



Energy Research and Development Division

FINAL PROJECT REPORT

DPRShield Water Treatment System for Failsafe Low-Energy Direct Potable Reuse

Gavin Newsom, Governor May 2023 | CEC-500-2023-014

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Contract Number: EPC-16-009

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ACKNOWLEDGEMENTS

This project was made possible through the California Energy Commission program, Electric Program Investment Charge, which provided funding for the advancement of energy efficiency for California's food and beverage manufacturing industry. Support from the California Energy Commission provides companies like Porifera the opportunity to bring cutting-edge research to commercial scale where benefits can be realized for private industry and the public at-large. Partnerships created through the EPIC program provide small companies with the chance to collaborate with industry to explore research concepts. This collaboration enables discovery of practical solutions for industry and lends brand-name credibility to the innovations of small businesses. Porifera is thankful to our study partners at Orange County Water District, Stanford University, and CDM Smith, each of whom demonstrated professionalism and persistence throughout the project. We'd also thank the Plant Operations, Maintenance, and Laboratory staff, as well as Mehul Patel, Dr. Ken Ishida, and Dr. Julio Polanco at the Orange County Water District, Farid Ramezanzadeh and Ray Busch with the City of Hayward Water Pollution and Control Facility, and Richard Danielson and Jim Truscott at Biovir Laboratories. Porifera is grateful for the opportunities provided by the California Energy Commission to further the development of this technology for wideranging commercial use. This project provided the engineering team the chance to define and solve processing challenges and discover solutions applicable across industries.

PREFACE

The California Energy Commission's Energy Research and Development Division supports energy research and development programs to spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution and transportation.

In 2012, the Electric Program Investment Charge (EPIC) was established by the California Public Utilities Commission to fund public investments in research to create and advance new energy solutions, foster regional innovation and bring ideas from the lab to the marketplace. The California Energy Commission and the state's three largest investor-owned utilities—Pacific Gas and Electric Company, San Diego Gas & Electric Company and Southern California Edison Company—were selected to administer the EPIC funds and advance novel technologies, tools, and strategies that provide benefits to their electric ratepayers.

The Energy Commission is committed to ensuring public participation in its research and development programs that promote greater reliability, lower costs, and increase safety for the California electric ratepayer and include:

- Providing societal benefits.
- Reducing greenhouse gas emission in the electricity sector at the lowest possible cost.
- Supporting California's loading order to meet energy needs first with energy efficiency and demand response, next with renewable energy (distributed generation and utility scale), and finally with clean, conventional electricity supply.
- Supporting low-emission vehicles and transportation.
- Providing economic development.
- Using ratepayer funds efficiently.

DPR Shield Water Treatment System For Failsafe Low-Energy Direct Potable Reuse is the final report for the Advance Wastewater Treatment Using Forward Osmosis to Produce High Quality Water project (Contract Number EPC-16-009) conducted by Porifera, Inc. The information from this project contributes to the Energy Research and Development Division's EPIC Program.

For more information about the Energy Research and Development Division, please visit the <u>Energy Commission's research website</u> (www.energy.ca.gov/research/).

ABSTRACT

Potable water demand in California is expected to grow, especially as droughts and water shortages are likely to become more common. Compared to other new water sources, potable reuse of water requires less energy, but is not widely used because of the advanced treatment required and negative public perception. DPRShield is a new low-energy, dual-barrier water treatment system for potable reuse that removes trace contaminants through two membranes—forward osmosis and reverse osmosis—and includes a dye marker in the draw loop between the two membrane barriers that enables the system to detect even the smallest breaches. If one of the membrane barriers is breached, a third barrier, the "Breach-Activated Barrier," is activated and pushes the contaminants away from the clean water stream with a pressure differential.

A pilot study at Orange County Water District demonstrated that the DPRShield technology produces permeate with excellent water quality from highly contaminated and often variable-quality feed water. The DPRShield was used to extract water from the existing reverse osmosis concentrate produced at the Orange County Groundwater Replenishment System. The project produced water quality comparable to the full-scale system reverse osmosis permeate; and generated high quality permeate with respect to all contaminants examined (organic contaminants, disinfection biproducts, and other regulated and unregulated compounds) using water with a contaminant level seven times higher than the feed water into the full-scale reverse osmosis system. The results demonstrated that DPRShield required 70 percent less energy than desalination, 33 percent less energy than competing direct potable reuse technologies, and up to 50 percent less energy than long-distance state water project transfers.

This new paradigm in water reuse provides evidence that the purification system works as designed and provides a counterpoint to negative public perception. The results are promising and further demonstrations and design improvements of the DPRShield technology will be needed before ready for sale to early adopters for commercial use. In addition, for municipal direct potable reuse, further work will be required to satisfy regulatory requirements.

Keywords: water reuse, direct potable reuse, indirect potable reuse, forward osmosis, reverse osmosis, real-time monitoring

Please use the following citation for this report: Desormeaux, Erik, et al. 2020. *DPR Shield Water Treatment System For Failsafe Low-Energy Direct Potable Reuse*. 2020. California Energy Commission. Publication Number: CEC-500-2023-014.

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EXECUTIVE SUMMARY

Introduction

Water has become a scarce resource in many arid regions of the world, including California. Agricultural, industrial, residential, and other users often share local and/or statewide water resources, and the pressure to conserve, reuse, and find alternative sources of water increases as demand continues to grow and droughts occur. Conservation requires the least energy of the three options; however, it will not be sufficient to meet demand, leaving reuse and alternative sources to fill the gap in California's diversified water resource portfolio.

The demand for potable water is expected to grow as California's population grows. Coupled with the expected increase of droughts, population growth will tax traditional potable water resources. California's main sources for new potable water supplies are importing water over long distances, desalination, and two types of reuse: indirect potable reuse and direct potable reuse.

Indirect potable reuse has been successful in parts of California. However, its development is limited by the availability of aquifers (or surface water reservoirs if allowed in the future) into which to inject water that has been purified from wastewater and mixed with other water for months or years before being pumped out of wells (or reservoirs), disinfected, and sent to the tap.

Direct potable reuse has broader applicability than indirect potable reuse. This method purifies wastewater to drinking water quality without the use of a groundwater aquifer or surface water reservoir and sends purified water directly to a municipal potable water system. Although direct potable reuse can effectively address California's potable water needs by providing a new source of water that can be implemented anywhere, with less energy use than seawater desalination and water transfers, California has not permitted a direct potable reuse project, even after years of study. Negative public perception and public and regulatory concern over perceived public health risks have been the primary hurdles to permitting.

Real-time detection and fail-safe operation are key features that would allow municipal water providers to overcome regulatory barriers to enable direct potable water reuse.

Project Description and Goals

DPRShield is a new low-energy, dual-barrier water treatment system for potable reuse that addresses public and regulatory concerns and impressions by enabling real-time detection of breaches and by ensuring fail-safe removal of pathogens and improved rejection of trace contaminants. It does this by utilizing two tight membrane barriers to remove trace contaminants, includes a dye marker between these two barriers that enables the system to detect even the smallest breaches in real time, and activates a third barrier to clear contaminants from the clean water stream in the event of a breach.

The DPRShield process, (1) combines forward osmosis with reverse osmosis; (2) adds a dye marker into the draw loop between the two processes so the marker is continuously recycled; (3) operates with a higher pressure within the loop than the process streams outside the loop, pushing the dye through any breaches that occur between the membrane barriers and the draw loop to signal rapid, high resolution, real-time detection; and (4) in the event that one of the membrane barriers is breached, activates a third barrier—the Breach-Activated Barrier illustrated in Figure 1—and pushes the contaminants away from the clean water system with hydrostatic pressure.



Figure 1: Ensuring Purity with Breach-Activated Barrier Technology

Source: Porifera, Inc.

The project met the following goals:

- Demonstrated DPRShield is feasible and will result in a reliable and cost-effective solution for water and wastewater treatment for potable water reuse.
- Demonstrated increased energy savings and water volumes at pilot scale for direct potable reuse at a municipal wastewater treatment facility.
- Demonstrated unprecedented pathogen removal using Breach-Activated Barrier technology with real-time high-resolution membrane integrity monitoring and contamination prevention (that is, high log removal credits using low energy membranes).

The project also met its goals to:

• Facilitate regulatory approval of water reuse projects by improving public health safeguards in direct potable reuse and indirect potable reuse.

• Reduce the electrical energy, chemicals, maintenance, and overall cost of potable reuse of wastewater.

The successful demonstration of the technology at scale during the project will accelerate broad technology adoption of DPRShield across California, resulting in energy savings and more water reuse.

Project Approach

Porifera piloted DPRShield system at Orange County Water District (OCWD), a municipal partner site, in collaboration with Stanford University and CDM Smith.

The approach was planned in partnership with OCWD staff to address the goals and objectives of the district's planned expansion to reuse more water at its Groundwater Replenishment System facility. The resulting approach separated the planned testing into three phases, each of which contained planned performance and water quality assessments.

Project Results

Porifera demonstrated DPRShield as a successful low-energy technology that can produce a high-quality forward osmosis/reverse osmosis permeate out of highly contaminated and often variable-quality feed water.

The study demonstrated that the DPRShield system required 70 percent less energy than desalination, 33 percent less energy than competing direct potable reuse technologies, and up to 50 percent less energy than long distance state water project transfers.

DPRShield generated this high quality permeate with respect to the levels of all contaminants examined: organic contaminants, disinfection byproducts, and other regulated and unregulated compounds of interest evaluated by Stanford University and OCWD despite treating water with approximately seven-fold higher contaminant levels than what enters Orange County's Groundwater Replenishment System. Spiking of MS2 coliphage, a commonly used surrogate for human virus, demonstrated the effectiveness of the Breach-Activated Barrier inherent to the operation of DPRShield, as it successfully pushed the MS2 coliphage away from the clean water stream during testing.

Overall, the results indicate that the DPRShield system can serve as a robust barrier to the passage of salts, bulk organic matter, organic contaminants, and disinfection byproducts and their precursors. Thus, DPRShield treatment of reverse osmosis concentrate could be a valuable tool to enhance water recovery at centralized facilities, without jeopardizing the quality of the potable product water. Real-time detection of even the smallest membrane breach and fail-safe operation that multiple membranes provide present a new paradigm in water reuse systems, providing evidence that the purification system works as designed, which would lead to greater public confidence in the process and in potable water reuse.

Technology/Knowledge Transfer/Market Adoption

The Orange County demonstration enabled Porifera to generate data on the DPRShield's efficient technology to share with customers. Porifera designed outreach and educational tools and materials including presentations, posters, and handouts to inform stakeholders of the technology and facilitate penetration in the marketplace. These materials were provided for in-person tours and presented at multiple conferences. The project team also published papers and articles in scientific journals and industry trade publications and will continue to do so. Commercial-scale demonstrations showed Porifera's ability to scale up and support industry users' operational needs that will benefit wider technology adoption. The data was shared with the US Bureau of Reclamation, as well as with engineering firms that are on the forefront of leading water reuse adoption in California such as CDM Smith, Corollo Engineers and Greely Hansen. More extensive testing and further demonstrations will be needed to move forward with technology adoption. Orange County Water District is interested in continuing to follow progress and demonstration.

Benefits to California

Employing DPRShield technology for potable reuse to address California's increased demand and water shortages will make California cities more drought resilient and help them remain operational even during periods of high demand for local and statewide water resources. DPRShield can be employed in areas served by either centralized treatment facilities or decentralized satellite treatment facilities for potable and other high-quality water uses.

DPRShield provides significant reductions in energy use, carbon dioxide emissions, and costs compared to more energy-intensive alternatives. Based on the assumptions and estimates derived from this project, implementing DPRShield technology at scale could offset on the order of 200,000 to 600,000 megawatt-hours per year and 60,000 to 200,000 metric tons of carbon dioxide emissions.

CHAPTER 1: Introduction

The Problem

Water has become a scarce resource in many arid regions around the world, including California, where agricultural, industrial, residential, and other users often share local and/or statewide water resources. As droughts occur and demand grows, the pressure to conserve, reuse, and find alternative sources of water increases. While conservation requires the least energy of the three options (Cooley, 2013), it will not be sufficient to meet demand. Reuse and alternative sources, such as increased water imports and desalination, are expected to be part of California's diversified water resource portfolio. This report specifically discusses a new technology for reusing municipal wastewater as a resource for potable water.

Potable water demand in California is expected to grow with population growth, especially because droughts are likely to become more common and tax traditional water resources (Diffenbaugh, 2015). The main sources for new water supplies in California are importing water over long distances, desalination, and reuse. There are two types of reuse:

- Indirect potable reuse (IPR) via groundwater recharge is the purification of wastewater to drinking water quality followed by injection or percolation of the purified water into a groundwater aquifer. In the aquifer, the purified water mixes with other groundwater for months or years before it is pumped out of a well, disinfected, and sent to the tap.
- Direct potable reuse (DPR) is the purification of wastewater to drinking water quality without use of an environmental buffer such as a groundwater aquifer or surface water reservoir. The purified water is sent directly to a municipal potable water system.

Implementation of IPR in Southern California has already provided a new source of potable water. It has reduced the energy required to meet water demands by offsetting pumping water from Northern to Southern California and reducing the need for more energy-intensive seawater desalination plants in Southern California (NRDC, 2004). Development of IPR is, however, limited by the availability of aquifers into which purified water can be injected, and few ideal locations remain.

Although DPR has broader applicability than IPR and may use less energy, California has not yet permitted a DPR project, even with municipalities having studied DPR projects for years. A primary hurdle is the public and regulatory concern over the public health risks associated with implementing DPR, which previously has been called "toilet

to tap." This concern is perpetuated by the lack of real-time, fail-safe methods to ensure that contaminant barriers are intact and performing as designed. Due to this lack of real-time, fail-safe methods and other data, regulators are opting for further study of DPR options rather than permitting them. Regulators continue to permit IPR projects despite IPR being more energy-intensive due to the energy needed for the treatment process combined with additional pumping energy needed for aquifer injection and well extraction.

Additionally, some existing IPR projects would benefit from extracting more potable water out of their existing municipal wastewater resources. Therefore, there is interest in identifying new technologies that can maximize reuse while minimizing energy use and costs.

The Solution

Porifera demonstrated DPRShield as a new technology for reuse applications that (1) adds an additional contaminant barrier to protect public health, (2) provides real-time monitoring to ensure that the barriers are performing as designed, (3) provides additional protection activated when barrier breaches occur (Breach-Activated Barrier technology), and (4) requires 40 percent to 50 percent less energy than desalination, 33 percent less energy than competing direct potable reuse technologies, and up to 50 percent less energy than long-distance state water project transfers.

Project Team and Site Selection

Porifera Overview

Serving as lead investigator, Porifera is a San Leandro, California-based company, which manufactures proprietary forward osmosis membranes and provides process solutions to a variety of industries. Porifera's innovative forward osmosis-based solutions enable users to efficiently remove water and (1) reuse high purity water and minimize waste or (2) concentrate valuable products to enable savings in shipping and storage. This unique technology facilitates the reduction of water waste, improvements to water reuse, and more efficient processing solutions to create better products using less energy.

Forward osmosis (FO) is the osmotically driven purification of water or concentration of products using a semi-permeable membrane. Water molecules migrate across the membrane by diffusion into a salt (draw) solution. Because FO is chemically driven by osmosis, only a small input of energy is needed to pump water across the membrane. Porifera's solutions combine forward osmosis technology with reverse osmosis (RO) for recovery of the draw solution.

Although FO has been studied for decades, it has only recently obtained broader commercial adoption. FO has unique advantages because it can operate reliably when processing challenging liquids that quickly clog or foul other types of membranes such as RO. Previous versions of FO technology were large and expensive systems that did not operate efficiently. Porifera has made advancements in membrane development and module design that address the cost, footprint, and performance constraints of existing treatment technologies. Porifera's patented DPRShield technology demonstrated in this project is unique to forward osmosis processing, providing extra protection from contaminants that fosters greater confidence in wastewater quality and its reuse.

Orange County Water District

Orange County Water District is at the forefront of municipal wastewater reuse in California and the world. It currently produces 100 million gallons per day (mgd) of purified water at its Groundwater Replenishment System (GWRS) advanced water purification facility (AWPF), the largest potable reuse plant in the world. OCWD's approach to potable reuse and advanced treatment train has been replicated throughout the world.

Stanford University

Porifera worked with Dr. William Mitch and his research group at Stanford University. Dr. Mitch is an expert researching DPR and key emerging contaminants.

CDM Smith

Porifera engaged CDM Smith to perform independent measurement and verification for the pilots, working with Greg Wetterau, BCEE, from CDM Smith, a lead expert on IPR and DPR projects, including the City of San Diego IPR demonstration facility and the operating emergency IPR facility in Cambria, California. CDM Smith is an engineering and construction company that provides solutions in water, energy, transportation, and facilities projects for government and private clients. The employee-owned CDM Smith was founded in 1947 and has more than 5,000 employees worldwide.

