

Groundwater Replenishment Performance and Operations: Lessons Learned During Clearwater's One-Year Pilot

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Challenged by the demand for affordable, safe drinking water and the need to reduce the impact of a high urban density on the coastal environment, the City of Clearwater investigated potable reuse through a pilot testing program for groundwater replenishment. Goals of this project include improving groundwater levels within the City through the recharge of the aquifer with purified water and minimizing the impact of potential increases in groundwater withdrawal from the City's existing wellfields. The Southwest Florida Water Management District (SWFWMD) is providing support and funding for the Clearwater Groundwater Replenishment Project as an alternate water supply that beneficially uses reclaimed water to help meet the Tampa Bay region's water supply needs.

To demonstrate the performance and reliability of the water purification process, the City conducted a one-year pilot of the water purification treatment system from June 2013 to June 2014. This article presents a summary of performance results from the treatment system. The results are presented after a brief description of the pilot treatment train.

Treatment Approach

The water treatment processes included in the purification process (Figure 1) were ultrafiltration (UF), reverse osmosis (RO), advanced oxidation process (AOP) with hydrogen peroxide and ultraviolet (UV), and membrane contactors to remove dissolved oxygen (DO) to help control the potential for metals mobilization from the aquifer formation. Reclaimed water was received from the City's Northeast Water Reclamation Facility. Piloting included an extensive water quality sampling and analyses program.

Groundwater recharge regulations include the requirement that the treatment process shall provide multiple barriers for organics and pathogens and that additional pollutant reduction for parameters reasonably expected to pose a risk to public health due to acute or chronic toxicity be provided. Based on available aquifer characteristics and groundwater quality data, the projected injection zone for the recharge wells at this time is within the underground source of drinking water (USDW) in lower zone A of the upper Floridan aquifer, which is likely to have total dissolved solids (TDS) between 800

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and 3,000 mg/L. This requires a minimum of 12 months of data from a pilot test per Chapter 62-610.564(3) of the Florida Administrative Code, in addition to multiple regulatory requirements pertaining to water quality. Requirements are discussed in the individual results sections where appropriate.

Results

Treatment process results are presented within the following summary categories: full treatment and disinfection requirements, drinking water standards, microorganisms, mutagenicity, microconstituents, and compatibility with native groundwater in the aquifer. Important operational insights gained during testing are interwoven into the discussion of each unit process.

Full Treatment and Disinfection Requirements

Total Organic Carbon

Sampling results indicated that the treatment train provided effective treatment for removal of total organic carbon (TOC). Typically, the treatment train reduced TOC by more than 99 percent from about 10 mg/L in the reclaimed water (RW-1) to below a detection limit of 0.06 mg/L in the purified water (PW-1). The TOC is regulated according to the full treatment and disinfection requirements given in 62-610.563(3)(d) to not exceed 3.0 mg/L (monthly average), with no single sample exceeding 5.0 mg/L.

