per year, only 144,000 AF per year above 2002 values, meaning that significantly more recycled water use is in California's future. Most recycled water use to date has been applied to the agricultural sector, which makes sense considering that over 75% of water used in California goes to this sector. In the municipal sector experience has shown that the most cost effective approach to water reuse is ground water replenishment, rather than using recycled water to replace irrigation of urban landscaping, golf courses and cemeteries. This is because groundwater recharge projects typically can be significantly larger in scale, and generally result in lower infrastructure costs per AF.

This paper discusses the treatment approaches used for water replenishment systems and the evaluation of contaminants of emerging concern (CECs) that are rejected into the waste streams produced by these processes.

**Indirect Potable Reuse (IPR)**

Indirect potable reuse (IPR) is one of the water recycling applications that has developed, largely as a result of advances in treatment technology that enables the production of high quality recycled water at increasingly reasonable costs and reduced energy inputs. In IPR, municipal wastewater is highly treated and discharged directly into groundwater or surface water sources as environmental buffers (Leverenz et al., 2011), with the intent of augmenting drinking water supplies (planned IPR). The environmental buffer is a key component of an IPR system and provides an additional barrier for the removal of contaminants, such as organics and microbiological constituents. In planned IPR systems, as opposed to *de facto* reuse resulting from natural replenishment of treated water that is discharged to streams higher in a watershed, treatment ranges from conventional wastewater treatment, which includes the headworks, primary clarification, and a secondary biological process, to ‘full advanced treatment’ (FAT), a term introduced by the California Department of Public Health (CDPH) that encompasses reverse osmosis (RO), and an advanced oxidation process (AOP) applied to an oxidized wastewater (CDPH 2014).

The world famous Groundwater Replenishment System (GWRS) project undertaken jointly by the Orange County Water District (OCWD) and the Orange County Sanitation District (OCSD) is the largest IPR project of its kind in the world. It currently produces 100,000 AF per year of FAT effluent that is recharged into Orange County's Groundwater Basin. The project will soon undertake its final expansion to 130,000 AF per year. Just north of this plant in Los Angeles County, the Metropolitan Water District of Southern California and the Los Angeles County Sanitation Districts are in the early phases of developing a similar project that will have an initial capacity of 150,000 AF per year. There is a push in southern California to reduce the discharge of treated wastewater effluent to the ocean and rather convert this water into a reusable source, and these two projects are examples of how this trend is taking hold.

**Direct Potable Reuse (DPR)**

The major difference between IPR and DPR is the absence of the environmental buffer and in California, regulations for implementation of DPR are still in the early stages of development. In DPR treated water from a FAT facility would be discharged into the raw water supply immediately upstream of a water treatment plant or introduced into a potable water supply distribution system, downstream of a water treatment plant with or without an engineered storage
buffer. The target of engineered storage buffer is to satisfy sufficient capacity or buffer time (Tchobanoglous et al., 2011) to allow for the measurement and reporting of specific water quality parameters. DPR, has been effectively implemented in Namibia for more than 40 years and it has been used in Texas since 2013.

Contaminants of Emerging Concern (CECs) and Brine Management

CECs and effect on Human Health

Contaminants of emerging concern originate from industrial and domestic products such as pesticides, personal care products, preservatives, surfactants, flame retardants, and perfluorochemicals. These contaminants are also excreted by humans, for example pharmaceutical residues or steroidal hormones. CECs are also present as chemicals formed during wastewater and drinking water treatment, so called disinfection byproducts (DBPs). The Environmental Protection Agency (EPA) has defined CECs as “pollutants not currently included in routine monitoring programs” that “may be candidates for future regulation depending on their (eco)toxicity, potential health effects, public perception, and frequency of occurrence in environmental media” (EPA, 2008a). For wastewater to be part of the reuse system including the de facto reuse (Asano et al., 2007), wastewater constituents should be considered in the design of the treatment and recycled water systems.