The project team is presented in Figure 2.

Project Site

The Hayward Water Pollution Control Facility, a wastewater treatment plant that has implemented multiple advanced technologies to improve energy use, was originally chosen as the demonstration site. Although initial testing using samples collected at this facility were promising, further pilot testing was not performed at the facility for a variety of management, priority, scheduling, and technical reasons.

Porifera ultimately chose OCWD, which had communicated that this project was a high priority with potential for full-scale implementation, if successful, and which was also awarded a grant from the U.S. Bureau of Reclamation to study Porifera's FO- and RO-based DPRShield system.



Source: Porifera, Inc.

Project Goals and Objectives

The objectives of this agreement were to:

- Demonstrate DPRShield is feasible and will result in a reliable and cost-effective solution for water and wastewater treatment.
- Demonstrate increased energy savings and water volumes at pilot-scale for potable reuse at a municipal wastewater plant in a disadvantaged community.
- Demonstrate unprecedented pathogen and chemical removal using Breach-Activated Barrier technology with real-time high-resolution membrane integrity monitoring and contamination prevention (that is, high log removal credits using low energy membranes).

The goals of this project were to:

- Improve public health safeguards in DPR and IPR, facilitating regulatory approval of water reuse projects.
- Reduce the electrical energy, chemicals, maintenance, and overall cost of potable reuse of wastewater.

The pilot demonstration at Orange County Water District was intended to help accelerate adoption of DPRShield across California. Broad adoption of this technology would result in energy savings and more water reuse, and as such be beneficial to California ratepayers and society at large. The following chapters detail the study process, discuss results, highlight how the technology is being shared, make recommendations, and discuss benefits to California ratepayers.



Figure 3: Site Visit to OCWD GWRS

California Energy Commission Project Manager and Porifera Principal Investigator visiting the pilot at Orange County Water District.

Source: Porifera, Inc.

CHAPTER 2: DPRShield Description and Theory

Introduction

DPRShield is the trade name for an integrated system that (1) combines a forward osmosis (FO) treatment process with a reverse osmosis (RO) treatment process, (2) adds a dye or other marker into the internal draw loop between the FO and RO processes, and (3) operates with the internal draw loop at a higher pressure than the FO feed and RO permeate streams so that the dye will be rapidly discharged into these streams if a breach occurs. Figure 4 shows an illustration of the DPRShield Process.



Figure 4: Simple Illustration of DPRShield

Schematic of DPRShield System with Breach-Activated Barrier technology under normal operation (a) and when breach is detected (b).

Source: Porifera, Inc.

Although there are companies working on developing new monitoring tools, existing water quality instruments do not detect emerging contaminants or pathogens in real time. Instead, samples are sent to a lab for analysis delaying both detection and responses. Instead, conductivity, total organic content (TOC), turbidity, and other water quality parameters are used as surrogates of contaminant removal. While they can be monitored in real time, it is easily argued that this monitoring is low resolution compared to using high concentrations of a dye as a surrogate.

In DPRShield, the dye can be (1) monitored in real time, (2) used to rapidly detect breaches in *membrane* integrity, and (3) correlated to pathogen rejection and emerging contaminants with a degree of confidence.

DPRShield also adds an additional pathogen rejection mechanism called Breach-Activated Barrier. This mechanism is inherent to system operation and acts as a fail-safe method to ensure pathogens and emerging contaminants are rejected even when significant breaches happen, a common occurrence in large-scale systems that contain hundreds or thousands of membranes.

If a significant breach occurs in the first membrane barrier (FO), this Breach-Activated Barrier is automatically activated by the breach itself, forcing contaminants away from the purified water. Figure 5 shows an illustration of the Breach-Activated Barrier.



Figure 5: Simple Illustration of Breach-Activated Barrier

Source: Porifera, Inc.

When a breach occurs, a small portion of the draw solution will be pushed via pressure through the breach into the feed solution because the hydrostatic pressure is higher in the draw channel than in the feed channel across the entire membrane surface. Pilot testing included tests to confirm that this mechanism excludes pathogen surrogates (for example, MS2) after membrane breaches are intentionally created within the FO elements tested.

This mechanism is different than typical membrane rejection and is not possible with filters or separation technologies that are pressure driven. It is only possible with filters that are driven via osmotic pressure combined with a hydrostatic pressure differential that is pushing in the opposite direction of the flow of purified water.

DPRShield is a new tool for potable reuse that offers assurance that the purification system is working in real time and has a backup mechanism (that is, the Breach-Activated Barrier) to continue to work even when integrity breaches occur.

Figure 6 provides an alternate illustration of the Breach-Activated Barrier in the context of a Porifera FO (PFO) element. If a breach occurs at any point within the white membrane area, the breach is addressed instantaneously via a pressure jet of draw solution that is pushed into the feed solution. This will reduce the result of the log removal calculation or purification effectiveness until the breach is remedied, but the treatment process will continue to exclude contaminants during this time.



Figure 6: Illustration of Breach-Activated Barrier

Alternate Breach-Activated Barrier illustration on single membrane plate within a PFO-100 element.

Source: Porifera, Inc.

In Figure 6, the feed solution is shown in green arrows flowing from the element feed inlet to the element outlet. For DPRShield, assume 8 pounds per square inch (psi) in and 3 psi out for the feed stream. The draw solution is shown in blue flowing from the element draw inlet to the element draw outlet; assume 13 psi in and 8 psi out for an average draw overpressure of 5 psi. Note that low pressure drops are typical across the PFO membrane in the modified plate and frame type modules used by Porifera.

Theoretical Background for Breach-Activated Barrier

The following section summarizes the theory of using draw overpressure to create a new type of rejection mechanism. The conclusion of the theory is that:

- A very small amount of draw overpressure (1–3 psi) can provide fail-safe rejection of viruses and larger pathogens for any size breach (see Chapter 5 section titled, "Porifera MS2 Spiking Test Results and Fail-Safe Breach-Activated Barrier Assessment," for MS2 spike data supporting this theory)
- 2. Higher draw overpressures (greater than 5 psi) may begin to increase the rejection of small, dissolved contaminants that are not typically rejected by FO and RO membranes.

An FO membrane consists of two separate sides: (1) a "feed side" with constituents (for example, molecules, contaminants, particles, or pathogens) present at concentration "C," and (2) a "draw side" pressurized to pressure "P" consisting of clean water with a draw solute and dye (Figure 7). For the sake of building a simple model, assume that with the breach present the two sides are connected by a cylindrical pore with a radius "r."



Figure 7: Pathogen Diffusion and Transport

(A) Schematic of constituent (such as, pathogens or molecules) diffusion through a cylindrical pore retarded by overpressure "P."

(B) Constituent transport as a function of the critical pore radius (breach size). The solid red line represents the combined constituent transport due to both diffusion and mass transfer. Negative transport means that no constituents of this size would enter the draw side from the feed side at a given pore radius (breach size).

Source: Porifera, Inc.

In steady state operation, the transport of molecules and contaminants from the feed side to the draw side is described by Fick's law of diffusion:

$$J = D \frac{dC}{dx} \approx D \frac{\Delta C}{L}$$
(1)

where "J'' is the diffusion flux in mol/m²s, "D'' is the diffusion coefficient, "L'' is the pore length, and " $\Delta C''$ is the concentration gradient of unwanted constituents including contaminants and/or pathogens.

The number of constituents " M_{diff} " transported through a cylindrical pore with radius "r" due to diffusion is as follows by adding the geometry of a cylinder to the equation:

$$M_{diff} = \pi r^2 \cdot J = \frac{\pi r^2 \Delta CD}{L} \tag{2}$$

On the draw side of the membrane, assuming pressure gradient " $\Delta P''$ is applied to the pore of radius "r'' with a length "L'' in the direction of the draw side to the feed side, then the volumetric flow "Q'' through this pore is defined by the Hagen-Poiseuille equation:

$$Q = \Delta P \cdot \frac{\pi r^2}{8\mu L} \tag{3}$$

where " μ " is dynamic viscosity.

Note that the volumetric flow thought the pore depends on the pore radius to the 4th power, which arises from the parabolic flow profile that occurs in a cylindrical pore. Also note that " ΔP " is the differential pressure across the membrane and for DPRShield is pushing in the opposite direction of the flow of filtration (e.g., a ΔP of 5 psi could be, for example, 9 psi of average fluid working pressure on the draw side and 4 psi of average fluid working pressure on the feed side).

The number of constituents " M_{mt} " transported by applied pressure (a.k.a., washed back from draw to feed) through the pore is equal to:

$$M_{mt} = C \cdot Q = \Delta P \cdot \frac{\pi r^4 C}{8\mu L} \tag{4}$$

Combining these equations, the combined mass transport of constituents " M_{total} " through the cylindrical pore can be calculated as the difference between " M_{diff} " (equation 2) and " M_{mt} " (equation 4) assuming that the average pore concentration "C" is equal to " ΔC ".

$$M_{total} = M_{diff} - M_{mt} = \frac{\pi r^2 C}{L} \left(D - \frac{\Delta P}{8\mu} r^2 \right)$$
(5)

Next, assume that the "critical defect radius" " r_0 " is the radius of a defect or breach in the membrane in which diffusion transport is equal to mass transport. Assuming equation (5) is equal to zero and that the average pore concentration "C" is equal to " ΔC ," the equation becomes:

$$r_0 = \sqrt{\frac{8\mu D}{\Delta P}} \tag{6}$$

Note that the size of critical defect radius " r_0 " is dependent on " ΔP " and that the higher the ΔP , the smaller the defect protected by Breach-Activated Barrier.

Figure 7B shows a graph of the combined transport of constituents (calculated using equation 5) as "pathogen transport" as an example of an unwanted constituent versus "relative pore radius" defined as " r/r_0 ." One dashed curve labeled "diffusion" represents constituent transport via diffusion only (calculated using equation 2) and a second dashed curve labeled "mass transport" represents transport in the opposite direction from reverse overpressure (calculated using equation 4). A dotted vertical line is shown

at a relative pore radius of 1 (assumes $r=r_0$). The results of the combined graphs on Figure 7B show two interesting conclusions.

First, the transport of constituents via diffusion (Fick's law) will be greater than the same constituents transported in the reverse direction via pressurized flow (Hagen-Poiseuille equation) if the radius of a defect "r" is smaller than " r_0 ." This means that the defect size is small enough that diffusion will dictate and that constituents, including unwanted constituents, can diffuse from the feed side to the draw side (assuming that size exclusion doesn't apply as a rejection mechanism). For DPRShield, this is the size of defect where it is very important to have high-resolution integrity monitoring to detect variations in this type of transport, especially, if real-time dye retention can be correlated to real-time pathogen and emerging contaminant rejection as proposed later in this paper.

Second, the transport of constituents via reverse overpressure will be greater (Hagen-Poiseuille equation) than the same constituents transported via diffusion if the radius of a defect "r" is larger than " r_0 . "Therefore, the flow of constituents would be reversed by draw overpressure *P* shown in Figure 7 and the constituents would not cross from the feed side to the draw side even through the breach would be larger in this second case than in the first case. This is a different type of rejection mechanism than those that occur in pressure-driven membrane separation processes like nanofiltration (NF) and RO.

Next, consider several constituents and calculate what this would mean in practice within a DPRShield process. Table 1 includes the calculated critical defect radiuses for different constituents assuming: (1) the viscosity of water of 10⁻³ (pascal-second (Pa/sec), (2) a draw overpressure of 5 psi (0.35 bar, typical for FO applications with Porifera modified flat sheet elements), and (3) known diffusion coefficients.

	Molecular Weight, MW	Stokes Radius or Approximate Size, nm	Diffusion Coefficient, 10 ⁻⁹ m ² /s	Critical Defect Radius, nm
NaCl	57.5	0.14	2	22
Urea	61	0.2–0.3	1.67	20
Fluorescein	376	3.4	0.78	13
Hemoglobin	64K	5-6	0.1	1.5
Virus Herpes Simplex	N/A	120-300	0.3	2

Table 1: Diffusion Coefficients and Critical Defect Radius for SelectedConstituents at 5 psi (0.34 bar) Overpressure

Source: Porifera, Inc.

These critical defect radius estimates suggest that diffusion will dictate transport of small constituents for small defects in the less than 1–20 nanometer (nm) range. For example, urea has a Stokes radius of 0.2–0.3 nm and an estimated critical defect radius of approximately 20 nm. According to the estimates in Table 1, urea would be able to pass through a breach smaller than 20 nm at 5 psi overpressure by diffusion, but not through a breach larger than 20 nm because the mass transport due to pressure will push the urea molecules back to the feed side more quickly than it can diffuse to the draw side.

Note that for larger constituents (for example, Hemoglobin and viruses), the critical defect radius is smaller than it's physical size and therefore it will not be able to diffuse to the draw side of an FO membrane through small defects due to size exclusion. For defects larger than a constituent's size, it will be kept out of the draw side by overpressure—by the Breach-Activated Barrier.

Fluorescein dye has a Stokes radius of 3.4 nm, but an estimated critical defect radius of approximately 13 nm. This suggests that dye transport will be dictated by diffusion for defects smaller than 13 nm and by pressure for defects larger than 13 nm. Also note the dye's rapid diffusion rate, which highlights its sensitivity for membrane integrity monitoring in case of very small defects where diffusion is greater than mass transport. In summary for a DPRShield process with Breach-Activated Barrier:

- In theory, only small molecules will be able to diffuse to the draw side of the FO membrane from the feed side and only through small defects in FO.
- Unwanted pathogens and potentially targeted emerging contaminants of concern (ECOCs) will not pass through large breaches because reverse pressure will effectively reject them.
- Dye retention measurements combined with draw overpressure is a new and practical membrane integrity-monitoring method because: (1) dye diffuses through small breaches, (2) proper dye formulations can provide very high resolution and be rapidly detected for both small and large breaches due to the dye's small size and rapid diffusion rate, and (3) the reverse pressure acts as an inherent backup barrier to reject contaminants when large breaches occur.

Most importantly, this means that reverse overpressure (that is, the Breach-Activated Barrier) will block even many small constituents from bulk transfer or passage through a barrier when there is a moderate to large breach (for example, the breach is greater than 30 nm, such as mechanical tears, glue line failures) when there is the highest risk for bulk contaminant and pathogen passage.

In other words, the larger the breach in an FO membrane in a DPRShield process, the less likely key contaminants will pass into the filtrate and the more quickly the breach will be detected.

This is not the case for pressure-driven filters (such as microfiltration (MF)/ ultrafiltration (UF), nanofiltration (NF), RO) where the pressurized flow pushes more of the contaminants of concern through a breach.

Benefits of Real-Time Monitoring

Real-time monitoring technology may accelerate regulatory approval of DPR in California by addressing one of the main concerns of DPR: undetected integrity leaks that could allow contaminants into the water supply. The DPRShield system (1) adds an additional tight contaminant barrier, (2) provides real-time monitoring to ensure that the barriers perform as designed, and (3) provides additional protection activated by the barrier breach itself (the Breach-Activated Barrier) that prevents contaminants from passing into the permeate.

Potable reuse systems in California have permitted microfiltration (MF) and reverse osmosis (RO) systems with low-resolution membrane integrity monitoring followed by an advanced oxidation potential (AOP) post-treatment step.

Figure 8 describes different types of water treatment membranes used as barriers in potable reuse systems and compares them based on the integrity testing methods applicable to each membrane. For example, MF and ultrafiltration (UF) membranes can have integrity breaches for days, while nanofiltration (NF) and RO membranes can have breaches for days, months, or sometimes years, before the integrity breach is detected due to current low-resolution methods.

Figure 8: Comparison of Membrane Integrity Test Methods and Monitoring Resolution



MF/UF hollow fiber membranes. Integrity test: daily or weekly via pressure decay. Several fibers must be broken before the test detects an integrity breach. Pressure decay resolution covers 99.99% rejection = 4-log removal value (LRV).

Breach-Activated Barrier technology is not applicable to MF/UF membranes.



Flat-sheet NF & RO membranes cannot be pressure decay tested. Salinity rejection (approx. 99% or 2-log LRV) is used for integrity testing. O-ring, cuts, and other small breaches may not be detected for years in municipal scale plants.

Breach-Activated Barrier technology can increase resolution to >99.99% rejection = 4-log LRV in a DPRShield process.



Flat-sheet FO membranes also cannot be pressure decay tested. Salinity rejection (approximately 99% or 2-log LRV) has been planned for integrity testing.

Breach-Activated Barrier technology can increase resolution to >99.99% rejection = 4-log LRV for FO

Source: Porifera, Inc.

Combining FO and RO with a dye marker and draw overpressure can provide greater than 4-log rejection of dye in real time for both the FO and RO membrane unit processes.

While real-time monitoring can provide assurance to regulators and operators, the potential log reduction value (LRV) credits may also make it easier to permit for DPR applications. Table 2 compares the estimated LRV credits from a DPRShield system based on pilot results and the anticipated requirements for a DPR project in California. While LRV credits are just one requirement of many that would be needed to permit a DPR project, they are a very important requirement, and the more fail-safe a project is or the higher the resolution for real-time monitoring it offers, the better the case that can be made for a reliable and functioning solution. Table 3 shows the LRV credits at GWRS for comparison.