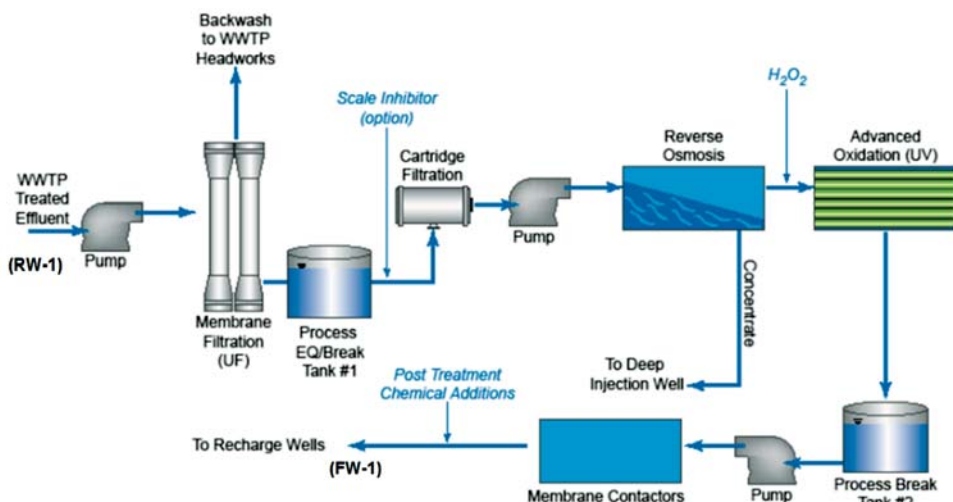


Figure 1. Groundwater Replenishment Pilot Process Flow Diagram and Sampling Points

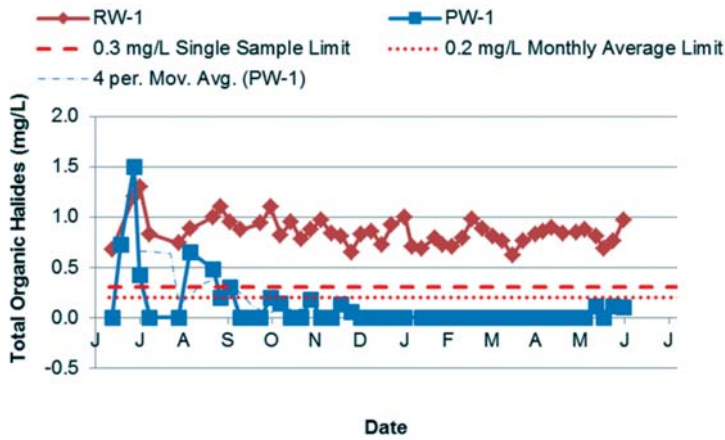


Figure 2. Total Organic Halides in Reclaimed Water and Purified Water

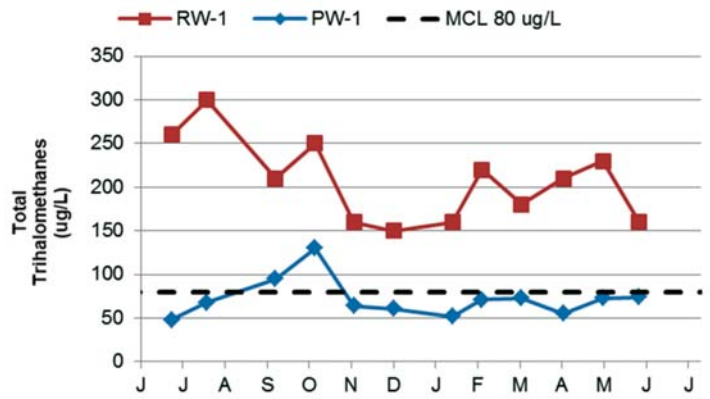


Figure 3. Total Trihalomethanes in Reclaimed Water and Purified Water

Total Organic Halides

Sampling results indicated that the treatment train provided effective treatment for removal of total organic halides (TOX). Earlier in the pilot study, TOX samples were typically taken after the sample taps had been wiped down with sodium hypochlorite and flushed. High TOX levels in the purified water dropped after sample tap bleaching and coliform sampling were moved to the end of the order of weekly parameter samples collected (Figure 2). The practice of bleaching and then flushing the sample tap may have introduced some TOX that were not naturally present in the purified water, increasing the observed value.

The TOX are regulated according to the full treatment and disinfection requirements given in 62-610.563(3)(e) to not exceed 0.2 mg/L (monthly average), with no single sample exceeding 0.3 mg/L.

Drinking Water Standards

Disinfection Byproducts

Sampling results indicated that the treatment train provided effective removal of disinfection byproducts (DBPs). The DBPs, including total trihalomethanes (TTHMs) and haloacetic acids (HAA5), are regulated to the levels listed in the Primary Drinking Water Standards. The maximum contaminant level for TTHMs is 80 µg/L, and for HAA5 is 60 µg/L.