To evaluate the effect of CECs on human health, pharmacology and toxicology of the Active Pharmaceutical Ingredients (APIs) must be analyzed to determine if it has an acceptable daily intake (ADIs). The ADIs are to be without pharmacological or toxicological effect with the exception of anti-cancer drugs and some antibiotics. The minimum dose producing the intended therapeutic effect is typically used as a basis to calculate the ADIs. Those values demonstrated no effect of concentration from the environmental exposure on human health (PNEC_{HHS}) from drinking water or sea life consumption. The PNECs were compared to predict environmental concentrations (PECs) calculated using the regional assessment models PhATETM for North America and GREAT-ER for Europe. Risk factors can be characterized as the ratio of the 90th percentile PECs to the PNEC_{HHS} (Cunningham, Binks, & Olson, 2009). The target CECs that will be considered in the analysis for this project are as shown in Table 1.

Evaluation of the environmental risk caused by CECs (most of which are pharmaceuticals) in secondary effluent or other treatment trains was carried out by means of the risk quotient (RQ), that is the ratio between the average pharmaceutical concentrations measured in the effluent and its corresponding "predicted no effect concentration" (PNEC) (EMEA, 2001). A criteria based on de Souza et al. (2009) and Hernando et al. (2006), was applied which stated that: RQ<0.1, low risk to aquatic organisms, 0.1≤RQ≤1, medium risk; RQ≥1, high risk. The occurrence of some pharmaceuticals in secondary effluent discharged into surface water may pose a medium–high (acute) risk to aquatic life. In addition, many other constitutions, even if their environmental risk was found to be low, are disposed of at high daily mass loads, which could contribute to negative
effects on aquatic organisms in the long term due to chronic and mixture toxicities. (Verlicchi, Al Aukidy, & Zambello, 2012)

For the removal of CECs, reverse osmosis (RO) is often used due to its effectiveness and ability to produce very high quality water. The process concentrates the removed contaminants into a brine concentrate stream that increases toxicity levels that require additional treatment (Romeyn et al., 2015). A common form used to resolve this issue has been to dilute the concentrate by thoroughly mixing the flow with other plant effluents, however it has been proven to provide no net improvement in environmental safety (Snyder et al., 2007). The most viable treatment options to destroy CECs and prevent them from returning to the environment have been proven to be UV/H₂O₂ and ozone-BAC. The UV advanced oxidation process (UV/H₂O₂ system) has been implemented for drinking water and wastewater treatment due to the amount of knowledge that has been attained. The system removes a broad range of CECs, but has the implementation issue of high power requirement to create conditions for advanced oxidation to occur. Further studies are required for other typical operating parameters to determine if high CEC levels need higher contact-time values (Romeyn et al., 2015).