Table 2: Estimated DPRShield Log Reduction Value Credits Vs. AnticipatedRequirements for Permitting a DPR Project

Pathogen	Wastewater Treatment Plant	FO	RO	UVAOP*	Total LRV	Anticipated Regulatory Credits to Permit DPR in California
Virus & Pathogen LRV	0-2	4	4	6	14–16	>12-log via 3 or more barriers
NDMA* LRV	0	0.5—1.0 (0.9 to 1.3) from pilot data	0.5—1.0 (0.9 to 1.3) from pilot data	>1.5	>2.0	May depend on facility and likely be >1.4-LRV

* NDMA = N-nitrosodimethylamine UVAOP = ultraviolet advanced oxidation process

Source: Porifera, Inc.

Table 3: Summary of GWRS Pathogen and NDMA Log Reduction CreditsAchieved in 2018

Pathogen	OCSD*	MF	RO	UVAOP*	Underground Retention Time	Total LRV	Regulatory Credits for Permit
Virus & Pathogen LRV	0	0 for virus; 4.2 for others	2	6	4 for virus	12	12-log via 3 or more barriers
NDMA* LRV	0	0	>0.1	1.9	0	>1.5	Depends of facility

* NDMA = N-nitrosodimethylamine OCSD = Orange County Sanitation District UVAOP = ultraviolet advanced oxidation process

Source: Porifera, Inc.

CHAPTER 3: Maximizing Potable Reuse Potential

Pilot Site and Site Partner Goals

This pilot project investigated increased reuse at the OCWD Groundwater Replenishment System (GWRS) AWPF, while also demonstrating potential benefits of DPRShield technology including energy savings, high purity water, real-time membrane integrity monitoring, Breach-Activated Barrier, cleaning frequencies, and other potential benefits.



Figure 9: DPRShield Pilot Site

Picture of Porifera DPRShield Pilot (Left) installed in the GWRS RO building (Right)

Source: Porifera, Inc.

Figure 10 shows a schematic of the OCWD GWRS potable reuse process. The GWRS treats municipal secondary wastewater from the Orange County Sanitation District (OCSD) with an advanced treatment system, which uses microfiltration (MF) and reverse osmosis (RO) membranes to create a high quality permeate. This permeate is further treated by a combination of high intensity ultraviolet light and hydrogen peroxide known as the ultraviolet advanced oxidation process (UVAOP) to further remove contaminants that may not be sufficiently removed upstream. After UVAOP, partial decarbonation (20 percent of flow) and lime addition are used to reduce the corrosiveness of the water. There is no disinfection; however, a low residual chloramine as well as hydrogen peroxide remain in the finished water as a result of the upstream treatment process. Lastly, the final product water (FPW) is injected (via injection wells) or percolated (via recharge basins) into the groundwater basin to provide drinking water via various city-owned production wells and to provide a robust barrier to seawater intrusion.



Figure 10: OCWD GWRS Advanced Treatment System

A red circle and arrow indicating the DPRShield pilot treated water in the reverse osmosis concentrate brine waste stream with the goal of producing water similar to the ROP (RO permeate) stream.

Source: Porifera, Inc.

OCWD is evaluating various technologies to further treat a portion of its existing RO concentrate (ROC) reject stream (red circle in Figure 10) that is currently discharged to the sea along with other local brines to increase overall plant production and therefore water recovery. The existing GWRS conventional three-stage RO system shown in Figure 10 (the primary RO system) removes most salts and dissolved organics, including emerging contaminants that are concentrated in this ROC stream by approximately six to seven-fold relative to the RO feed stream. Therefore, robust treatment is important prior to potable reuse.

OCWD is currently limited to reusing approximately 85 percent of the wastewater that enters the facility, due to the inherent recovery limitations of the primary RO system. The district is evaluating the potential for maximizing the recovery from the facility with a goal of increasing nominal reuse from 85 percent to approximately 95 percent. This pilot project is a key component of OCWD's current investigations.

Ideally, this additional reuse water could be blended directly with OCWD's existing RO permeate (ROP), as shown by the red arrow in Figure 10. However, additional review with regulators is necessary to determine the necessary treatment and credits for this approach.

Existing and Planned IPR and DPR Projects in the United States

Today, the United States produces 32 billion gallons of municipal wastewater effluent per day, of which 7 percent to 8 percent is reclaimed (U.S. Environmental Protection Agency, 2012a). Currently, planned IPR and DPR projects account for a negligible fraction of the reused water volume (NRC, 2012a). However, potable reuse is a significant portion of the nation's water supply when considering de facto reuse—where treated wastewater affects drinking water sources (NRC, 2012a). The map in Figure 11 shows locations of planned IPR and DPR projects around the United States, many of which are in California.



Figure 11: Planned and Constructed IPR and DPR Projects in United States as of 2017

Source: CDM Smith

Planned Reuse in California

The California Water Action Plan, adopted in 2014 and updated in 2016 to guide the state's water resource efforts, specifically cites recycled water as a key strategy for meeting the state's water demand. The state's recycled water goals, which were adopted to set a target for water recycling efforts throughout California, aim to increase annual recycled water production by 497 billion gallons (1 million acre-feet) by 2020 and 823 billion gallons (2 million acre-feet) by 2030 above the 2002 baseline of 171 billion gallons (.525 million acre-feet). More generally, the state's recycled water policy encourages the substitution of "as much recycled water for potable water as possible by 2030." Furthermore, recycled water is an increasingly important component of California's water portfolio. The California Department of Water Resources (DWR) and the State Water Resources Control Board (State Water Board) found that California reused approximately 233 billion gallons (714,000 acre-feet per year) of recycled water in 2015, representing an increase of 45,000 acre-feet since 2009.

There are multiple limitations and barriers to increasing water reuse in California including:

- Demand vs. Supply. In some areas, there are low demands for non-potable water supplies (agriculture, irrigation of parks, golf courses, and others) and the geology is not suitable for IPR. Therefore, DPR is the ideal type of reuse, but DPR projects are not yet being permitted in California.
- Infiltration and Inflow. Most recycled water systems are designed for a target capacity and water quality. However, the effects of stormwater and seasonal variability either limit the percentage of combined discharge (wastewater and stormwater) that can be reused or significantly increase cost.
- Financial Costs. The cost to recycle water varies depending on the level of treatment required, capital investment, and operating costs, which are typically high compared to the current cost of cheaper water supplies such as wells, state and federal water projects, and local surface water in California. Also, the costs of recycled water projects are highly variable and depend on site-specific factors, treatment requirements, proximity to end-users, and other factors. The costs in different locations may vary significantly.
- Public and Regulatory Acceptance. Although DPR projects are not yet permitted in California, the state is currently developing regulations. The level of public support, concern, and resistance varies widely throughout the state.
- Brine Generation: Indirect and direct potable reuse are promising water resource strategies for further expanding the state's recycled water production. The technologies employed in potable reuse projects, however, result in the generation of concentrated discharges (brine) in volumes that may require special considerations for disposal or potentially cap the possible volume of recycled water production at individual facilities. As potable reuse production

increases at individual facilities, there will be less diluent wastewater available to mitigate concentrations of various constituents. At high enough concentrations (that is, at high enough production levels), brine from potable reuse projects could risk violating existing National Pollutant Discharge Elimination System permit pollution standards indicated in the U.S. Environmental Protection Agency's (EPA's) 1972 Clean Water Act.

In 2015, municipal wastewater treatment plants (WWTPs) in California discharged 417.5 billion gallons of treated effluent at 57 discharge locations into the Pacific Ocean or a coastal bay. These coastal locations are typically the most ideal locations for potable reuse facilities due to the proximity to the sea for discharge of the concentrated waste stream produced during potable reuse process. Figure 12 shows a map of the jurisdictional boundaries for six of the nine regional water quality control board within California, as well as the total treated municipal flows for WWTPs in each region. WWTPs serving California's largest population centers, particularly WWTPs in the San Francisco Bay and Los Angeles regions, generate the largest volumes of treated effluent.


Figure 12: Coastal Wastewater Discharges Offer Greatest Potential for Increased Potable Reuse

Coastal wastewater discharges by region in billions of gallons per year.

Source: Heal the Ocean, "Inventory of Municipal Wastewater Discharges to California Coastal Waters," September 2018

California-based coastal wastewater treatment plants discharge a significant volume of treated municipal effluent to coastal water bodies. The state's efforts to increase drought resiliency could benefit from greater use of this treated effluent in recycled water projects, offsetting the need to use drinking water in irrigation or other non-potable reuse projects and increasing water supplies through indirect or future direct potable reuse projects.

If coastal wastewater treatment plants were able to recycle an aggressive 85 percent of their treated municipal effluent, 28.61 percent of California's coastal urban water needs could be supplied, illustrated by region in Figure 13.



Figure 13: Percent of Current Coastal Urban Water Use That Can Be Offset by High Recovery Reuse

Source: Heal the Ocean, "Inventory of Municipal Wastewater Discharges to California Coastal Waters" September 2018

Current Process and Activities at OCWD

OCWD is located in Fountain Valley, California, and was created as a special district by state law in 1933 for the protection and preservation of the Orange County groundwater basin. The mandate of the special district is to ensure adequate water supplies, while also protecting the integrity of the basin's groundwater quality and quantity. As groundwater resources began to decline, OCWD used Santa Ana River water or other imported water resources to replenish the groundwater basin and began planning an indirect potable reuse project for groundwater replenishment in 1994.

In 2008, OCWD began operating the GWRS, which uses advanced water treatment technologies to purify treated wastewater to high quality before injecting and percolating the water into the groundwater basin to replenish local drinking water resources and to provide a barrier to salt water intrusion.

Jointly developed by OCWD and the OCSD, GWRS is the largest water purification project of its kind in the world and treats enough water to supply 850,000 people. It is estimated that in the next 20 years the population of Orange County will increase from 2.3 million to 3 million people. It is also projected that by 2020, the water requirement for central and north Orange County will be 600,000 acre-feet. To fulfill the future water demand for agricultural, industrial, and indirect potable use, it was decided to expand the GWRS, and the original plant was constructed with plans for two future expansions, one of which has been completed and the other is underway. The project provides an additional 31,000 acre-feet a year (AFY) of water supplies, bringing the total to 103,000 AFY.

Approximately 30 mgd, or 113,000 cubic meters, of the final product water is conveyed by the barrier pump station to injection wells along the seawater intrusion barrier. The remaining 70 mgd (265,000 cubic meters) final product water is conveyed by the product water pump station to the Kraemer, Miller, La Palma, and Mira Loma Recharge Basins in Anaheim, California.



Figure 14: GWRS Advanced Water Purification Facility and Water Replenishment Basin

Site location and map of GWRS site (advanced water purification facility), reuse injection areas, and ocean outfall.

Source: <u>OCWD GWRS Technical Brochure 2018</u>. Retrieved from https://www.ocwd.com/media/ 6203/sarwqh-final-nwri-panel-report-2004.pdf

Technology Evaluation for Capacity Increase

While it currently reuses approximately 85 percent of the wastewater that enters the facility, OCWD is interested in maximizing the recovery from the facility with a goal of increasing nominal reuse from 85 percent to approximately 95 percent, and this pilot project is a key component of their current investigations.

Increasing the capacity of the current GWRS treatment process could be carried out by extracting more potable water from the existing RO concentrate (ROC) stream, which is currently disposed of via ocean discharge. Whether or not this additional purified water recovered from the RO concentrate can be blended with the existing RO permeate stream prior to UVAOP, as opposed to for example introducing the new permeate to the AWPF influent (secondary effluent), is unknown and would require additional regulatory review.

For example, increasing recovery from 85 percent to 92 percent would increase the total planned future capacity from 103,000 AFY to 111,500 AFY, sufficient for 920,000 people. After discussing Porifera's DPRShield technology and OCWD's goals and objectives, extraction of potable water from existing RO concentrate was the application selected for pilot testing at their site as opposed to the other potential application like treatment of secondary or tertiary effluent.

The existing GWRS RO system removes most salts and dissolved organics (including emerging contaminants), which are concentrated in this ROC stream by approximately six-fold relative to the RO feed stream. Therefore, robust treatment of the ROC to recover more water is important prior to potable reuse.

In parallel to evaluating DPRShield technology for increasing water recovery at the GWRS, OCWD evaluated a different technology called closed-circuit reverse osmosis (CCRO). OCWD received a grant from the U.S. Bureau of Reclamation to perform operational optimization, water quality testing, and other studies to evaluate both CCRO and DPRShield. Therefore, some of the data collected for that evaluation is included for completeness in this report with OCWD's permission. Furthermore, some of the data in this report will be presented in OCWD's final report to USBR.

CHAPTER 4: Project Approach

Goals and Objectives

The primary purpose of the testing was to demonstrate energy savings and water quality in a way that would benefit municipalities and other water reuse facilities throughout California.

The objectives of this agreement were to:

- Demonstrate DPRShield is feasible and will result in a reliable and cost-effective solution for water and wastewater treatment
- Demonstrate increased energy savings and water volumes at pilot-scale for DPR at a municipal wastewater plant in a disadvantaged community.
- Demonstrate unprecedented pathogen and chemical removal using Breach-Activated Barrier technology with real-time high-resolution membrane integrity monitoring and contamination prevention (that is, >4-log removal credits using low energy membranes).

The goals of this project were to:

- Improve public health safeguards in DPR and IPR, facilitating regulatory approval of water reuse projects.
- Reduce the electrical energy, chemicals, maintenance, and overall cost of potable reuse of wastewater.

OCWD Goals and Objectives

OCWD's goal for the testing was to evaluate DPRShield and CCRO at pilot scale to recover water from reverse osmosis concentrate (ROC) generated from the advanced potable reuse treatment facility (Figure 15). The RO concentrate is a liquid waste stream that otherwise must be disposed of via ocean discharge or other means. Successful treatment and recovery of RO concentrate at advanced potable reuse facilities will minimize the volume of the waste stream while generating more water, increasing overall water recovery (plant efficiency) from 85 percent to greater than 90 percent. Objectives included evaluating pilot operational feasibility, recovery optimization, water quality, treatability (confirmation of suitability for subsequent UVAOP treatment), and cost.

Figure 15: Process Streams at GWRS

A sample sink at an OCWD GWRS tour stop with RO permeate (left); RO feed water, which is microfiltration effluent (center); and RO concentrate (right).

Source: OCWD

Approach

The approach was planned in partnership with OCWD staff to incorporate the goals and objectives of OCWD's planned expansion to reuse more water at the GWRS facility. The resulting approach separated the planned testing into two major periods, each of which contained planned performance or water quality assessments. However, as is common with most pilot projects, there were some unplanned site issues and equipment component failures impacted the assessments and required troubleshooting and modifications to either the pilot equipment or the approach to provide realistic assessments.

Equipment and Materials

The equipment and materials used for testing were different for each phase of the test and are summarized in the following subsections. The main components needed for testing were as follows:

- PFO laboratory scale and pilot-scale test system at Porifera lab.
- RO concentrate feed solution at OCWD GWRS.
- Dechlorinated secondary effluent from the Hayward Water Pollution Control Facility.

- Draw solution salts (sodium chloride (NaCl) table salt and magnesium chloride (MgCl₂) - road salt).
- Tankless FO plus RO system without prefiltration equipment for the majority of testing; a 1-micron pre-filter was added in the final month, but did not appear to remove foulants.
- Turner Designs fluorescein and uranine dyes.
- AWC C-227 high pH proprietary cleaning chemical for FO and RO membranes (recommended by OCWD for existing RO membranes).
- Miscellaneous piping, electrical, and containment work to install and operate pilot.
- Sample containers suitable for selected water quality testing.

The test equipment, treatment process, and site modifications were primarily designed, installed and operated by Porifera with some assistance from OCWD; the feed solution was provided by the OCWD; and draw solution and other chemicals were supplied by Porifera. The majority of the pilot operation was unmanned with remote support and occasional on-site support provided by Porifera with assistance from OCWD staff.

Test Phases and Schedule

The testing occurred in the following phases:

- 1. Phase 1: Preliminary lab testing 10/1/15 to 10/1/16.
- 2. Phase 2: Site assessment, pilot system fabrication and installation 10/1/15 to 12/1/16.
- 3. Phase 3: Site Demonstration, optimization, and sampling 12/1/16 to 11/1/19.

Phase 1: Preliminary Laboratory Testing

Initial tests were performed at coupon scale using Porifera's custom FO membrane coupon test setup and FO element setup shown in Figure 16. The results achieved on the coupon setup provided data and information to guide tests at element scale. The tests from the element setup provided initial operating data and design information for the pilot system.



Figure 16: FO Membrane Element Test System

Source: Porifera, Inc.