Haloacetic Acids

The treatment train consistently reduced HAA5 below the maximum contaminant level (MCL) of 60 µg/L to less than 10 µg/L starting from reclaimed water concentrations ranging from approximately 30 µg/L to 60 µg/L. The HAA5 are the sum of five regulated haloacetic acids: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid.

Total Trihalomethanes

The treatment train consistently reduced TTHMs to between approximately 50 µg/L and 125 µg/L, starting from reclaimed water concentrations ranging from approximately 150 µg/L to 300 µg/L (Figure 3). The TTHMs are the sum of four regulated trihalomethanes (THMs): chloroform, bromodichloromethane, dibromochloromethane, and bromoform, and the TTHM levels were above and below the 80 µg/L MCL.

The pilot process was sampled for TTHMs in January 2014 to investigate the possibility of reducing TTHMs and to identify the portions of the treatment process that were removing most of them. Figure 4 shows the results of the system profile by location in the pilot plant. The profile includes two sample points before the pilot plant: post filters (after the reclaimed water filters) and postchlorine contact chamber. The sampling location MF-F-1 represents reclaimed water that has passed through the reclaimed water storage tank and before the membrane filtration step with UF membranes.

The total THMs in MF-F-1, 190 µg/L (corresponding to reclaimed water), were greater than the levels after the chlorine contact chamber, 89 µg/L, and after the reclaimed water filters, <1 µg/L. This suggests that moving the pilot treatment source from the reclaimed water storage tank to the contact chamber effluent could reduce TTHM concentrations by nearly 50 percent. Assuming a corresponding 50 percent reduction in purified water TTHMs, the pilot treatment system would be capable of bringing the TTHMs below the MCL.

Typically, the whole pilot treatment process reduced the TTHMs by about 50 percent. This reduction was not attributable to one single process, but rather several processes working in series. The RO removed about 25 percent of TTHMs, with no significant difference by type of THM. The UV and hydrogen peroxide advanced oxidation process (UVAOP) removed about 30 percent of TTHMs, with chlorodibromomethane being much higher (85 percent removal) than the other species and no significant

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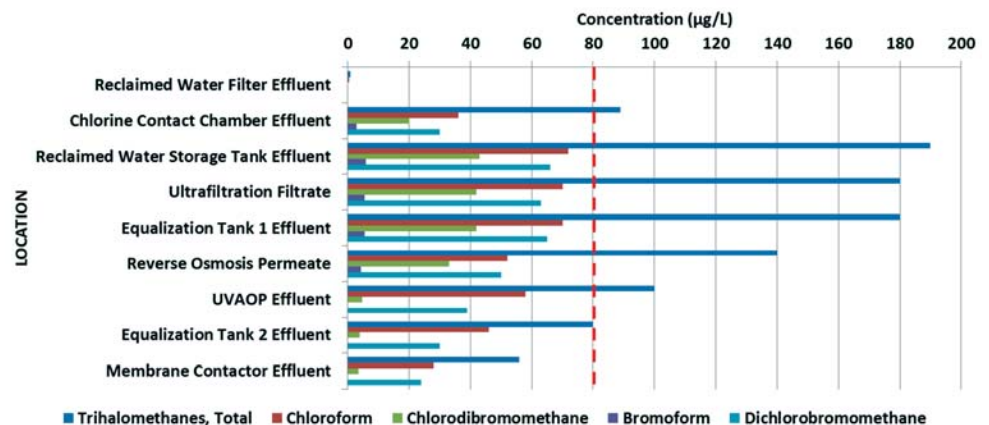


Figure 4. Profile of Trihalomethanes Through the Treatment Process

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removal of chloroform. Equalization tank 2 allowed for UVAOP water to fall a short distance into the tank, providing natural aeration that removed approximately 20 percent of all TTHMs.