Table 1. Target CECs

<table>
<thead>
<tr>
<th>Type</th>
<th>Pharmaceutical compound</th>
<th>MW</th>
<th>Chemical formula</th>
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<tr>
<td>Analgesics/ anti-inflammatories</td>
<td>Acetaminophen</td>
<td>151</td>
<td>C₈H₁₉NO₂</td>
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<td></td>
<td>Diclofenac</td>
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<td>C₁₄H₁₁Cl₂NO₂</td>
</tr>
<tr>
<td></td>
<td>Ibuprofen</td>
<td>206</td>
<td>C₁₃H₁₈O₂</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>230</td>
<td>C₁₄H₁₄O₃</td>
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<td></td>
<td>Salicylic acid</td>
<td>138</td>
<td>C₇H₆O₃</td>
</tr>
<tr>
<td>Antibiotic</td>
<td>Amoxicillin</td>
<td>365</td>
<td>C₁₆H₁₉N₃O₅S</td>
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<tr>
<td></td>
<td>Azithromycin</td>
<td>749</td>
<td>C₃₈H₇₂N₂O₁₂</td>
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<tr>
<td></td>
<td>Ciprofloxacin</td>
<td>331</td>
<td>C₁₇H₁₈FN₃O₈</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>253</td>
<td>C₁₀H₁₁N₃O₃S</td>
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<tr>
<td></td>
<td>Trimethoprim</td>
<td>290</td>
<td>C₁₄H₁₈N₄O₃</td>
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<tr>
<td>Beta-blockers</td>
<td>Atenolol</td>
<td>266</td>
<td>C₁₄H₂₂N₂O₃</td>
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<tr>
<td>Lipid regulators</td>
<td>Gemfibrozil</td>
<td>250</td>
<td>C₁₅H₂₂O₃</td>
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<tr>
<td>Psychiatric drugs</td>
<td>Carbamazepine</td>
<td>236</td>
<td>C₁₅H₁₂N₂O</td>
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<td></td>
<td>Diazepam</td>
<td>285</td>
<td>C₁₆H₁₃ClN₂O</td>
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<tr>
<td></td>
<td>Fluoxetine</td>
<td>309</td>
<td>C₁₇H₁₈F₃NO</td>
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<td>Hormones</td>
<td>Estrone</td>
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<td>C₁₈H₂₂O₂</td>
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<td></td>
<td>Testosterone</td>
<td>288</td>
<td>C₁₉H₂₈O₂</td>
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<td></td>
<td>17-α-Ethynylestradiol</td>
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<td></td>
<td>Progesterone</td>
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<td>Antiseptics</td>
<td>Triclosan</td>
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<td>C₁₂H₇Cl₃O₂</td>
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<tr>
<td>Contrast media</td>
<td>Iopromide</td>
<td>791</td>
<td>C₁₈H₂₄I₃N₃O₈</td>
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<td>Psychostimulants</td>
<td>Caffeine</td>
<td>194</td>
<td>C₈H₁₀N₄O₂</td>
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<tr>
<td>Component of plastics</td>
<td>Bisphenol A</td>
<td>228</td>
<td>C₁₅H₁₆O₂</td>
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<tr>
<td>Drugs of abuse</td>
<td>Cotinine</td>
<td>176</td>
<td>C₁₀H₁₂N₄O</td>
</tr>
<tr>
<td>Pesticides</td>
<td>DEET</td>
<td>191</td>
<td>C₁₂H₁₁NO</td>
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<tr>
<td>DBPs</td>
<td>NDMA</td>
<td>74</td>
<td>C₂H₆N₂O</td>
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<tr>
<td>1,4 Dioxane</td>
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<td>C₄H₈O₂</td>
<td></td>
</tr>
<tr>
<td>Atianxiety</td>
<td>Meprobamate</td>
<td>218</td>
<td>C₉H₁₈N₂O₄</td>
</tr>
<tr>
<td>Flame retardant</td>
<td>TCEP</td>
<td>250</td>
<td>C₁₀H₁₅O₆P</td>
</tr>
<tr>
<td>TCPP</td>
<td>327</td>
<td>C₁₉H₁₈Cl₃O₄P</td>
<td></td>
</tr>
<tr>
<td>TDCPP</td>
<td>430</td>
<td>C₁₀H₁₅Cl₆O₄P</td>
<td></td>
</tr>
<tr>
<td>HMG CoA reductase</td>
<td>Atorvastatin</td>
<td>558</td>
<td>C₃₃H₃₅FN₂O₅</td>
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<tr>
<td>Opioid</td>
<td>Methadone</td>
<td>309</td>
<td>C₂₁H₂₇NO</td>
</tr>
<tr>
<td>Hydantoin</td>
<td>Phenytoin (Dilantin)</td>
<td>252</td>
<td>C₁₅H₁₂N₃O₂</td>
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</tbody>
</table>

**Brine Management**

The FAT system employs RO, which therefore results in the need for brine management. In the coastal regions, brine typically is discharged to the ocean using an ocean outfall. By comparison, an inland location where a brine line to the ocean is not available or in coastal location where ocean discharge is not allowed or is restricted, other concentrate disposal options need to be considered. These could include surface water discharge (though probably unlikely); discharge to a wastewater collection system; deep well injection, and additional concentration followed by lined evaporation ponds to create a zero liquid discharge (ZLD) system. The costs associated concentrate disposal are site specific and vary depending on the characteristics and volume of brine that must be managed and the type of disposal option that is ultimately selected.

Management of CECs within RO concentrate from FAT systems has not received much attention to date. The focus has been on minimizing CECs remaining in the product stream to be recharged to a groundwater aquifer, and understandably so. This work is focused on the concentrate stream and evaluating the treatability of CECs in RO concentrate and the environmental benefits that this might have overall.