An FO setup (schematic in Figure 17) was constructed particularly for assessing dye while also being able to operate the FO membrane element in both feed and draw overpressure mode.



Figure 17: Custom Dye Laboratory Test System Schematic

Source: Porifera, Inc.

Phase 2: Site Assessment, Pilot System Fabrication, and Installation

Following the preliminary lab tests, Porifera designed and constructed the DPRShield pilot system based on a previous tankless FO plus RO system design. Figure 18 is a diagram of the process flow. This system was designed to fit within a small footprint and to use commercial Porifera FO membrane elements. As the diagram indicates, system recovery is equal to FO recovery and that make up draw solution is occasionally injected into the regenerated draw stream.



Figure 18: DPRShield Pilot Process Flow Diagram

Source: Porifera, Inc.

The DPRShield pilot was configured to run on:

- FO: one FO module with 1 to 2 PFO-100 elements each (7-14 m2).
- RO: two pressure vessels in series with one 2.5-inch diameter by 40-inch long Dow seawater element (Dow SW2540) per vessel.
- Tankless design: no feed or draw tanks were needed; only a small draw dose tank.
- Table salt (NaCl) draw and magnesium chloride (MgCl2) draw solutions.
- No pretreatment until the final two months of the study, when a 1-micron prefilter was added to the feed in stream. However, no increase of pressure was observed across the pre-filter, and no change in fouling propensity was observed.
- No chemicals were added to the process with the exception of the NaCl draw salt (99 percent of operation), MgCl2 draw salt (1 percent of operation), fluorescein dye (added during the first two months) and uranine dye (added during the final month), and AWC C-227 for FO and RO membrane cleanings.
- Chloramine and antiscalant residuals were continuously present in the DPRShield feed from dosing prior to the GWRS feed.

A unique aspect of this pilot system was its design to operate without a draw storage tank. This means that the draw out of the RO system would flow directly into the FO

draw inlet and the dilute draw from the FO would feed directly into the RO pump suction without any draw storage. While this can have many benefits in terms of small footprint and small draw volumes, it does change the system starts and stops, and the system is more difficult to control when there are rapid changes in feed water salinity and/or temperature.

Phase 3: Site Demonstration, Optimization, and Sampling

During Phase 3, the initial plan was to investigate the ideal water recovery for the system so that the system could operate at a stable recovery for sampling events. However, numerous small issues required changing multiple parameters, resulting in the initial optimization period being conducted at a constant water recovery to minimize the numbers of variables that could affect operation and troubleshooting. During this phase, several minor modifications were made to change where certain water quality parameters were monitored in the process to better automate the blowdown frequency, improve draw overpressure, and reduce nuisance alarms and shutdowns. Eventually dye was turned off to assess the effect of dye on membrane fouling.

Table 4 shows the different operating parameters of the system. Following initial optimization, the system was adjusted to the final operating values, which were largely held constant until the final two months of operation, when the FO module was upgraded with a 1-micron pre-filter and a recirculation pump to increase surface velocity on the feed side of the FO membrane, and a new dye was injected into the system.

Multiple water quality sampling and analysis events occurred during pilot testing including:

- Four water quality sampling events conducted by Stanford University that focused on NDMA, 1,4 dioxane, disinfection byproducts (DBPs), and selected emerging contaminants of concern (ECOCs).
- Four water quality sampling events conducted by OCWD.
- One MS2 spiking event conducted by Porifera with OCWD assistance.
- Three MS2 spiking events conducted by OCWD in October/November 2019 (not included in this report as results were unavailable during report preparation).
- Four planned microbial/pathogen assessment sampling events conducted by OCWD in October through November 2019 (not included in this report as results were unavailable during report preparation).

Stream/ Parameter	Feed In ¹ (1)	Reject Concentrate Out (2)	Dilute Draw (3)	Regenerated Draw ² (4)	Permeate Out ³ (5)	Draw Blowdown Out⁴(6)
Avg. Flow (gpm)	0.97	0.65	1.4	1.1	0.32	0.0008
Max. Flow (gpm)	1.1	0.7	1.8	1.5	0.45	0.006
Min. Flow (gpm)	0.9	0.5	1.2	0.9	0.27	0
Avg Pressure (psi)	5	3	FO/RO 6/350	FO/RO 8/340	<10	<10
Max Pressure (psi)	8	5	FO/RO 10/45	FO/RO 13/430		
Min Pressure (psi)	3	2	FO: 5/270	FO/RO 6/260		
Avg. Conductivity (mS/cm)	9.6	13.4	28	37	0.3	Same as dilute draw
Max. Conductivity (mS/cm)	11.5	16.5	35	42	0.6	Same as dilute draw
Min Conductivity (mS/cm).	8.0	10.9	22	28	<0.1	Same as dilute draw

Table 4: Representative Range of Operating Parameters During Pilot Operation

Numbers in parentheses correspond to those in Figure 18.

1. ROC feed in conductivity data was not collected on the pilot, but provided to Porifera by OCWD.

- 2. The regenerated draw pressure was controlled by the RO pump within the draw loop to maintain approximately 3 psi draw overpressure compared to the feed in pressure for the majority of pilot testing. Higher draw overpressures were tested; however, this increased the likelihood of glue line failures during GWRS RO flush and power variation events.
- 3. The 2.5-inch diameter RO elements do not typically include the best membrane from RO membrane manufacturers and produce lower quality RO permeate than commercial 4-inch and 8-inch diameter RO membranes. Also, the RO system was not operating at ideal design parameters especially in terms of surface velocity, so a commercial scale DPRShield system would provide better permeate conductivity values at similar operating conditions.
- 4. Blowdown is shown at representative continuous flow rates. Blowdown was evaluated at rates of 0% to 2% of system permeate flow in both continuous and intermittent mode. Blowdown was set at 0.25% in intermittent mode for the majority of pilot operation.

Source: Porifera, Inc.

Sampling Approach by Stanford

The focus of measurements for this study was on 1,4-dioxane, *N*-nitrosamines, and an array of regulated and unregulated disinfection byproducts (DBPs). DBPs result from chemical reactions between organic and inorganic matter in water with chemical treatment agents during the water disinfection process. Chlorinated disinfection agents are strong oxidizing agents introduced into water to destroy pathogenic microbes, to oxidize taste/odor-forming compounds, and to form a disinfectant residual so water can reach the consumer tap safe from microbial contamination. These disinfectants may react with natural organic matter, as well as iodide and bromide ions, to produce a range of toxic DBPs.

In California, there is significant regulatory concern over 1,4-dioxane and N-nitrosamines, particularly N-nitrosodimethylamine (NDMA), within advanced treatment trains for potable reuse. Chloramine has become a popular disinfectant in the United States, and it has been found to produce NDMA. California has established notification levels of 10 nanograms per liter (ng/L) for *N*-nitrosoamines and 1 mg/L for 1,4-dioxane in drinking water.

Porifera targeted these analytes for two reasons. First, while the public fears pharmaceuticals, the National Research Council (NRC) indicated that DBPs are of far greater human health concern for potable reuse trains (NRC, 2012). The NRC divided chemicals associated with human health risks by concentrations typically measured under potable reuse scenarios to derive margins of safety. DBP concentrations, particularly nitrosamines, were within an order of magnitude of levels associated with health risks, while pharmaceuticals and other compound classes (for example, estrogens, chlorinated flame retardants such as tris(2-chloroethyl) phosphate, and others) were orders of magnitude lower than levels of concern (margins of safety are approximately 10⁶; see Table 5). Second, N-nitrosamines, halogenated DBPs, and 1,4-dioxane represent challenge chemicals for potable reuse trains because, compared to pharmaceuticals, they are less successfully removed by RO membranes (Agus, 2010).

Emerging Contaminants	Margin of Safety
Nitrosamines: NDMA	>0.4
Other DBPs: Bromate	>2
Other DBPs: Bromoform & DBCM	>160
Chloroform	16
DBCA & DCAA	>60
HAA5	12
THMs	8
Pharmaceuticals: Acetaminophen	>35,000,000
Pharmaceuticals: Ibuprofen	>280,000,000
Pharmaceuticals: Carbamazepine	>190,000,000
Pharmaceuticals: Gemfibrozil	>140,000,000
Pharmaceuticals: Sulfamethoxazole	>160,000,000
Pharmaceuticals: Meprobamate	>930,000,000
Pharmaceuticals: Primidone	>58,000,000
Other ECOC: Caffeine	>23,000,000
Other ECOC: 17-β Estradiol	>35,000,000
Other ECOC: Triclosan	>2,100,000
Other ECOC: tris(2-chloroethyl) phosphate	>210,000
Other ECOC: PFOS	>200
Other ECOC: PFOA	>80

Table 5: Margin of Safety Comparison of DBPs and Other ECOCs

Source: Porifera, Inc.

Some of these ECOCs, such as NDMA and other DPBs, were present in detectable concentrations in the ROC at the GWRS. Most others were not, so concentrated solutions of 16 organic contaminant stock contaminants were spiked during four events into a dedicated FO feed tank targeting concentrations of 200 nM. These contaminants included benzotriazole, ibuprofen, acyclovir, naproxen, diuron, carbamazepine, sulfamethoxazole, atenolol, hydrochlorothiazide, diclofenac, ranitidine, ciprofloxacin, oryzalin, bezafibrate, fipronil, and 1,4-dioxane. Samples (500 mL) were collected from the FO feed, the FO draw solution tap located on the FO module, and the RO permeate tap and stored at 4°C prior to analysis. During each spike, one sample was collected

prior to spiking, and three samples were collected throughout the run after at least 40 gallons of water were processed.

The 1,4-dioxane was measured in 40 mL samples by extraction and analyzed by gas chromatography mass spectrometry (Chuang et al., 2017). For analysis of the remaining compounds, samples (250 mL) were passed through 6 mL Oasis HLB cartridges (Waters Corp.), which had been pre-rinsed with 12 mL of methanol and 12 mL of deionized water. The cartridges were then rinsed with 12 mL of deionized water and eluted with 12 mL of methanol (McCurry et al., 2014). The resulting extract was then analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS).

For disinfection byproducts (DBPs), two sets of grab samples were collected. One sample set was treated with 33 mg/L ascorbic acid immediately after collection to quench residual disinfectants to measure the DBPs already present in the samples. To measure the levels of DBP precursors, the other sample set was collected without ascorbic acid to enable treatment in the laboratory with chloramines. Samples were stored at 4°C prior to analysis.

The set of samples treated with 33 mg/L ascorbic acid was measured directly for 43 DBPs belonging to seven classes, including four trihalomethanes (THMs), ten haloacetic acids (HAAs), four haloacetamides (HAMs), four haloacetaldehydes (HALs), six iodinated-THMs, two haloketones (HKs), one halonitromethane (chloropicrin), and eight *N*-nitrosamines. The HAAs and all other halogenated DBPs were quantified using modified EPA Methods 552.3 and 551.1, respectively, with approximately 0.2 μ g/L reporting limits. The *N*-nitrosamines were measured using a modified EPA Method 521 with approximately 2 ng/L reporting limits.

Prior to analysis using the same methods, the second set of samples collected without ascorbic acid was treated with chlorine or chloramines to evaluate the concentrations of chlorine- or chloramine-reactive precursors. Free chlorine stock solutions were constituted by dilution of a 5 percent sodium hypochlorite solution (Fisher Scientific) into deionized water and were standardized by ultraviolet (UV) absorbance at 292 nm ($\lambda_{292} = 365 \text{ M}^{-1} \text{ cm}^{-1}$; Feng et al., 2007). Preformed monochloramine stock solutions were prepared daily by adding sodium hypochlorite dropwise to ammonium chloride (1:1.2 molar ratio) and standardized by measuring UV absorbance at 245 nm and 295 nm (Schreiber and Mitch, 2005). Samples were buffered at pH 8 by the addition of a 4 mM bromate buffer. Samples were treated with 5 mg/L as Cl₂ of preformed monochloramine residual (greater than 1 mg/L as Cl₂) was then quenched with ascorbic acid prior to analysis for DBPs.

OCWD Sampling Approach

The focus of measurements was on regulated compounds and other water quality parameters needed to compare the permeate from the DPRShield pilot with OCWD GWRS RO permeate and to determine what additional treatment or post-treatment may

be needed to properly implement a DPRShield-type solution at their facility. Samples were collected, stored, and analyzed using standard methods where available.

Porifera Sampling and MS2 Spiking Test Approach

Porifera collected continuous data for parameters including conductivity, temperature, and dye concentration throughout the study and also collected grab samples to confirm the accuracy of the data and to assess other parameters such as pH, oxidation reduction potential, and other data needed to assess performance and troubleshoot issues.

MS2 coliphage is a bacteriophage (a virus that infects bacteria) that is often used as a surrogate for human viruses (because it is a similar size or smaller than human viruses) when assessing advanced membrane treatment technologies. The principle of the use of this surrogate is that if a technology rejects (removes) MS2 due to size exclusion, then the technology would also reject larger viruses as well as larger pathogens such as cryptosporidium, giardia, and other protozoa and waterborne pathogens.

MS2 spikes were used to assess the effectiveness of the theory that Breach-Activated Barrier could provide fail-safe rejection of pathogens in the event of a spike. The first MS2 spike was conducted on synthetic feed without a breach to determine a baseline MS2 rejection and to provide a practice run. The second MS2 spike was performed on site at OCWD using an FO membrane element that had pinholes punched through three membrane sheets using sewing needles (Figure 19). The intent was to create intentional breaches orders of magnitude larger than MS2 to allow MS2 to pass through easily, while also not being so large that the breach would bleed too much salt from the system to alter operation.

Both spikes were planned for a starting feed concentration of greater than 1 million plaque forming units (pFu) per milliliter to provide a resolution of greater than 7-log removal (Figure 20).

Figure 19: Intentional Membrane Breaches



Two of the four pinholes created within a PFO-100 FO membrane element with 33 sheets total.

Source: Porifera, Inc.



Figure 20: MS2 Spiking Test

MS2 concentrate (left) spiked into a feed tank (right) of RO concentrate for the MS2 spike test.

Source: Porifera, Inc.

The pilot system was then reconfigured to treat water from a feed tank that could hold more than 100 gallons of ROC feed, and both the FO reject and the RO permeate were recycled back to the feed tank to retain the phage.

The spike test was planned to include two periods:

- 1. Breach-Activated Barrier active: FO operating with 3 psi or greater draw overpressure.
- 2. Breach-Activated Barrier inactive: FO operating with 5 psi or greater feed overpressure.

Preliminary tests indicated that the water processed from a feed tank through the FO and RO systems would pass through the system in less than 10 minutes, so each period was planned for 90 minutes to allow sufficient time for MS2 breakthrough to occur. Additionally, both OCWD's resident MS2 expert and lead investigator for the DPRShield pilot study were present during the start and portions of the spiking study and sampling activities.

CHAPTER 5: Project Data and Results

This section includes a summary of the data and results for each test and phase of the project. More detailed data is included in the Appendix.

Phase 1: Preliminary Laboratory Testing

Laboratory coupon and element tests were performed on wastewater from OCWD to evaluate the customer's wastewater and design an optimal draw solution for this site. Initially, the target was communicated as 30 to 50 percent water recovery.

At laboratory scale, Porifera's FO membrane was able to achieve 50 percent reuse at flux rates between 8 and 30 liters per square meter per hour (LMH), with variable draw salinities and fluorescein dye concentrations. Pictures of the tests are shown in Figure 21.



Figure 21: Laboratory Wastewater Testing

Source: Porifera, Inc.

Multiple tests were performed with Porifera PFO-20 FO elements to measure the amount of dye passing through an FO membrane and its correlation with membrane

integrity. PFO-20 elements use Porifera's high performance FO optimized thin film composite membrane and have an effective membrane surface area of 1 m². In the first set of experiments, an initial concentration of 2 mg/L of fluorescent dye FITC (fluorescein isocyanate) was mixed with a 5,000 parts per million (ppm) sodium chloride draw solution, and low total dissolved solids (TDS) water was used as the feed (dechlorinated tap water modified to approximately 500 ppm TDS). During normal operation and without an intentional breach, dye leakage was not measured above the background fluorescence level of water (approximately 2 parts per billion [ppb]) regardless of overpressure being applied from the feed or draw side. Even when the dye concentration in the draw solution was increased to 20 mg/L fluorescence, the dye concentration in the feed solution was still below the background level with a corresponding dye rejection of over 99.99% (greater than 4-log).

Next, small breaches were intentionally created by degrading the active rejection layer of the same PFO-20 membrane element used in initial tests. To do this, the membrane was exposed to free chlorine because it is known to disrupt the amide bond in a thinfilm composite membrane's selective layer and degrade membrane rejection. The free chlorine exposure increased reverse salt flux (RSF) by 10-fold from 0.2 to 2.0 g/L before and after chlorine degradation respectively. RSF is a measure of the grams of draw salt (for example, NaCl) that pass from the draw into the feed by diffusion for every liter of water that transfers from the feed to the draw by diffusion. During testing following the degradation, dye passage exceeded the minimum detection limit, thus, allowing rapid detection of minor breaches.