The membrane contactor removed about 30 percent of TTHMs.

These differences in removal by THM type provide insight into the specific role of each unit process in removing TTHMs. Nevertheless, relo-

cating the source from the reclaimed water storage tank to the chlorine contact chamber effluent would probably be adequate to address TTHM levels in the purified water.

Microorganisms

Pathogens

Sampling results indicated that the treatment train provided effective removal of all infectious pathogens tested. The purified water and reclaimed water were sampled for multiple types of pathogens in accordance with 62-610.564(4)(b), including enteroviruses, *Cryptosporidium*, *giardia*, and helminths. Large volumes of water were passed through sample filters, with 100 L of reclaimed water (RW-1) and purified water (PW-1) filtered on site and sent to a commercial laboratory for analysis. Table 1 summarizes the pathogen counts from testing.

A small amount of nonviable helminth ova were observed in the purified water on Oct. 8, 2013, and Dec. 3, 2013; however, since these helminth ova were nonviable, they would not present any risk of infection.

Coliform Bacteria

Sampling results indicated that the treatment train provided effective treatment for removal of coliform bacteria. The purified water and reclaimed water were sampled for total coliforms and *Escherichia coli* coliform bacteria on a weekly basis using a presence/absence method. In the purified water, neither total coliform bacteria nor *E.coli* were detected after 51 weekly samples. In the reclaimed water, *E.coli* were present in one out of 51 weekly samples and total coliform in 11 out of 51 weekly samples.

Maintaining Ultrafiltration Performance

The primary filtration process for physical removal of pathogens in the treatment train was UF. Chemically enhanced backwashes were carried out on a daily basis (high pH) and a weekly basis (low pH). Through the course of pilot testing, the UF membranes accumulated moderate fouling, as shown by the increase in transmembrane pressure (TMP), as shown in Figure 5. The pilot ran for approximately five months before requiring the first clean-in-place (CIP). High pH cleaning was effective for removing TOC from the membranes; low pH cleaning was effective in removing iron fouling.

Toward the end of the pilot testing period, the UF membrane fouled very rapidly after each, requiring three CIPs within a one-month period. In order to address this buildup of foulants, a procedure of repeated chemically enhanced backwashes (CEBs) over a few hours led

Table 1. Pathogen Counts for Reclaimed and Purified Water

| Pathogen | Units | Raw Water | | | | | |
|-----------------|----------------------------|--------------------|------------------------|------------------------|-------------------------|-------------------------|-------------------------|
| Date | | 07/19/13 | 10/08/13 | 12/03/13 | 02/04/14 | 04/03/14 | 05/27/14 |
| Cryptosporidium | Oocysts/100L | 16.3 | 14.4 | 3.2 | 1.3 | <1.4 | 1.3 |
| Enteroviruses | Infectious Units/100L | BDL | BDL | BDL | BDL | BDL | BDL |
| Giardia | Oocysts/100L | 2.8 | 12.5 | 7.0 | 22.6 | <1.4 | BDL |
| Helminth Ova | Total ³ ova/L | 45.0 | 27.0 | 26.0 | 12 | 375 | 324 |
| | Viable ova/L | BDL | BDL | BDL | BDL | BDL | BDL |
| Pathogen | Units | Purified Water | | | | | |
| Date | | 07/19/13 | 10/8/13 ⁽¹⁾ | 12/3/13 ⁽¹⁾ | 02/04/14 ⁽¹⁾ | 04/03/14 ⁽¹⁾ | 05/27/14 ⁽¹⁾ |
| Cryptosporidium | Oocysts/100L | N/A ⁽²⁾ | BDL | BDL | BDL | BDL | BDL |
| Enteroviruses | Infectious Units/100L | BDL | BDL | BDL | BDL | BDL | BDL |
| Giardia | Oocysts/100L | BDL | BDL | BDL | BDL | BDL | BDL |
| Helminth Ova | Total ⁽³⁾ ova/L | BDL | 0.07 | 0.16 | 0.07 | 0.10 | 0.16 |
| | Viable ova/L | BDL | BDL | BDL | BDL | BDL | BDL |