**Cost and Energy Saving via Innovative Treatment Train**

*Comparison between energy required for CAT and secondary treatment*

The cost and energy required for water reuse is related to the cost and energy of FAT, piping, pumping and brine management. Raucher and Tchobanoglous (2014) reported the energy required by the FAT and the benefit of eliminating the aerobic treatment train (Activated Sludge). The values for FAT energy consumption range between 1050 kWh/AF and 1140 kWh/AF (Raucher and Tchobanoglous, 2014), with the main energy requirement being for the secondary treatment processes. Raucher and Tchobanoglous, (2014) also showed that for a
module size of about 5 mgd, there was not much variation in energy usage by secondary
treatment processes. If the activated sludge process could be removed from the treatment train,
the cost and energy would reduce significantly.

Pilot Testing on Primary Effluent Using IMANS® Configuration

Background

There is a collaboration between academia (Cal Poly Pomona), government agencies (Bureau of
Reclamation), private sector (Carollo Engineers), and a local agency in Southern California
(Inland Empire Utilities Agency) to study the water reuse trains in IPR and DPR. The objective
of the study is to explore the feasibility of an innovative FAT system, and to understand the fate
and transport of CECs in aqueous forms in various systems of the treatment train.

In southern California, water agencies have been implementing IPR to replenish groundwater
basins for decades. The process has become more cost effective and can have a much larger
impact on the water supply portfolio. This is a suitable system in regions where the majority of
water used is imported, because these projects tend to be larger in scale than typical Title 22
irrigation projects.

The Inland Empire Utility Agency (IEUA) has applied the IPR system by using tertiary filtered
effluent to recharge the Chino Basin. IEUA has considered an advanced treatment option that
utilizes microfiltration (MF) and RO treatment of secondary effluent and an advanced oxidation
process (APO) treatment to produce higher quality water that could be injected directly into the
groundwater basin or used in spreading basins without the requirement for diluent water.

Direct, non-biological MF of primary effluent is a novel approach to wastewater processing that
has been tested at a number of locations over the last decade, including in the USA. The MF
treated primary effluent may be treated further before discharge or reuse, depending upon the
location or intended application. Because MF does such a good job of removing suspended
solids (including bacteria and other microorganisms), downstream treatment can include RO
treatment. RO could be followed by AOP treatment to address specific compounds such as
pharmaceuticals and personal care products (PPCPs) and CECs, to yield a very high quality
water. The effluent quality from this combination will be comparable to the quality obtained
when starting with secondary effluent, but at significantly reduced capital and operating costs
due to the elimination of the energy intensive activated sludge process. Figure 1 presents the
novel approach to producing a high quality effluent for IPR that incorporates MF treated primary
effluent and a second anaerobic digestion process (called the IMANS® configuration). As can be
seen in the IMANS® configuration there is no activated sludge secondary treatment step, but
rather primary treatment followed directly by MF, RO and UV/AOP. In this configuration,
ergy rich organic material that passes through the MF membrane will be rejected by the RO
membrane and concentrated into a smaller stream that can be treated using a high rate anaerobic
process, or other system to recover energy. Furthermore, the solids in the MF backwash stream
can be recovered and blended with the primary solids to yield additional biogas production in the
solids handling conventional anaerobic digestion process. Digestion of only primary solids leads to greater solids destruction, higher biogas production, better solids dewatering, lower polymer usage, and ultimately about 50-percent less biosolids for disposal.

Previous testing of MF on primary effluent in southern California has been successfully demonstrated at the Orange County Sanitation District (OCSD) and at the City of Corona. At OCSD, two projects were undertaken. The first, carried out at OCSD's Plant No. 1, included most of the IMANS® treatment configuration (MF, RO and the UASB reactor). The MF unit treated about 30 gpm of primary effluent and the study lasted about 18-months. In follow up work, a 200 gpm MF demonstration scale project was carried out utilizing two full-scale membrane racks, each containing 32 membrane elements, and it operated successfully on primary effluent for more than 2-years. The work at the City of Corona was carried out at treatment Plant 2, and a 6.5-gpm MF pilot unit was operated on primary effluent also for about two years. Periodically, MF permeate was treated in a downstream nanofiltration (NF) pilot unit.

**Purpose and Objectives of Pilot Test**

The overall purpose of this pilot plant project is to determine the feasibility of producing a high quality RO permeate stream suitable for direct injection into a groundwater basin. It is understood that post treatment of the RO permeate with UV/AOP would be needed to meet Regulatory Requirements, and such processes may be added to the pilot configuration if timing and budget considerations are suitable. The initial phase of pilot testing is expected to last between 6 - 9 months and specific objectives of the testwork include:

1. Demonstrate that the MF pilot unit can operate on primary effluent from the Carbon Canyon Wastewater Reclamation Plant, and achieve similar flux, recovery and cleaning requirements as obtained recently at the City of Corona.