Draw Over- pressure ¹ (psi)	Water Flux at 20°C (Imh)	Reverse Salt Flux (g/L)	Fluorescent Dye Passage (µg/hour)	Equivalent Single Pass Dye Rejection (%)	Equivalent Single Pass Dye Rejection (log)
2	25	0.4	8	99.995	~4.4
4	26.2	0.34	24	99.987	~3.9
6	27	0.3	20	99.989	~4.0
8	28	0.3	28	99.985	~3.8
11	27	0.55	48	99.974	~3.6

Table 6: Dye Rejection and Forward Osmosis Element Performance Data as aFunction of Draw Overpressure for Undamaged Membrane

Source: Porifera, Inc.

To quantify long-term dye rejection of FO element and sensitivity of dye monitoring method to the defects in the membrane, a second set of experiments were performed by recirculating both the feed and draw solutions in multiple passes as shown in Figure

^{1:} Note: 2 psi draw overpressure was the equivalent to the draw solution flowing at an average 2 psid higher pressure than the feed solution is flowing through an element on average.

17 and Figure 21. Both feed and draw solutions were circulated through the FO membrane element at a flow rate approximately 1.5 liters per minute (L/min) with the draw containing 2,000 ppb of dye and 57,500 ppm of salt (approximately 1 M NaCl solution, which is the draw concentration for a standard FO membrane performance test). Real-time membrane flux, RSF, and dye leakage rates were measured as a function of time and draw overpressure.

A typical undamaged $1m^2$ FO element circulated at 2 psi overpressure fluorescence in a 40-liter tank increased at roughly constant rates of 0.1 to 0.15 ppb/hour (see Figure 22A) and was stable for at least 18-20 hours.

Figure 22B, however, shows that when the draw overpressure was increased in increments from 2 to 11 psi, total dye passage, (calculated from dye concentration in known feed volume) increased from approximately 8 µg/hour at 2 psi to 48 µg/hour at 11 psi, which indicates that diffusion of the dye from the draw side to the feed side was aided by mass transport (note that for DPRShield, mass transport is designed to retard diffusion of pathogens but aids dye passage for rapid accurate detection). The last row in Table 6 and Figure 22B show that at 11 psi overpressure dye passage increased six times, while RSF and water flux changes were minor. This suggests that fluorescent dye is a better indicator of through the membrane than RSF or water flux.



Figure 22: Dye Characterization

Fluorescence increase due to dye passage through a Porifera PFO-20 element with 2 psidraw overpressure and (B) dye passage and RSF as a function of draw overpressure.

Source: Porifera, Inc.

Although the experiment was run in recirculation mode, a commercial-scale DPRShield process would operate in a single pass through mode so that no recirculation of the feed occurs. Therefore, Porifera converted the results shown in Table 7 to "equivalent single dye rejection" to indicate dye passage when the FO feed passes only once though the element. This was calculated by taking the test feed flow rate of 1.5 L/min (chosen to minimize effects of concentration polarization effect in the FO element) and

dividing it by the PFO-20 element volume of 0.7 liters to yield approximately 128 element-passes/hour. Using the number of passes per hour and the average dye amount increase, FO element dye rejection per single pass was calculated as $(C_{draw} - C_{feed})/C_{draw}$ where C_{draw} is the dye concentration in the draw and C_{feed} is the amount of dye that passed through membrane in one pass divided by FO element volume. The data in Table 7 indicates that the dye is highly rejected at overpressures of 8 psi (0.55 bar) or less, which is well within typical operation parameters and sufficiently high enough to allow for the Breach-Activated Barrier mechanism to occur as previously described.

During this round of testing, a different type of intentional breach was used to assess dye passage through the leak. This time experiments were conducted with a sharp spacer material inside the PFO-20 element pushing this sharp spacer against the membrane's selective layer during operation. Applied draw overpressure caused the sharp spacer to produce multiple defects of approximately 100 micron-scale in the membrane's selective layer. Figure 23A and Table 7 show that there was a significant increase in dye passage rate for the element with a sharp spacer compared to an undamaged element with a typical spacer material. Figure 23B shows methylene blue dye staining of an intentional defect, and Figure 23C shows a picture of a defect using scanning electron microscopy. RSF and water flux were not as sensitive measures of this membrane damage as dye passage. For example, dye passage increased 30 times from 2 psi to 8 psi overpressure while RSF increased only 1.8 times. This effect is likely due to the excellent rejection (4-log or greater) of fluorescent dye by the undamaged areas of the FO membrane.



Figure 23: Breach Detection Using Tracer Dye

(A) Dye passage and RSF as a function of differential pressure between the draw and feed side of an FO membrane damaged by a sharp spacer. (B) Optical image of a damaged area stained with methylene blue, and (C) scanning electron microscopy of the same area.

Source: Porifera, Inc.

Draw Over- pressure (psi) ¹	Water Flux (LMH) at 68°F (20°C)	Reverse Salt Flux (RSF, g/L)	Fluorescent Dye Passage, µg/hour	Equivalent Single Pass Dye Rejection, %	Equivalent Single Pass Dye Rejection, log
2	24	0.47	16	99.991	4.1
4	25.2	0.55	240	99.87	2.9
6	25.1	0.66	280	99.85	2.8
8	24.3	0.86	488	99.73	2.6
11	9.6	0.21	3360	98.16	1.7

Table 7: Dye Rejection and Forward Osmosis Element Performance Data asFunction of Draw Overpressure for Membrane Damaged with Sharp SpacerMaterial

Source: Porifera, Inc.

Phase 2: Site Assessment, Pilot Fabrication and Installation

Following laboratory testing, Porifera staff visited the site to determine the proper connection points and selected a location with an existing ROC connection, existing 120V electrical outlet, and an existing drain. The pilot unit was installed so that the ROC was fed directly into the pilot system via the pressure in the pipeline without a feed equalization tank, and a feed pump was selected to reduce feed pressure and control

feed flow. The three outputs from the system (RO permeate, FO reject, and draw blowdown) were sent directly to the drain.

A separate tote was filled with GWRS RO permeate to provide water for cleaning, draw makeup water, and maintenance as needed. Figure 24 shows installed and operational DPRShield Pilot at the GWRS.



Figure 24: Installed and Operational DPRShield Pilot at the GWRS

Source: Porifera, Inc.

Phase 3: Site Demonstration and Optimization

Once the pilot system was installed and started at the GWRS, it was configured to operate continuously unmanned, with remote monitoring by Porifera staff and occasional assistance from OCWD research and development staff. The DPRShield pilot input and output streams are shown in Figure 25.

Figure 25: DPRShield Pilot Input and Output Streams



DPRShield feed water (left), permeate (center left), draw with dye (center right) and FO reject (right).

Source: Porifera, Inc.

The pilot system initially operated well and continued to produce high quality water. However, as operation continued programming bugs, design issues, and operational challenges with the site eventually became apparent and required repairs and adjustments to keep the system running continuously. Figure 26 shows the months of operation and run time of the pilot system as well as the operating recovery of the FO and RO processes. Overall, the system was installed and piloted at OCWD site for more than 18 months, with continuous operation for approximately half of the time.

Figure 26: Pilot Run Time and Unit Process Recovery



Graph of RO (top) and FO (bottom) recovery vs. time; note that the FO recovery equals the system water recovery. Source: Porifera, Inc. The pilot experienced issues primarily due to the following reasons:

- Cleanable FO and RO membrane fouling due to initial fluorescein dye used in the system.
- Cleanable FO fouling primarily due to clay with some minor general organic fouling; minor scaling where the membrane came in contact with the feed spacer.
- PFO membrane delamination due to rapid spikes in draw overpressure often caused by power outages, cleaning, or other maintenance that occurred at the GWRS. This would typically cause the RO pressure to increase, which was misdiagnosed as FO membrane fouling. The misdiagnoses were confirmed after cleanings and membrane autopsies.
- Programming code that required modification due to unexpected or unforeseen conditions.
- Intermittent draw pressure relief valve malfunction (issue that was misinterpreted as other types of failure due to its intermittent nature); this is more common with very small valves than larger valves used for commercial systems.
- Failure or maintenance of other mechanical parts including the RO feed pump, FO feed pump, pressure transmitters, conductivity sensors, and other mechanical parts.

When dye was present, these issues were easy to troubleshoot and address; however, without the dye it was more difficult because minor salt leak/integrity issues if present were not significant enough to show up in real time as spikes in the FO reject conductivity.

Therefore, some of these issues were difficult to diagnose, often being misdiagnosed at first, making it challenging to fully understand long-term operational requirements such as the cleaning frequencies required. For example, although for one period the FO membranes did not need to be cleaned for more than two months, these and other FO elements were damaged due to membrane delamination before a proper assessment of cleaning requirements could be made. As another example, some FO elements were thought to be fouled or breached, but the issue was later identified as a faulty valve that intermittently would not fully close and would bleed salt from the draw loop. While these operational issues created challenges in terms of evaluating cleaning and maintenance frequencies, they also resulted in important lessons learned for future demonstrations.

Water Quality, Fail-Safe Barrier, and Real-Time Monitoring Performance Assessment

Despite operational challenges, DPRShield technology was successfully demonstrated during the periods of days and weeks in between the pilot mechanical challenges described. The pilot showed that the technology can produce a high quality permeate from highly contaminated and often variable quality feed water. DPRShield extracted water from the RO concentrate produced by the GWRS facility and was able to produce comparable water quality permeate to the GWRS RO facility permeate (Figure 27).



Figure 27: Influent for GWRS RO and DPRShield Treatment Processes

GWRS RO feed and DPRShield feed. Note that the DPRShield feed is considerably more contaminated than GWRS RO feed (microfiltered secondary effluent, tertiary effluent) as it is the concentrate produced by the GWRS RO system.

Source: Porifera, Inc.

Multiple water quality sampling and analysis events occurred during Phase 3 pilot testing at OCWD including:

- Four water quality sampling events conducted by Stanford University that focused on emerging contaminants of concern (ECOCs).
- Four water quality sampling events conducted by OCWD.
- One MS2 spiking event conducted by Porifera with OCWD assistance.

General Water Quality Results

The ROC produced from RO treatment of microfiltered secondary effluent at the GWRS facility was treated by the DPRShield pilot system to extract additional water. Since the DPRShield system treated GWRS RO facility concentrate, concentrations of all the contaminants in the feed of the DPRShield system were 5 to 7 times higher than concentrations in the feed of the GWRS system. Despite the considerably higher influent concentrations than for GWRS, the DPRShield pilot system permeate contained dissolved organic carbon, nitrate, nitrite, and bromide concentrations comparable to those in the permeate of the primary RO unit of the GWRS facility (Table 8). It should be noted that the chloride concentration in the DPRShield permeate is expected to be reduced in a full-scale installation due to availability of better RO membranes than those used in the DPRShield pilot (commercial systems that use 8-inch RO membranes typically achieve better performance than pilot systems that use 2.5-inch RO

membranes because the top grades are used for commercial-scale membranes where requirements are more stringent).

Further chloride reduction could also be achieved by using an alternate draw solution (for example, MgSO₄). These results suggest that blending the DPRShield permeate with the primary RO permeate should not significantly degrade the quality of the product water with respect to basic water quality parameters.

Table 8: Mean and Range (Minimum to Maximum) Concentrations of BasicWater Quality Parameters

Parameter	Influent to GWRS RO (MF effluent)	Permeate from GWRS RO	Influent to DPRShield (RO Concentrate from GWRS)	Permeate from DPRShield
DOC (mg-C/L)	43 (41-44)	0.1 (<0.1-0.2)	280 (250-300)	0.4 (<0.1-0.5)
NO₃ (mg-N/L)	10 (10-10)	3.0 (1.0-9.0)	58 (50-63)	1.4 (1.0-3.0)
NO ₂ (mg-N/L)	0.1 (<0.02-0.1)	<0.02	3.2 (0.8-7.6)	<0.02
Br (mg/L)	0.3 (0.3-0.3)	<0.1	2.3 (1.9-2.6)	<0.1
Cl (mg/L)	260 (240-280)	4.1 (3.5-4.7)	1830 (1630-1970)	110 (30-240)

Measured during four sample events for centralized RO treatment of microfiltered secondary effluent and FO/RO treatment of RO concentrate.

Source: Porifera, Inc.

Stanford Sampling Results: Pharmaceuticals, Pesticides, and Other Industrial Contaminants

It is critical for a potable water reuse system to reject contaminants such as pharmaceuticals, pesticides, and other industrial contaminants, and the DPRShield system demonstrated excellent rejection of these emerging (often unregulated) contaminants.

To evaluate emerging contaminant rejection, 200 nM of 15 compounds were spiked into the FO influent; chloroform was not spiked and will be discussed together with the DBPs. Rejection of the compounds by the FO membranes correlated primarily with molecular volume (Figure 28) but was well rejected at greater than 95 percent for nearly all of the compounds. Benzotriazole, the compound with the lowest molecular volume (88.3 cm³), exhibited the lowest rejection at 91 percent. However, rejection for 1,4-dioxane, which is only slightly larger than benzotriazole (88.5 cm³ molecular volume), was consistently greater than 96 percent. Overall rejection by the DPRShield system was excellent at greater than 99 percent for all of the compounds tested.

The list of the 15 compounds (1,4 dioxane, pharmaceuticals, and other ECOCs) and more detailed rejection data for each compound is included in the Appendix.



Percent rejection of 15 organic contaminants by the FO membrane alone (comparing the concentrations in the FO influent and draw solution) and by the combined FO/RO system (comparing the FO influent and RO effluent concentrations) for treatment of RO concentrate. Error bars represent the standard deviation of three sampling events. BTA= benzotriazole, DIOX = 1,4-dioxane, DIC=diclofenac.

Source: Stanford University

Stanford Sampling Results: Disinfection Biproducts

As mentioned previously, disinfection biproducts (DBPs) were the primary contaminants of interest in addition to 1,4 dioxane due to typical margins of safety for potable reuse projects (see Table 5). DBP removal and formation were evaluated in the permeate of the DPRShield system and in chloramine treated uniform formation conditions (UFC) permeate to determine its suitability for reuse. If implemented at OCWD, the permeate from DPRShield would ideally be combined with the permeate from the primary RO unit from the existing process train, which contains a chloramine residual, so it is important to determine the levels of DBPs that application of chloramine may generate. There are regulatory limits on the concentrations of certain DBPs for potable reuse applications, including maximum contaminant levels (MCLs) of 80 μ g/L for the sum of four trihalomethanes (THM4), 60 μ g/L for the sum of five haloacetic acids (HAA5) in the United States, and a 10 ng/L notification level for NDMA in California.

The removal of DBPs and chloramine-reactive DBP precursors was compared between (a) the GWRS RO process receiving microfiltered secondary municipal wastewater effluent within the existing advanced treatment train and (b) the DPRShield pilot treating the RO concentrate generated by the GWRS RO. This comparison is important since the two permeates could be blended in a future application, and there are concerns as to whether the addition of the DPRShield permeate would degrade the quality of the potable reuse product water.

Even though the total DBP concentration prior to chloramine application was on one occasion 10-fold higher in the DPRShield influent (260 μ g/L vs. 27 μ g/L), the DPRShield and GWRS RO treatment systems both reduced the average total DBP concentrations to 11 μ g/L (Figure 29A). While the total DBP concentrations were low, the NDMA concentrations exceeded the 10 ng/L notification level in both the DPRShield permeate (29 ng/L average) and primary RO permeate (15 ng/L average). The contribution of a DBP to toxicity is a function of both concentration and toxic potency. Regulated and unregulated DBP concentrations were weighted by metrics of toxic potency, using the same toxic potency weighting factors employed in previous publications (Chuang et al., 2019). On a toxic potency-weighted basis, the average total DBP concentrations were 37 percent higher in the DPRShield permeate than the GWRS RO permeate (Figure 29B), but still relatively low for potable reuse applications.

After chloramine application, the average total DBP concentrations (Figure 29C) were four-fold higher in the DPRShield influent (420 μ g/L) than in the primary RO influent (97 μ g/L), but the concentrations in the permeate were comparable (16 μ g/L and 12 μ g/L, respectively). The concentrations in the permeates were only slightly higher than the levels measured before chloramine addition, indicating the efficient removal of many of the DBP precursors. However, the NDMA concentrations exceeded the 10 ng/L notification level in both the DPRShield permeate (38 ng/L) and primary RO permeate (16 ng/L). The average total toxic potency-weighted DBP concentrations were 52 percent higher in the DPRShield permeate (0.0014) than in the GWRS RO permeate (0.0007) effluent. The total toxic potency-weighted DBP concentrations (Figure 29) were within the range or slightly higher than (0.0005 median; 0.0009 maximum) reported previously for chloraminated effluents of MF/RO/AOP-based potable reuse trains (Zeng et al., 2016).