Notes:

- ¹ Sampled from membrane contactor effluent (MC-E-1) to avoid turbidity interference from lime addition.
- ² Turbidity interference from lime addition in the purified water interfered with pathogen counts for July 19, 2013.
- ³ None of the ova were found to be viable, and therefore do not pose any infection risk.
- ⁴ The presence of pollen, insect eggs, and larvae from insect excrement complicate the process of enumeration as they resemble, microscopically, the ova that are being enumerated. Pollen, eggs, and biologicals may be misclassified as ova even by a trained person. Additionally, if insects gain access to the water system, then it is possible that they would release ova as part of the insects' natural life cycle.

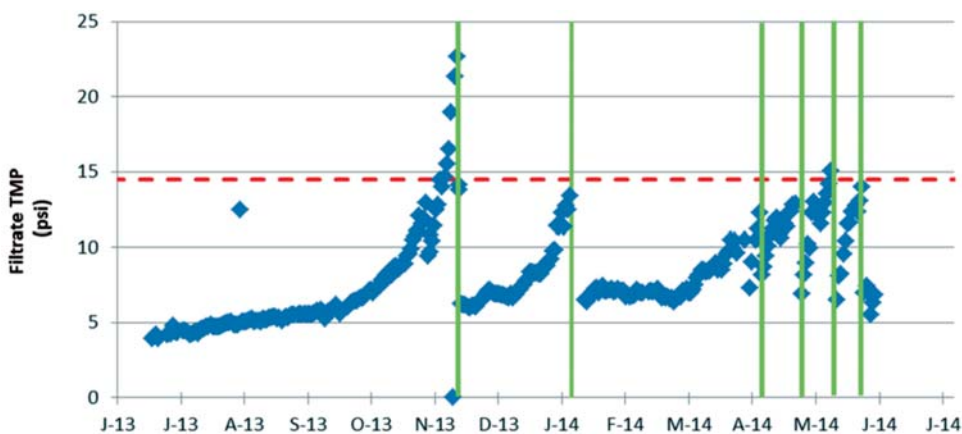


Figure 5. Ultrafiltration Transmembrane Pressure

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to significant drops in TMP by more than 7 pounds per sq in. (psi), dropping to near original levels, with the low pH CEB resulting in a greater than 5 psi drop. This suggests that the low pH CEBs may have removed large masses of accumulated iron fouling. With more frequent low pH CEBs, it is anticipated that fewer CIPs would be required. An autopsy of the UF module confirmed that iron had been accumulating on the UF modules.

This experience showed the importance of keeping the CEB program flexible and repeating CEBs until the improvements in pressure diminish entirely. If a CEB cycle shows a significant decrease in TMP (i.e., >1 psi), the CEB cycle should be repeated until the decrease in TMP diminishes with each test. If the TMP is still well above the clean startup pressure, another CEB solution should be tried. Otherwise, if the TMP drops to near the clean startup pressure, chemical backwashing should be discontinued and normal production resumed.

Maintaining Reverse Osmosis Performance

The RO was the secondary filtration process for physical removal of pathogens in the treatment train, and the primary treatment process for removal of microconstituents. The RO membranes operated smoothly during the year of pilot testing, with some scaling observed in the third stage. Evidence from a membrane autopsy and a “canary” element indicated that the scale was calcium phosphate. This scaling was removed using a combination of high pH and low pH CIPs. The RO process was converted from three-stage to two-stage during the testing and successful testing results supported use of two-stage operations as a more robust approach for the full-scale design.