2. Demonstrate stable performance of the MF pilot unit in combination with a downstream RO pilot unit.

3. Determine the performance of the RO pilot unit and the membrane cleaning requirements.

4. Determine the chemical make-up of the RO permeate stream and the requirements for downstream UV/AOP treatment to meet the Regulations for direct injection of the product water.

5. In conjunction with Cal Poly Pomona determine the treatment alternatives that could be considered for the concentrate stream from the RO unit; to recover energy and/or manage the CECs present in the stream.
Figure 1. The IMANS® Configuration utilizes MF treated Primary Effluent for Producing High Quality Recycled Water at lower cost

Pilot System Description

Primary treated effluent from the Carbon Canyon plant will be transferred to the pilot plant site. Residual streams (product and backwash streams) from the pilot plants will be directed to a drain near the headworks, for return to the main treatment plant.

A schematic of the proposed pilot plant configuration is shown in Figure 2. Approximately 20-gpm of primary effluent will be pumped to the pilot plant site from an existing collection box near the primary clarifiers. Ferric chloride, or a similar coagulant, will be dosed into the primary effluent just downstream of the transfer pump as a pretreatment ahead of the MF pilot unit. Mixing will be achieved in the transfer pipe and the travel time will allow for about 8 minutes of coagulation time.

The MF pilot plant will be a Pall Corporation Inc. (Pall) pilot unit, fitted with up to four full-scale modules, that will operate in an outside-in configuration. Each module will contain 538 square feet of membrane area. The membrane material will be polyvinylidenefluoride (PvDF) with a nominal pore size of 0.1 micron. The Pall MF pilot system is a fully automated membrane system designed with a range of capacity and capability intending to be applied to a wide range of process conditions. An industrial computer and a PLC will control the operation of the system during the pilot study. The system will also be monitored and controlled remotely through a wireless cellular router and remote access software. The pilot unit also includes a hot water
heater that will be fed with potable water and self-contained chemical pumps for the membrane cleaning cycles.

Initially, the MF unit will be set to produce approximately 13 gpm of product. The product water will be fed to an RO feed tank, with a capacity of about 500 gallons, that will provide some storage ahead of the RO pilot unit for when the MF unit goes into a backwash cycle. A small dose of chlorine will be added to the RO feed tank to create 2 to 3 mg/L of chloramine residual. Backwash water from the MF unit will be discharged to a drain line that will flow to a collection point that returns flow to the Carbon Canyon plant headworks.

The RO pilot unit was provided by the US Bureau of Reclamation. This unit will take about 12 gpm of feed from the RO feed tank and then boost the pressure to between 150 and 200 psi. Anti-scalant will be added to the RO feed stream ahead of the high pressure pumps. The RO unit will be fitted with both 4-inch and 2.5-inch membrane units arranged in two-stages to achieve a recovery of around 85%. Permeate from the RO unit will be collected for sampling and the remainder of the stream will be blended with the RO concentrate and directed to the common drain line to the plant headworks. If the RO unit has to be shut down, the unit will be flushed with RO permeate water from a 150-gallon flush tank (not shown on Figure 2) first.

![IEUA Pilot Plant Schematic](image)

**Figure 2. Schematic of Pilot Plant Arrangement**

Feed, concentrate and product streams from the RO pilot will be sampled for CECs to determine the removal efficiency of the RO membranes. The use of primary effluent as the feed source for the pilot is expected to provide higher concentrations of CECs in the RO feed, allowing for greater contrast between the feed and product stream concentrations and therefore better resolution of the results. This will help with the assessment of the membrane rejection capabilities of individual CECs.

Samples of RO concentrate will be evaluated for treatment of the organic material as a means to recover energy and simultaneously destroy CECs and control the discharge of such substances back to the environment.
Acknowledgements

The authors would like to extend a special thank you to Yatziri Enriquez, California State Polytechnic University, Pomona; Jeremy Chok, California State Polytechnic University, Pomona; Brian Noh, M. S., P.E., Senior Associate Engineer, Inland Empire Utilities Agency.

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