Figure 29: DPR Shield and GWRS DBP Removal and Formation Potential/Toxicity Results

DBP concentrations on a (A, C) mass- or (B, D) toxic potency-weighted basis in the influents and permeates of the FO/RO system fed with concentrate from the primary RO treatment unit and of the primary RO unit fed with microfiltered secondary effluent. DBP concentrations are provided before (A, B; "Raw") and after (C, D) chloramine application. Raw = before chloramine application. UFC = after chloramine application under uniform formation conditions. The bars show the concentrations of individual DBP classes during one sampling event. THM4 = four chlorinated and brominated trihalomethanes, HAA9 = nine brominated and chlorinated haloacetic acids, HAMs = haloacetamides, HALs = haloacetaldehydes, HANs = haloacetonitriles, HKs = haloketones, HNMs = chloropicrin, NAs = nitrosamines, I-THMs = iodinated trihalomethanes.

Source: Stanford University

The permeate from DPRShield treatment of the RO concentrate exhibited concentrations of basic water quality parameters comparable to those generated by RO treatment of the secondary wastewater effluent. Rejection of 15 organic contaminants spiked into

the FO influent was greater than 99% across the combined DPRShield system for all three matrices (test events).

The concentrations of DBPs that formed when chloramines were applied to the DPRShield permeate met regulatory limits except for NDMA. NDMA concentrations exceeded the 10 ng/L notification level when the DPRShield permeate was chloraminated. However, the NDMA concentrations in the permeate from the GWRS RO also exceeded the 10 ng/L notification level. These results indicate that the DPRShield trains should incorporate a UV-based AOP to control NDMA concentrations in the permeate, in the same fashion employed for treatment of RO permeate at the GWRS and other centralized potable reuse facilities (Marron et al., 2019). However, when DBP concentrations were weighted by their toxic potencies, the total DBP concentrations were comparable to those observed previously in RO permeates from centralized potable reuse treatment trains.

Overall, the results indicate that the DPRShield system can serve as a robust barrier to the passage of salts, bulk organic matter, organic contaminants, and DBPs and their precursors. However, additional treatment is needed to adequately control NDMA. Nonetheless, despite the approximately seven-fold higher DOC concentration in RO concentrate than in secondary effluent, the DPRShield permeate quality from RO concentrate was comparable in many respects to that of RO permeate from centralized potable reuse facilities including the GWRS.

Thus, DPRShield treatment of RO concentrate could be a valuable tool to enhance water recovery at existing centralized IPR facilities, without jeopardizing the quality of the potable product water.

OCWD Sampling Results for Regulated Components

OCWD's sampling and analysis protocol was primarily focused on the assessment of the DPRShield pilot systems removal of surrogated and regulated water quality parameters, without spiking.

The sampling events occurred on the following dates:

- February 21, 2019.
- April 29, 2019.
- June 25, 2019.
- September 25, 2019, consistent with Stanford's data, as shown in Table 9, OCWD data showed good rejection of all compounds by DPRShield. The DPRShield system was able to produce comparable permeate quality to that of the GWRS system despite starting from approximately seven-fold higher initial contaminant concentrations in the feed.

Table 9: Summary of OCWD's Key Pilot Water Quality Analysis

Water Quality Parameter and Units	GWRS RO Concen- trate	DPRShield Pilot Permeate ¹	GWRS Treated Water ²	GWRS RO Feed ²	Permit Limit
TDS (mg/L)	na	260	ROP: 19 FPW: 53	1,018	500
	6170	92	ROP: 19 FPW: 53	1,018	500
	6190	312	ROP: 19 FPW: 53	1,018	500
	TBD	145	ROP: 19 FPW: 53	1,018	500
Electrical conductivity	na	569	100	1,725	900; surrogate for salinity
(uS/cm)	8830	232	100	1,725	900; surrogate for salinity
	8850	604	100	1,725	900; surrogate for salinity
	TBD	308	100	1,725	900; surrogate for salinity
Turbidity NTU	na	<0.1	<0.1	0.1	0.5; surrogate for suspended solids
	0.3	<0.1	<0.1	0.1	0.5; surrogate for suspended solids
	0.3	<0.1	<0.1	0.1	0.5; surrogate for suspended solids
	TBD	<0.1	<0.1	0.1	0.5; surrogate for suspended solids
Ultraviolet Absorbance UVT% or cm ⁻¹	na	97.9% UVT	97.47% UVT	na	>90%; surrogate for organics
	0.969 cm ⁻¹	0.015 cm ⁻¹	97.47% UVT	na	>90%; surrogate for organics

		10.6% UVT	98.6% UVT	97.47% UVT	na	>90%; surrogate for organics
		TBD	98.5% UVT	97.47% UVT	na	>90%; surrogate for organics
Total Coliform Most probable number		na	<1	ROP: ND FPW: 0.3	na	<2.2; surrogate for harmful bacteria
		<1	<1	ROP: ND FPW: 0.3	na	<2.2; surrogate for harmful bacteria
		<1	<1	ROP: ND FPW: 0.3	na	<2.2; surrogate for harmful bacteria
		TBD	<1	ROP: ND FPW: 0.3	na	<2.2; surrogate for harmful bacteria
TOC mg/L		na	0.23	0.11	7.82	Measure of total organics
		45.9	0.25	0.11	7.82	Measure of total organics
		35.6	0.25	0.11	7.82	Measure of total organics
		TBD	0.76	0.11	7.82	Measure of total organics
Total All mg/L as	kalinity CaCO3	na	6.3	ROP: <1 FPW: 34.1	296	240
		1,190	9.2	ROP: <1 FPW: 34.1	296	240
		1130	6.4	ROP: <1 FPW: 34.1	296	240
		TBD	<5	ROP: <1 FPW: 34.1	296	240
TTHMs	ug/L	na	11	ROP: 4 FPW: 3	12.7	80
		69.7	4.3	ROP: 4 FPW: 3	12.7	80
		97.1	8.2	ROP: 4 FPW: 3	12.7	80

	TBD	18.6	ROP: 4 FPW: 3	12.7	80
Total Nitrogen	na	1.4	FPW: 1.0	na	5
mg/L	62.2	1.3	FPW: 1.0	na	5
	6.9	ND	FPW: 1.0	na	5
	TBD	4.9	FPW: 1.0	na	5
NDMA ng/L	na	na	ROP: 16.3 FPW: 1.6	27.9	10
	220	11	ROP: 16.3 FPW: 1.6	27.9	10
	160	16	ROP: 16.3 FPW: 1.6	27.9	10
	TBD	<1.0	ROP: 16.3 FPW: 1.6	27.9	10
1,4 dioxane ug/L	na	<0.5	<1	1.9	1
	na	<0.5	<1	1.9	1
	8.5	<0.5	<1	1.9	1
	TBD	<0.5	<1	1.9	1

1: DPRShield data collected from the pilot system in a different year than the GWRS data.

2: GWRS data is from the publicly available 2018 GWRS Annual Report retrieved from <u>https://www.ocwd.com/media/7934/2018-gwrs-annual-report.pdf</u>.

N/A = not applicable; ND = not detected; na = not analyzed; TBD = awaiting final results; ROP = RO permeate; FPW = final product water after UVAOP and remineralization.

Source: Porifera, Inc.

Porifera MS2 Spiking Test Results and Fail-Safe Breach-Activated Barrier Assessment

MS2 spiking demonstrated the effectiveness of the Breach-Activated Barrier inherent to the operation of DPRShield. As described in Chapter 4, small intentional membrane breaches were introduced to four FO membrane sheets within an FO element. With this damaged membrane in place and the Breach-Activated Barrier active (that is, draw held at 3 psi higher than the feed), the feed to the system was spiked with approximately 200 million/ml of MS2. Figure 30 shows that as long as the Breach-Activated Barrier is active, for about three hours, no MS2 passes into the draw and into RO permeate. As soon as the Breach-Activated Barrier is de-activated, the passage of MS2 into the draw and permeate is detected, with more than 10 million phage passing through the breaches in 90 minutes of the Breach-Activated Barrier being turned off. Note that no MS2 was detected in the RO permeate during this test.



Figure 30: MS2 Spiking Test Results

MS2 spiking data in all process stream (Top) and FO draw and RO permeate data only (Bottom).

Source: Porifera, Inc.

This indicates that the draw overpressure was keeping hundreds of millions of MS2 virus surrogates from passing through breaches in the FO membrane barrier that would be easily passed without draw overpressure. While this is only one event, the resolution of approximately 8-log removal with draw overpressure active and 7-log passage within 90 minutes of it being turned off is statistically significant. Also, a previous MS2 spike was performed on the DPRShield pilot system during the initial lab testing with draw overpressure active and there was only minor observable MS2 passage once draw overpressure was turned off.

Real-Time Dye Monitoring Assessment

The real-time monitoring resolution of dye was assessed and compared to the monitoring resolution of conductivity during the same time at the pilot. During this time, the dye concentration of the draw solution was maintained at a concentration of approximately
5 mg/L. Sensors that could measure at the selected wavelength as the dye was installed on the FO feed, FO reject, draw, and RO permeate. There was an extremely low background level of absorbance in the FO feed, FO reject, and RO permeate and with no known breaches, the resolution of real-time dye monitoring was well over 4-log between the draw and both the feed and permeate (Figure 31). During this same time, the resolution of conductivity real-time monitoring between the draw and RO permeate only was over 2-log. The real-time LRV was approximately equal for uranine dye and fluorescein dye.



Figure 31: Real-Time Dye vs. Conductivity Monitoring in the DPRShield Pilot System

Source: Porifera, Inc.

As previously described, California currently gives RO-based technologies 2-log pathogen removal credits based on continuous real-time salt rejection data (conductivity is converted to TDS according to the permit). Basically, as long as 2-log removal is shown of salt, the RO system maintains 2-log of pathogen removal credits even if it can reject more than 2-log of pathogens. If this same approach was used for DPRShield and real-time dye rejection is accepted as a monitoring tool for both FO and RO, then there is potential for both the FO and RO units processes to achieve 4-log removal of dye in real-time and be awarded 4-log pathogen removal credits each. Historically, 4-log credits have been the maximum allowable given by California, so further increasing the concentration of dye in the draw loop is not considered necessary. The real-time LRV was approximately equal for uranine dye and fluorescein dye.

Summary of Independent Measurement and Verification Data

CDM Smith was the measurement and verification (M&V) partner for this project and visited the site to observe pilot system operation and provide manual measurements to confirm general operational data. The graph in Figure 32 compare CDM Smith's independent readings with Porifera's readings shown at that time on the touchscreen, which are the same data used for data logging and creating data graphs shown in this section and the Appendix. The calculated unit energy use from M&V measurements ranged from approximately 3.4–4.2 kilowatt-hours (kWh)/1000 gallons of permeate while operating at onsite conditions. More details are provided in the Appendix.



Figure 32: Energy Consumption Measurement by M&V Partner

Source: Porifera, Inc.

Energy Use Comparison

The energy use observed during pilot testing was higher than the anticipated energy use of a commercial DPRShield system that was estimated at 3.1 kWh/1000 gallons prior to piloting. However, this is excellent when compared to other alternative water supplies and ranges from competitive to attractive compared to other potable reuse alternatives. Also, it should be noted that a commercial DPRShield will operate more efficiently with commercial-size RO membranes and a RO system designed and operated at more ideal efficiency conditions and with a larger scale, more efficient energy recovery device. Based on these considerations, it is expected that a commercial scale DPRShield system would operate more in the range of 3.5-3.7 kWh/1000 gallons than the approximately 4.0 kWh/1000 gallons usage demonstrated in the pilot.

DPRShield's energy use was compared to energy required for the main sources for new water supplies in California: (1) importing more water over long distances, (2) water desalination, and (3) other reuse options. Of these three options, reuse requires the least amount of energy (Cooley, 2013). As shown in Figure 33, Porifera's DPRShield

system for direct potable reuse would require approximately 70 percent less energy than desalination, 33 percent less energy than competing direct potable reuse technologies, and up to 50 percent less energy than long-distance state water project transfers.



Figure 33: Energy Use Comparison

Energy use comparison for production of potable water from different water sources available in California. State log removal credits required for permitting are assumed for each process.

Source: Porifera, Inc.

Assumptions for these calculations include the following:

- Energy use for seawater desalination, IPR State Water Project (SWP) transfers, and competing DPR alternatives are from published and/or publicly presented data (Cooley, 2013).
- Energy use for IPR was based on average data shared by OCWD for the GWRS in 2017.
- DPRShield would require similar feed, storage, and transmission infrastructure as other DPR or IPR ROC+ (enhanced reuse from existing RO concentrate) projects.
- DPRShield permeate would require UVAOP similar to that of GWRS RO permeate for IRP ROC+ and approximately double that for DPR projects.
- DPRShield pumps and ERDs are high efficiency types typically used for seawater reverse osmosis (SWRO).

There is little useful data on the commercial energy use of competing DPR technologies suitable for California regulations because there are no permitted projects in California. Regulations are in the process of being developed and reviewed. Also, there have been many different technologies proposed and a leading option that includes ozone and

granular activated carbon (GAC) may actually be lower energy than shown in Figure 33 if RO is not included or required.

Establishment of Cleaning and Maintenance Frequency Requirements

Additional piloting is recommended to better assess the technology before commercial installation. However, while the pilot data is incomplete for portions of the test due to replacement of FO membranes, useful data was collected at times throughout the study. Additional data and information can be found in the Appendix.

RO Cleaning and Maintenance Frequency

The RO cleaning frequency is conservatively estimated to be once every six months; however, the data showed that without dye the RO membrane tested had near new permeability (+/10 percent) when autopsied after eight months of continuous operation. Only two RO cleanings were performed during the entire study, and one was directly linked to the fluorescein dye. The second cleaning was performed proactively after six months of operation (with little apparent change) as a part of troubleshooting an issue that was related to a faulty valve. There were also some RO replacements due to installing new RO elements that did not perform well immediately after installation, but these replacements did not adversely affect cleaning assessment.

FO Cleaning and Maintenance Frequency

The FO cleaning frequency is estimated to be once every 4-8 weeks, and it is recommended that (1) the FO be operated in feed circulation mode to maximize crossflow velocity, and (2) a feed flush option be implemented occasionally to maintain or extend cleaning frequency as needed. Unfortunately, these last two modifications were not evaluated until the final two months of testing but appeared to have positive results.

Initial operation with and without fluorescein suggested that the presence of the fluorescein dye was reducing the FO cleaning frequency from once every 4-8 weeks to once every 2-3 weeks with the dye present. Uranine dye, which is similar to fluorescein in terms of wavelength, did not seem to have the same negative effect over a period of less than two months.

After the fluorescein dye was discontinued there were multiple runs with cleaning periods of four weeks and one run of eight weeks before the FO membranes were replaced due to membrane delamination associated with GWRS maintenance events or incorrect diagnosis (FO membranes were replaced due to perceived delamination, but standard tests and autopsies indicated no fouling, delamination, or other breach). Those FO membranes that were not delaminated were cleaned prior to testing and reuse.

Summary of Pilot Demonstration Results

The DPRShield pilot showed that the technology can produce excellent permeate water quality out of highly contaminated and often variable quality feed water. The DPRShield extracted water from the GWRS RO facility concentrate and was able to produce comparable water quality permeate to the GWRS permeate. DPRShield system operation was demonstrated to require 70 percent less energy than desalination, 33 percent less energy than competing direct potable reuse technologies, and up to 50 percent less energy than long distance state water project transfers.

DPRShield generated this high quality permeate with respect to the levels of all contaminants examined: organic contaminants, disinfection byproducts, and other regulated and unregulated compounds of interest evaluated by Stanford and OCWD, despite treating water with approximately seven-fold higher contaminant levels than GWRS. Overall, the results indicate that the DPRShield system can serve as a robust barrier to the passage of salts, bulk organic matter, organic contaminants, and DBPs and their precursors. Thus, DPRShield treatment of RO concentrate could be a valuable tool to enhance water recovery at centralized facilities without jeopardizing the quality of the potable product water.

MS2 spiking demonstrated the effectiveness of the Breach-Activated Barrier inherent to the operation of DPRShield. The Breach-Activated Barrier is activated by the breach itself and the contaminants are pushed away from the clean water stream, ensuring fail-safe operation. This combined with real-time detection of even the smallest FO or RO membrane breach by detection of tracer dyes, presents a new paradigm in water reuse systems providing solid evidence that the purification system continues to work as designed, offering a counterpoint to public and regulatory concern over the public health risks and perceived "toilet to tap" image associated with implementing DPR. Real-time detection and fail-safe operation are key features that will allow municipal water providers to overcome regulatory barriers to enable direct potable water reuse.

CHAPTER 6: Path to Commercialization

There are now multiple Porifera FO+RO commercial and commercial-scale demonstration systems operating in North America and Asia on food and beverage and challenging wastewater applications (for example, animal manure). However, only a limited number have been operating for more than a year and none are designed to operate continuously in draw overpressure mode with a dye.