Mutagenicity

Sampling results indicated that the treatment train produced water without significant observable mutagenic effects. Mutagenicity testing was performed as required by FAC 62-610.564(4)(c). The “Ames Test” (EPA 600/4-82-068) was selected as the mutagenicity test method since it has been in widespread use over the past 30 years, is relatively easy to carry out, and is partly quantitative. A standard commercial test kit was used for all mutagenicity testing. Each test kit incorporated standard, 96-well microplates and five different strains of salmonella bacteria. Each sample was exposed to five different types of bacteria (T-97a, T-98, T-100, T-102, and T-1535) so that several different base pair and frame shift mutations can be investigated.

The reagents were prepared, then distributed into each microplate and incubated at 37°C for five days. Mutagenicity was indicated by a positive color change from purple to yellow, which indicated that the reverse mutation of the bacteria by the sample had allowed synthesis of the histidine reagent. The kit included a sterile blank, reagents, and a positive control to perform necessary quality controls. Potential mutagenicity was quantified by counting the number of wells that change color and comparing the results to the control blank using statistical significance tables. Mutagenicity testing was performed in triplicate and plate counts for each sample averaged.

A summary of the mutagenicity test results by location, date, and strain of test bacteria is shown in Table 2, with the level of mutagenicity indicated by color. Early tests had shown some signs of mutagenic effects in the purified water; however, during these tests (Oct. 8, 2013, and Oct. 22, 2013) it was observed that sodium

bisulfide was underdosed, therefore allowing peroxide, an oxidant added to support the UVAOP process, to remain unquenched in the purified water. When peroxide was fully quenched, with a slight sulfide residual of about 0.5 mg/L left over, no significant mutagenic effects were observed (Nov. 19, 2013, and Jan. 24, 2014)

Microconstituents

This section includes the results of microconstituent sampling and UVAOP challenge testing for destruction of microconstituents N-nitrosodimethylamine (NDMA) and 1,4 dioxane.

Microconstituent Sampling

The pilot water purification process was designed to be effective at removing a wide variety of unregulated organics and small molecular weight compounds known as microconstituents. The microconstituents analyzed include compounds spanning a broad range, such as pharmaceutically active agents (drugs and antibiotics), personal care products, and hormones. Reclaimed water, purified water, and target aquifer injection zone water samples were analyzed for 62 different microconstituents in October 2013 and January 2014.

The results indicated that some microconstituents were present in the reclaimed water, but in the purified water, all microconstituents present, except one, were removed by the pilot process to below the reporting limits. The minimum reporting limit is the smallest measured concentration of a substance that can be reliably measured by using a given analytical method. Over the course of five separate sampling events, 30 out of 62 microconstituents were detected in the reclaimed water.

Sampling results have indicated that the treatment train is effectively reducing nearly all microconstituents tested to below minimum reporting levels; these microconstituents are shown in Table 3. In the purified water, none of the 62 microconstituents were detected for four out of the five sampling events; however, one compound, atenolol, was found in the purified water in one sampling event (January 2014). Similarly, in the lower zone A of the upper Floridan aquifer, none of the 62 microconstituents tested were detected.

Atenolol, which is a high blood pressure medication, was the only microconstituent that was detected in the purified water. In January 2014, it was detected in the reclaimed water at a concentration of 75 ng/L. The pilot treatment train removed 79 percent of atenolol from the water, resulting in a purified water concentration of 16 ng/L; this concentration is above the

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Table 2. Summary of Mutagenicity Results for Reclaimed Water and Purified Water

| Sample Date | RW-1 | | | | | PW-1 | | | | |
|-------------|------------------|--------|-------|-------|-------|------------------|--------|-------|-------|--------|
| | Bacterial Strain | | | | | Bacterial Strain | | | | |
| | TA100 | TA1535 | TA97 | TA98 | WP2 | TA100 | TA1535 | TA97 | TA98 | WP2 |
| 8/22/13 | Green | Green | Red | Green | Red | Green | Red | Green | Green | Green |
| 10/8/13 | Green | Green | Green | Green | Green | Green | Green | Green | Green | Yellow |
| 11/19/13 | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green |
| 1/24/14 | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green |
| 3/11/14 | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green |

Notes:

8/22 and 10/8: Peroxide residuals not quenched

3/11: WP2 Laboratory control showed signs of contamination within laboratory

- Green: Negligible mutagenic effects observed
- Red: Strong mutagenic effects observed
- Yellow: Moderate-weak mutagenic effects observed
- White: Not available

Table 3. Microconstituent Concentrations

| Item | Reporting Limit (PQL) (ng/L) | Reclaimed Water (ng/L) | | Purified Water (ng/L) | |
|--------------------------------|------------------------------|------------------------|---------|-----------------------|---------|
| | | Average | Maximum | Average | Maximum |
| Sucralose | 100 | 47400 | 56000 | ND | ND |
| Iohexal | 10 | 726 | 980 | ND | ND |
| TCEP | 10 | 266 | 400 | ND | ND |
| Lopressor | 20 | 230 | 350 | ND | ND |
| Hexachlorocyclopentadiene | 50 | 211 | 760 | ND | ND |
| TCPP | 100 | 198 | 430 | ND | ND |
| Acesulfame-K | 20 | 184 | 740 | ND | ND |
| Primidone | 5 | 158 | 170 | ND | ND |
| TDCPP | 100 | 154 | 390 | ND | ND |
| Carisoprodol | 5 | 135 | 300 | ND | ND |
| Carbamazepine | 5 | 134 | 190 | ND | ND |
| Dehydronifedipine | 5 | 98 | 200 | ND | ND |
| Dilantin | 20 | 90 | 120 | ND | ND |
| Meprobamate | 5 | 70 | 200 | ND | ND |
| Acetaminophen | 5 | 46 | 220 | ND | ND |
| Caffeine | 5 | 26 | 120 | ND | ND |
| Atrazine | 5 | 23 | 30 | ND | ND |
| Atenolol | 5 | 21 | 75 | 5.2 | 16 |
| DEET | 10 | 20 | 64 | ND | ND |
| 1,7-Dimethylxanthine | 10 | 18 | 71 | ND | ND |
| Fluoxetine | 10 | 17 | 28 | ND | ND |
| Methylparaben | 20 | 15 | 34 | ND | ND |
| Cotinine | 10 | 12 | 18 | ND | ND |
| Diuron | 5 | 8.4 | 32 | ND | ND |
| Gemfibrozil | 5 | 6.3 | 14 | ND | ND |
| N-Nitroso-dimethylamine (NDMA) | 2 | 4.7 | 5.5 | ND | ND |
| DEA | 5 | 4.0 | 10 | ND | ND |
| Sulfamethoxazole | 5 | 3.3 | 6.5 | ND | ND |
| Diazepam | 5 | 3.1 | 5.3 | ND | ND |
| 4-androstene-3,17-dione | 0.3 | 0.30 | 0.41 | ND | ND |

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analytical laboratories minimum reporting limit of 5 ng/L. Without a regulatory limit for atenolol, some other point of reference is needed in order to understand the significance of the reported concentration.

In order to quantify the risk of adverse health effects from unregulated chemicals, the National Research Council states that a margin of safety (MOS) can be used. This MOS is the ratio of a contaminant-specific risk reference value and the concentration of the contaminant in the purified water. An MOS>1 suggests that the contaminant in the water is unlikely to pose significant risk of adverse health effects. A risk reference value for atenolol of 70,000 ng/L¹ was recently reported in the potable reuse literature. Since the concentration of atenolol measured in the purified water was 16 ng/L, the MOS is 4,375, indicating that 16 ng/L of atenolol is not likely to pose significant risk of adverse health effects. Atenolol was added to the UVAOP challenge testing program.