Based on the pilot results, the general process design and water quality performance were sufficient to envision what a commercial system would look like for this application. Additionally, the pilot revealed valuable information about additional technology and process modifications necessary to provide a reliable, affordable, and scalable commercial system for both OCWD's application and other IPR and DPR potable reuse applications.

Commercial Scale-Up Assumptions from Pilot Results

Based on the results from pilot testing, an overall process schematic was developed in coordination with Carollo Engineers working on behalf of OCWD. The treatment process schematic for a commercial system treating ROC at OCWD is shown in Figure 34 and Table 10 includes expected operating parameters based on pilot data as well as expectations of higher efficiency that would come with larger scale components.



Figure 34: Commercial Scale DPRShield Process for OCWD

Process flow diagram illustrates how the DPRShield treatment process can integrate into the existing GWRS process.

Source: Carollo Engineers and OCWD

The numbers shown on each stream in Figure 34 correspond to the same numbers in Table 10 and assume 10 mgd of ROC and 4 mgd of DPRShield permeate that would be blended with existing GWRS permeate prior to UVAOP and post-treatment.

A few items to note are that the ability to add an antiscalant to the draw is included in case scaling were to be observed on the FO membrane. Additionally, the amount of calcium added during post-treatment may decrease if a magnesium-based draw solution (for example, MgCl₂–road salt or MgSO₄–Epsom salt) were mixed with NaCl in the draw solution. Adding a magnesium-based salt would slightly increase energy use of the DPRShield process, but it would also produce a higher quality permeate and potentially reduce costs and operations challenges associated with post-treatment.

1 4 FO 2 3 RO 5 6 7 8 9 Feed Dilute RO Permeate RO Regen Blow FO Total Draw Feed Reject Draw Reject Reject Stream In Out down Flow (mgd) 4 3.98 6.02 10 8 8 3.98 0.02 6 5³ 5³ 5³ 10¹ 15 350² <25 10 Pressure (psi) 325 6,500 20,000 20,000 <200 39,800 40,000 39,800 11,000 TDS (mg/L) 11,100

 Table 10: Flow, Pressure, and Salinity Estimation Corresponding to Figure 35

1: Assumed FO feed pressure 10 psi; however, could be higher to increase FO reject pressure.

2: Assumes average RO pressure if RO is cleaned between 300 to 400 psi assuming a full-scale RO would operate more efficiently than the less efficient RO pilot system.

3: Assumed reject pressure; however, could be higher if needed for discharge.

Source: Porifera, Inc.

Technology and Process Modifications

First, the majority of reliability issues observed during pilot operations will be addressed with system design modifications. It is recommended that Porifera add a draw tank, pilot at a larger capacity to allow for commercial-size RO membranes and ancillary equipment like pressure-reducing valves and to improve feed maintenance options such as feed flush and recirculation to maximize crossflow to minimize fouling and improve cleaning frequencies.

Second, an upgrade is recommended to improve FO element reliability for operation in continuous draw overpressure mode. This would include (1) either making the current element adhesion stronger or (2) flipping the membrane prior to adhesion. While the first option would provide a nominal improvement, the latter would provide an improvement of 5 to 10 times in the safety factor in terms of draw overpressure prior to delamination, assuming proper manufacturing.

Third, a larger capacity element is recommended to reduce both the footprint and cost of any systems larger than 0.3 mgd. The design of this element is complete, and first

articles have been developed for other applications. A minor modification would allow for the membrane to be flipped within this larger element without any expected reduction in efficiency to improve reliability while operating in draw overpressure mode.

Lastly, additional demonstration is recommended to continue to optimize the DPRShield process, confirm uranine as the preferred draw marker, and confirm cleaning frequencies and reliability once upgrades are made to commercial elements.

Production Readiness Summary

The goal of this project was to clearly demonstrate the benefits of the DPRShield technology at a world-recognized municipal potable reuse facility.

While DPRShield technology had already been developed and patent protected, there was insufficient, non-confidential pilot-scale or commercial data demonstrating the technology's effectiveness to grow demand. Furthermore, the FO market at the time of this project award was virtually non-existent with insufficient demand to drive technology growth or investment in scaling up manufacturing to reduce cost. Finally, insufficient data were available for regulators to clearly understand the benefits of this technology. With the support of this project, Porifera was able to demonstrate the FO-based technology innovations to reduce energy and maximize protection while also integrating lessons learned into design and control protocols. This demonstration also uncovered a Porifera FO element design problem that needs to be addressed before the DPRShield technology will be sufficiently ready for sale to early adopters for commercial use. In addition, for municipal direct potable reuse, further work will be required to satisfy regulatory requirements.

Although useful pilot operation data were obtained and goals were demonstrated, no patentable inventions were conceived or reduced to practice during the project term. The project allowed Porifera to demonstrate continuous system operation and the Breach-Activated Barrier concept. The operational data and independent measurement and verification data from this pilot are not confidential and will be used to create case studies, presentations, and other marketing materials that will allow market professionals and customers to assess the technology for their needs and will promote future adoption of the technology. Porifera will also engage with regulators to understand further data needed to satisfy regulatory requirements and eventually provide a new technology to improve the permitting and implementation of direct potable reuse in California and worldwide.

CHAPTER 7: Technology and Market Transfer Activities

The scope of this project included development of a plan to share the knowledge gained and results of this pilot project with policy makers and industry decision makers as part of a broad, multi-pronged effort to advance and promote statewide and industrywide adoption of this new technology that offers tremendous promise of increasing potable use of waste streams.

Porifera's multi-pronged plan to inform stakeholders about this technology and encourage acceptance of it includes working with industry influencers, creating educational outreach materials, including published articles and papers, for distribution; updating its website for use as an information resource; making presentations; and participating in industry trade shows and exhibits.

Working with Industry Influencers

Porifera chose as its partners for this project organizations and individuals known worldwide for their work in advancing technologies related to water reuse. CDM Smith, a technology-neutral engineering firm known for evaluating advanced technologies for water reuse, served as the measurement and verification partner. Stanford University's Dr. William Mitch and his research colleagues are on the forefront of assessing disinfectant biproducts and emerging contaminant removal and potential toxicity for direct and indirect potable reuse research. Orange County Water District's Groundwater Replenishment System was the first of its kind IPR facility that revolutionized potable reuse in California and worldwide. Many of the staff are considered to be at the top of their field as well as in potable reuse applications.

Data generated by this project is also being evaluated by the US Bureau of Reclamation.

Outreach Materials and Publications

Porifera designed outreach materials to increase the speed and penetration of innovative energy efficient technologies into the marketplace. Porifera has also published articles and papers in industry trade magazines, including:

- <u>Advantages and Applications of Forward Osmosis</u>, Food Technology Magazine (an IFT publication), March 2017: <u>https://www.ift.org/news-and-publications/</u> <u>food-technology-magazine/issues/2017/march/columns/processing-forwardosmosis-and-applications-in-industry</u>.
- Forward Osmosis for the Food Industry, article for Commonwealth Scientific and Industrial Research Organisation (CSIRO) website, 2017: <u>https://www.csiro.au/</u> <u>en/Research/AF/Areas/Food-manufacturing/Making-new-sustainable-foods/</u> <u>Forward-osmosis</u>.

<u>Porifera is developing additional articles, including a case study</u>, Demonstration of Fail-Safe Water Reuse at OCWD, for publication on Porifera's website (<u>https://www.porifera.</u> <u>com/news-events</u>) and in industry trade publications.

Porifera revamped the company website to provide information and details of benefits that are being realized by the demonstration of the DPRShield and forward osmosis technologies. The website is a resource for case studies and product and system specification documents and includes sections specific to several different markets sectors to which the technology is applicable.

Presentations and Trade Show Participation

Porifera has made presentations and participated in numerous industry showcases and exhibits to expand the sphere of outreach to additional industry professionals and plans to continue outreach efforts, including the California Energy Commission Water Opportunities Workshop in November 2019.

- Oral presentation: EPIC Symposium, Sacramento, Calif., February 2017.
- Booth exhibit: California League of Food Processors, Sacramento, Calif., February 2018.
- Booth exhibit: Institute of Food Technologists Conference, Chicago, Ill., June 2018.
- Booth exhibit: California League of Food Processors, Sacramento, Calif., February 2019.
- Oral presentation: EPIC Symposium, Sacramento, Calif., February 2019.
- Oral presentation: California WateReuse Symposium, Garden Grove, Calif., March 2019.
- Booth exhibit: Institute of Food Technologists Conference, New Orleans, Louisiana, June 2019.
- Oral presentation: Membrane Technology Forum, Minneapolis, Minn., June 2019.
- The Emerging Technologies Coordinating Council/California Energy Commission Webinar, August 2019.

The multi-faceted approach of the technology transfer plan enables Porifera to showcase to stakeholders the potential the DPRShield technology offers for a safe, high quality potable product, but through education and information sharing to also bring the technology closer to commercialization, thus realizing increased water reuse and significant energy savings for all users.

CHAPTER 8: Conclusions and Recommendations

This pilot demonstration had multiple goals and objectives, including demonstrating the benefits of DPRShield in terms of water quality performance, pathogen rejection, realtime integrity monitoring, reducing energy requirements for reuse and new water supplies in California, and making potable reuse more "fail-safe" in the perceptions of regulators and public, as well as demonstrating commercial viability. While the majority of the project goals and objectives were demonstrated, there were also numerous challenges in terms of practical operations and implementation of this new technology.

Outstanding Challenges

The primary technical challenge—membrane delamination—can be easily addressed as the technology is improved. Pilot operations revealed outstanding questions in terms of maximum water recovery and design cleaning frequency. These questions can be addressed with a follow-up demonstration using a larger system configuration based on the lessons learned from this initial demonstration.

The conclusions were as follows:

- Water Quality: DPRShield provided permeate with a similar water quality to the existing GWRS permeate, while treating a feed water with 3 to 7 times higher concentrations of contaminants than the GWRS system.
- Pathogen Rejection: The Breach-Activated Barrier showed "fail-safe" rejection of pathogens when intentional FO membrane integrity breaches were made. Forward osmosis (FO) achieved greater than 8-log removal, and reverse osmosis (RO) achieved greater than 7-log removal. Initial data suggests that both the FO and RO unit processes can achieve greater than 4-log reduction value (LRV) credits for (the maximum allowable LRV credit per unit process is 6-log per the California Department of Water Resources).
- Real-Time Membrane Integrity Monitoring: Adding a dye to the draw solution increased real-time breach monitoring resolution by more than 100 times from 2-log (greater than 99 percent removal) to greater than 4.5-log (greater than 99.995 percent removal). This may give regulators confidence to grant FO and RO at least 4-log LRV credits each based on dye removal instead of the 2-log LRV credits currently granted to RO based on real-time total organic carbon (TOC) or conductivity measurements.
- Dye Selection: The selection of the proper dye had an observable effect on cleaning frequency, and additional dye fouling tests were needed to select the proper dye.
- Emerging Contaminant Rejection: DPRShield provided excellent rejection of emerging contaminants including 1.4 dioxane, NDMA, disinfectant byproducts, selected pharmaceuticals, and other selected emerging contaminants. FO membrane

element and system improvements that would allow higher draw overpressure could, in theory, improve DPRShield rejection in the future.

- Water Recovery for Reuse: DPRShield achieved a recovery as high as 45 percent of the RO concentrate volume generating a FO plus RO permeate. However, due to the operational challenges of this particular pilot system in draw overpressure mode, the system operated between 30 percent and 35 percent recovery for the majority of testing. Based on final data review, it is anticipated that a commercial DPRShield system modified for high feed surface velocity, occasional feed water flushes, and automated cleanings could achieve between 35 percent and 45 percent water recovery from the OCWD ROC.
- Cleaning Frequency: Due to onsite challenges with the system and current element design, there are still questions on sustainable feed water flush and cleaning frequencies for the FO membrane. Although during one period the FO membranes did not need to be cleaned for more than months, membrane delamination damaged these and other FO elements before a proper assessment could be made. Porifera's existing FO elements were not originally designed for draw overpressure mode, and new designs could easily address this issue.
- System Design: A dedicated draw tank should be added to improve system reliability, in both pilot and full-scale designs. While the "tankless system design" for this pilot system achieved its primary goals in terms of maintaining stable draw overpressure and achieving a small-footprint and energy-efficient operation, the lack of a dedicated draw equalization tank made it difficult to manage draw overpressure when there were abrupt changes in ROC water quality. This was especially true when power outages, cleaning, or other maintenance occurred at the GWRS, such as when full-scale RO skids were flushed, which caused low salinity water to enter the reverse osmosis concentrate line that fed the DPRShield pilot. This low salinity caused the FO flux to spike and caused FO membrane delamination due to rapid spikes in draw overpressure. With a dedicated draw equalization tank, the tank level would rise; however, because there was no tank, the draw pressure increased rapidly until the RO pump could speed up sufficiently to relieve the pressure.
- IPR versus DPR: Since the demonstration testing was primarily for a pretreated IPR application in which the majority of solids and pathogens were already removed, additional testing is needed to fully demonstrate reliability for DPR applications treating raw sewage, secondary effluent, and tertiary effluent. Initial data indicates that raw sewage and tertiary effluent may be easier applications than secondary effluent. As noted in this report, studies conducted in South Korea (on secondary and tertiary effluent) and at Stanford University (on greywater and raw sewage) indicate that PFO plus RO systems like DPRShield may be a potential solution for direct potable reuse.

Recommendations

Recommendations for additional research include:

- Engage Regulators to Attain LRV credits: Work with regulators in the California Department of Water Resources to determine additional demonstration necessary to attain up to 8-log (4 for FO and 4 for RO) pathogen LRV advanced treatment technology credits.
- Additional Testing and Demonstration: A larger scale demonstration could better evaluate cleaning frequency and reliability for IPR and DPR on raw sewage, secondary effluent, and tertiary effluent.
- Upgrade Technology to Improve Reliability in DPRShield Mode: Design new and larger Porifera FO elements to improve reliability with constant and higher draw overpressures.
- Evaluate Enhanced Emerging Contaminants of Concern (ECOC) Rejection: Engage a third-party research partner or university to assess the effect of higher draw overpressure on further increasing ECOC rejection.

CHAPTER 9: Benefits to Ratepayers

The project demonstrated that DPRShield technology has the potential to benefit industrial and municipal ratepayers in several ways:

- Provide potentially fail-safe pathogen removal . membrane integrity breaches occur by incorporating draw overpressure.
- Provide real-time, high resolution membrane integrity monitoring for FO and RO, which may allow both FO and RO to achieve greater pathogen removal credits for permitting.
- Generate high purity water for potable reuse even when treating a waste that has 5 times higher concentrations of contaminants than most potable reuse projects.
- Provide excellent rejection of pharmaceuticals, pesticides, DBPs, and other emerging contaminants of concern.
- Provide excellent rejection of pharmaceuticals, pesticides, disinfection byproducts, and other emerging contaminants of concern.
- Provide excellent rejection of disinfection byproducts precursors to alleviate concerns with mixing the properly permitted purified water into a potable distribution system.

It is difficult to estimate the potential energy savings for implementing DPRShield technology in California, so assumptions are needed to estimate the applicability and potential savings if a certain percentage of municipalities were to reuse their wastewater for potable reuse via IPR, DPR, or other high purity reuse instead of obtaining water from a more energy intensive source.

Benefits to California ratepayers would be both direct and indirect. Direct benefits include the potential for lower cost of power and water. Indirect benefits may include benefits to the environment, utilities that want to permit DPR projects, energy producers that can generate more electricity with smaller water diversions, and the economy.

Potential Energy and Emissions Savings for California

Potential statewide energy savings have been estimated in two different ways (top down and bottom up) to provide a range of potential savings based on industry adoption and assumptions listed below.

Based on these two approaches, it is anticipated that 162,000 MWh/year of energy could be saved from early adoption and on the order of 600,000 MWh/year assuming

widespread adoption and being selected over energy intensive alternatives such as seawater desalination.

Estimate 1: Top Down Approach for Increased Municipal and Satellite Potable Reuse

Implementing DPRShield technology for potable reuse at wastewater treatment plants and in smaller satellite reuse locations can reduce energy and water resource demands throughout the state, especially when the alternatives are long distance water transfers or seawater desalination. The energy savings can be lower processing energy to purify the water and/or reduced energy to transport the water from the location of treatment to the location of use.

The Natural Resources Defense Council and the Pacific Institute (NRDC&PI, 2014) estimated for California "that the water reuse potential (...) ranges from 1.9 million to 2.5 million AFY. Approximately 64 percent of the water reuse potential is from residences; the remainder is from commercial businesses and institutions (21 percent) and industry (15 percent). Some of this reuse is already occurring. According to a recent state survey, recycled water use in California is 670,000 AFY. Thus, the potential for additional water reuse in California today is 1.2 million to 1.8 million AFY (NRDC&PI, 2014)." Therefore, the maximum estimated potential for potable reuse for residential and commercial reuse is on the order of 1 to 1.5 million AFY (85 percent of 1.2 to 1.8 million AFY) of wastewater that was not reused at the time of the survey.

On average, we expect our technology to save between 1-10 kWh per every 1,000 gallons reused for most potable reuse applications based on savings compared to other potable reuse technologies, long distance State Water Project transfers, and seawater desalination.

If we assume that 20% of the 1 million AFY (178.5 million gallons/day) of new municipal wastewater is reused in California at an average of 3 kwh/1000 gal of energy savings on average per project, then the total energy savings would equate to approximately 195,000 MWh/year with an associated emissions reduction of 64,000 metric tons of CO_2 emissions.

Estimate 2: Energy Offsets Versus Other New Water Supply Alternatives (Bottom Up)

The second approach is to make assumptions about how increased potable reuse can offset higher energy requirements from other alternative new water supplies such as seawater desalination and increased long distance State Water Project transfers. Table 11 provides a summary of the estimates for estimated capacities and assumed offsets.

Table 11: Competing Water Resources that can be Offset by IncreasedPotable Reuse

Water Resource	Total Estimated Capacity	Assumed Percentage Offset	Assumed offset Capacity for Calculations
Planned Seawater Desalination Projects in CA ¹	514 million gallons per day (576,000 AFY) ¹	33%	170 million gallons per day (192,000 AFY)
California Urban Water Use Offset from Long Distance SWP Transfers	8.1 billion gallons per day (9.1 million AFY)	5%	406 million gallons per day (455,000 AFY)

1: Approximately 50 million gallons per day has already been implemented with additional projects in the works including projects in Monterey County.

2: Assumes this SWP water can be used near point of origin for significantly less energy.

Source: Porifera, Inc.

If we assume that 33 percent of the planned seawater desalination plant capacity were offset by DPRShield, the energy savings would equate to approximately 613,000 MWh/year. While if 5 percent of urban water that comes from SWP transfers were offset by DPRShield, the energy savings would equate to approximately 711,000 MWh/year.

Summary

Table 12 provides a summary of these different scenarios and the associated energy and emissions savings.

Table 12: Estimated Energy and Water Saving Benefits to Ratepayers

Scenario	Percent Converted to Potable Reuse	Annual Capacity	Unit Energy Savings Assumption	Annual Savings
1 million AFY available for reuse	20%	200,000 AFY	3 kWh/1000 gallons	195,000 MWh and 64,000 metric tons of CO_2 emissions
514 mgd of planned seawater desalination plants	33%	192,000 AFY	9.9 kWh/1000 gallons	613,000 MWh and 203,000 metric tons of CO ₂ emissions
9.1 million AFY urban water use from State Water Project	5%	455,000 AFY	4.9 kWh/1000 gallons	711,000 MWh and 235,000 metric tons of CO_2 emissions

Source: Porifera, Inc.

Underlying Assumptions for Top Down Energy Savings

Assumptions for supporting our projected growth rates include:

- DPRShield would save 3 kWh per 1000 gallons on average vs. competing alternatives.
- 178.5 million gallons per day. 3 kWh times 1785 units of 1000 gallons *365 days
 = 195,457,500 kWh/year = 195,457 MWh/year.

Underlying Assumptions for Bottom Up Energy Savings

- DPRShield would save 9.9 kWh per 1000 gallons on average vs. seawater desalination and offset 33 percent of the planned 514 mgd of planned SWRO facilities in CA.
- DPRShield would save 4.9 kWh per 1000 gallons on average vs. long distance SWP transfers and offset 5 percent of urban water use from this source.

Other Assumptions for All Energy Savings

- Emissions factor (CO₂): 0.73 pounds CO₂ saved per kWh saved and 2204 pounds per metric ton.
- There is increasing economic pressure to conserve water & energy resources.
- Strategic partnering with a large company will accelerate market penetration.
- DPRShield technology will be improved for reliable, mostly unmanned operation.
- A portion of California cities planning drought mitigation projects would implement DPR and DPRShield technology provides an easier way to permit DPR projects.

Note that key assumptions for energy and emissions calculations are based on the relevant results and conclusions from the pilot results while also incorporating efficiency improvements expected from scaling up the process from pilot-scale to commercial scale.

Benefits and Conclusions

The benefits for implementing DPRShield technology for potable reuse in California may provide significant energy reductions, CO₂ emissions, and other benefits compared to addressing droughts and water shortages with more energy intensive alternatives. Based on the estimates summarized above, it is estimated that implementing DPRShield technology at significant scale could offset on the order of 200,000 to 600,000 MWh per year and 60,000 to 200,000 metric tons of CO₂ emissions.

This obviously assumes that DPRShield technology can address key regulator concerns, work as or better than expected, and be selected for DPR projects over competing DPR technologies. It also is based on the following assumptions:

• More DPR projects will either maintain average water costs or limit future increases.

Assumption: more water reused = greater water sustainability and lower statewide costs.

- DPRShield will address some regulator and public concerns to improve DPR permitting.
 Assumption: fail-safe barrier and improved real-time monitoring = improved story & data.
- More potable reuse will lead to less electricity demand than seawater desalination.
 Assumption: reduced electricity demand = lower projected future demand.
- More potable reuse will decrease groundwater pumping and surface water diversions.
 Assumption: less water diverted = more water for hydroelectricity and the

Assumption: less water diverted = more water for hydroelectricity and the environment.

If these assumptions turn out to be correct and even a portion of the energy and emissions reductions are realized, then it would provide benefits to California ratepayers that would be both direct and indirect.

Direct benefits include the potential for lower cost of power and water, while indirect benefits may include:

- Increased water availability during droughts while increasing safety of the water supply.
- Improved permitting success of potable and advanced treatment reuse projects.

- Improved groundwater and surface water resources due to increased reuse.
- Decreased diversions from rivers and reservoirs equals more water available:
 - o to generate hydroelectric power,
 - o for power plant hybrid cooling projects,
 - and environmental benefits environmental benefits related to water temperature, such as improved native fish and wildlife habitat.
- Potable reuse equals softer and less salty water than typical non-potable recycled water; soft water improves energy efficiency of cooling towers, boilers, refrigeration, and other industrial and commercial equipment.
- Reduced energy demand and emissions and associated savings n terms of infrastructure.
- Stable economy due to industry benefiting from consistent water availability and pricing.
- Potential for reliable sources of potable reuse water for new developments or rural areas that require satellite treatment systems.
- Associated increases in local, state and federal tax income.
- Reduce the electrical energy, chemicals, maintenance, and overall cost of potable reuse of wastewater.

If demonstrated at sufficient scale, this work will accelerate broad technology adoption of DPRShield across California, resulting in energy savings and more water reuse.

LIST OF ACRONYMS

Term	Definition
AOP	advanced oxidation potential
BOD	biological oxygen demand
°C	Celsius
CCRO	closed circuit reverse osmosis
COD	chemical oxygen demand
DBP	disinfection biproduct
DP	differential pressure
DPR	direct potable reuse
ECOC	emerging contaminants of concern
EPA	Environmental Protection Agency
EPIC	Electric Program Investment Charge
ERD	energy recovery device
°F	Fahrenheit
FPW	final product water
FO	forward osmosis
GAC	granular activated carbon
Gal	Gallons
gpm	gallons per minute
GWh	gigawatt hours
GWRS	Groundwater Replenishment System
HAA	ten haloacetic acids
HAMs	four haloacetamides
HALs	Haloacetaldehydes
HANs	Haloacetonitriles
HKs	Haloketones
HNMs	Chloropicrin
I-THMs	iodinated trihalomethanes
IPR	indirect potable reuse
kg/l	kilograms per liter
kWh	kilowatt hours
Lb	Pounds

Term	Definition
LMH	liters per square meters per hour
MBR	membrane bioreactor
LRV	log reduction value
M&V	measurement and verification
m ²	meter squared
MCL	maximum contaminant levels
MF	Microfiltration
mg/L	milligrams per liter
mS	Microsiemens
mS/cm	microsiemens per centimeter
MTCO ₂	metric tons of carbon dioxide
NAs	Nitrosamines
NDMA	n-nitrosodimethylamine
OCSD	Orange County Sanitation District
OCWD	Orange County Water District
ppb	parts per billion
R&D	research and development
RO	reverse osmosis
ROC	reverse osmosis concentrate
RSF	reverse salt flux
SWP	state water project
SWRO	seawater reverse osmosis
TDS	total dissolved solids
ТОС	total organic carbon
TSS	total suspended solids
ТНМ	Trihalomethanes
UF	Ultrafiltration
USBR	U.S. Bureau of Reclamation
UVAOP	ultraviolet advanced oxidation process
V	Volt
Wh	watt hours
Wh/gal	watt hours per gallon
WWTP	wastewater treatment plants

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APPENDIX A: Additional Supporting Data

The water quality of the RO Concentrate that fed the pilot was quite variable in terms of foulants, but moderately stable in terms of osmotic pressure and salinity. Figure A-1 shows a typical variation in Total Organic Carbon (TOC) and electrical conductance (EC) (surrogate for salinity) of the RO Concentrate over a 3-week period. The TOC seems fairly stable during this period; however, there was a period in which fouling of the FO membrane increased more in a 12-hour period, than typically occurred over a 4 week period as shown in the increase in RO pressure in Figure A-2. The DPRShield pilot operated at a constant FO and RO permeate production, which meant that as the FO membrane fouled, the system would dose draw salinity as needed to maintain the permeate flow setpoint. This would cause the RO pressure to increase due to the higher RO feed salinity.



Figure A-1: Typical RO Concentrate Feed Salinity and Organic Loading

Graph of RO Concentrate Conductivity (red) and Total Organic Carbon (blue) loading over a 3week period



Figure A-2: Graph of a High Fouling Event

Source: Porifera, Inc.

Figure A-3 shows a graph which indicates drops in the conductivity of the ROC stream at the GWRS in green. Drops in this graph typically correlate to the flush of one of the RO skids at the GWRS, which would introduce very low salinity ROP flush water into the ROC line. This low salinity (low osmotic pressure) feed water would cause rapid spikes in FO flux in the DPRShield system. For most FO+RO systems, this would not cause an issue because this would only cause the draw tank level to increase, however, this DPRShield pilot was configured to operate without a draw tank in an effort to reduce energy, reduce footprint, and improve draw overpressure reliability. Since the draw tank level could not increase, then the draw pressure would spike, which would signal the RO pump to increase speed to expel sufficient permeate to match the increase in water flow into the system from the FO. If the RO pump response time was not sufficient, the spike in draw overpressure would cause delamination in the FO membrane, which were difficult to troubleshoot without the presence of dye



Figure A-3: Graph of GWRS RO System Flush Events

Source: Porifera, Inc.

FO and RO membrane autopsies were performed occasionally to assist in troubleshooting of these issues. There was no apparent irreversible scaling or fouling present on the elements selected for autopsy, all of which had been cleaned (CIP) at least once, since a CIP was one of the first troubleshooting methods used when the RO Pressure had increased. Unfortunately, most membrane delamination events also showed up as increased RO pressure, since salt that leaked into the feed required a greater draw salinity to maintain a constant FO flux.

Figure A-4 shows a SEM image of one of the FO membrane surface and its spacers from the first autopsy. The conclusions of the autopsy for an element that had run for 8 weeks including one CIP were as follows:

- The organic content of the foulant could not be determined as the membrane surface was virtually free of material. No reaction occurred during acid testing which is indicative of the absence of carbonates and metals.
- Microbiological analysis identified small amounts of amorphous inorganic material (e.g., clay), particles and biological material.
- Energy Dispersive Spectroscopy (EDS) identified sodium as the primary inorganic element present on the membrane surface with lesser amounts of silicon and trace amounts (<0.50 wt%) of chloride and aluminum.
- Scanning Electron Microscope (SEM) imaging revealed small amounts of foulant material along the feed spacer contact point. Close-up SEM imaging (5000x) of the feed spacer contact revealed a thin layer of smooth foulant with few particles.
- Chromatic Elemental ImagingSM (CEISM) identified the smooth foulant as clay (aluminum silicates) with particles composed of colloidal silica and aluminum. The membrane surface is represented by carbon and was visible away from the feed spacer contact point.

Figure A-4: FO Membrane Autopsy 1



Source: Porifera, Inc.

Figure A-5 shows an image of one of the FO membrane surface and spacers from a second autopsy, which showed extremely minor scaling at membrane contact points. The conclusions of the autopsy for an element that had run for 4 weeks including one CIP were as follows:

- No mechanical damage was detected on the external components of the two modules.
- Minimal foulant was visible on the membrane surface. Of the foulant that was isolated to the feed spacer contact points.
- The foulant in the contact points was identified as calcium phosphate in both the top and bottom membrane. Silica was also present in the feed spacer contact points of the bottom membrane.

Figure A-5: FO Membrane Autopsy 2



Source: Porifera, Inc. via Avista Technologies, Inc.

Figure A-6 shows a graph of fouling assessment tests using uranine and fluorescein dyes at Porifera's facility. This test was performed on a synthetic feedwater after it was determined that fluorescein seemed to impact cleaning frequencies. Other dyes were also evaluated; however, uranine was selected both in terms of fouling potential and having a similar wavelengths for detection so that the existing dye monitors in the DPRShield pilot would work without significant changes. In conclusion, uranine shows less fouling propensity than fluorescein.



Figure A-6: Dye Fouling Assessment and Comparison

Table A-1 summarizes the results for DBPs from their sampling events. NDMA is the key DBP for potable reuse projects and along with 1,4 dioxane is one of the top two ECOCs that regulators in the state of California use to determine the level of treatment required to meet potable reuse regulations. Total Trihalomethanes (TTHMs) and Haleoacetic acids (HAA5) are other DPBs regulated in drinking water, while iTTHMs and iHAAs iodated versions of these DBPs that are not currently regulated, but are considered to be potentially more toxic than the regulated DBPs. Stanford's team was particularly interested to see if the formation of iodated DPBs may be higher with DPRShield because there is some iodine in table salt (NaCl), which was used as the draw solution during all of this testing. The data indicates that this is not a concentrations observed at the GWRS, even though the concentrations of DBP precursors (organics needed to form DBPs) were at higher concentrations in the RO Concentrate (DPRShield feed) than in the feed to the GWRS RO.

The sampling events occurred on the following dates:

- 1. March 29, 2018
- 2. August 2, 2018
- 3. November 19, 2018
- 4. December 14, 2018

Water Quality Parameter	Sampling Event	GWRS ROC/ DPRShield Feed	DPRShield Pilot Permeate	GWRS Permeate on the Same Day	Regulated Limit
NDMA (ng/L)	1	149	22	21	10; UVAOP required to achieve regulation
	2	57	24	11	10; UVAOP required to achieve regulation
	3	131	26	11	10; UVAOP required to achieve regulation
	4	235	45	16	10; UVAOP required to achieve regulation
TTHM (ug/L)	1	56	1.8	2.4	80
	2	66	1.9	3.8	80
	3	81	14	6.5	80
	4	47	11	4.2	80
HAA (ug/L)	1	126	ND(<0.2)	ND(<0.2)	60
	2	64	0.8	4.1	60
	3	121	ND(<0.2)	1.3	60

Table A-1: Summary of Stanford University's Key Pilot Water Quality Analysis

Water Quality Parameter	Sampling Event	GWRS ROC/ DPRShield Feed	DPRShield Pilot Permeate	GWRS Permeate on the Same Day	Regulated Limit
	4	102	0.6	ND(<0.2)	60
iTTHM + iHAA (ug/L)	1	2.9	0.1	0.1	N/A; not currently regulated
	2	0.2	ND(<0.2)	0.2	N/A; not currently regulated
	3	4.5	ND(<0.2)	ND(<0.2)	N/A; not currently regulated
	4	3.1	0.3	ND(<0.2)	N/A; not currently regulated
1,4 Dioxane (ug/L)	1	35 (spiked)	ND (<0.1)	N/A	1
	2	41 (spiked)	ND (<0.1)	N/A	1
	3	42 (spiked)	ND (<0.1)	N/A	1
	4	60 (spiked)	ND (<0.1)	N/A	1

Figure A-9.1 and Figure A-9.2 summarize the data for each of the ECOCs spiked during these events with the exception of 1,4 dioxane, which is presented in Table A-1.



Figure A-4.1: Stanford ECOC Spiking Results (part one)

Graphs of the Results for Different Spiked ECOCs with sampling event 2 (green circles), sampling event 3 (dark red triangles), and sampling event 4 (purple rectangles).



Figure A-5.2: Stanford ECOC Spiking Results (part two)

Graphs of the Results for Different Spiked ECOCs with sampling event 2 (green circles), sampling event 3 (dark red triangles), and sampling event 4 (purple rectangles).

Figure A-10 summarizes the additional measurement and verification data collected by CDM Smith. Note that majority of measurements were within typical variations based on the specified accuracy of the instrument except for the feed and permeate conductivity meters which had to be re-calibrated multiple times throughout testing.



Figure A-6: Measurement and Verification Comparison

Source: Porifera, Inc.