Ultraviolet and Hydrogen Peroxide Advanced Oxidation Process Challenge Testing

The UVAOP process is intended to reduce concentrations of microconstituents that remain after RO. Concentrations of microconstituents are very low and often variable due to changes in community use of products and treatment plant performance. Consequently, it can be difficult to show that the UVAOP process is reducing microconstituents as intended. Temporarily spiking the concentration of a few target contaminants above background levels raises the influent and effluent concentrations high enough to be measured, allowing UVAOP performance to be quantified.

Sampling results indicated that the UVAOP process met the log removal goals for NDMA at 1.4 log removal and 1,4-dioxane, or 0.5 log removal. These goals and target contaminants were based on the California Department of Public Health (CDPH) draft criteria for groundwater recharge with reclaimed water, and are widely used as a benchmark for measuring UVAOP performance in groundwater recharge applications.

The NDMA was removed below detection limits at all peroxide doses tested for all but one sample that still met the 1.4 log removal target. Removal to detection limits corresponds to at least 2.6 log removal, well above the 1.4 log removal value target. The NDMA removal is based on UV irradiation only and does not require any peroxide addition.

On average, 1,4-dioxane was removed beyond the log removal target of 0.5 log removal, for tested peroxide doses greater than 2 mg/L (Figure 6). The removal of 1,4-dioxane was de-

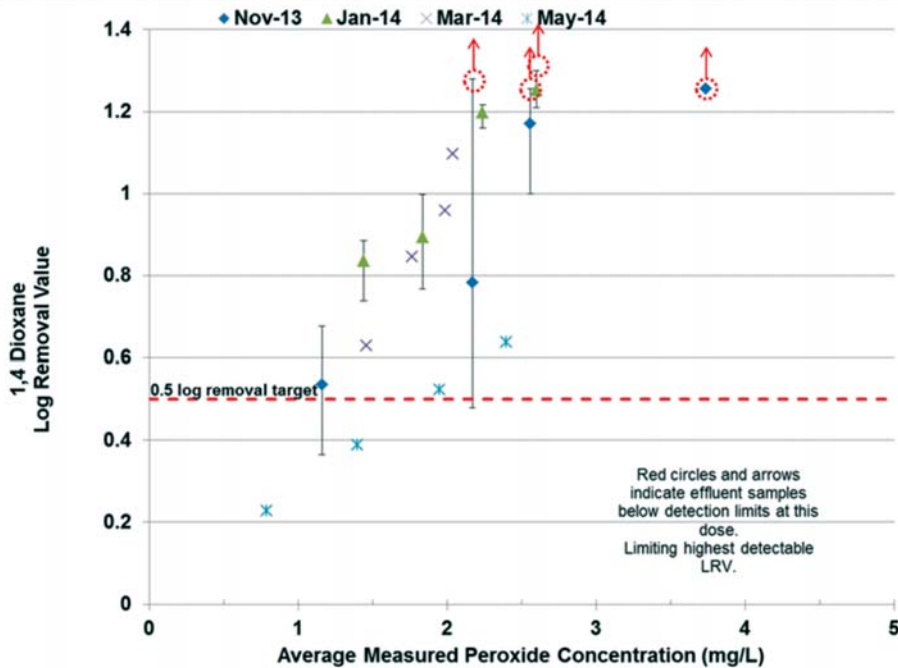


Figure 6. Log Removal of 1,4-Dioxane Versus Peroxide Dose for the Ultraviolet and Hydrogen Peroxide Advanced Oxidation Process

pendent on peroxide dose, with higher doses of peroxide providing greater degrees of removal of 1,4-dioxane. The 1,4-dioxane is destroyed by hydroxyl radicals (OH•) that are formed when UV light splits hydrogen peroxide (H₂O₂) molecules.

Atenolol was included in the third and fourth rounds of challenge testing since it was detected once in the purified water at 16 ng/L. Atenolol removal during spike testing exceeded the 0.5 log (68 percent) removal requirement from the CDPH Groundwater Replenishment Reuse Draft Regulation (2011) at the lowest peroxide dose tested, 0.8 mg/L. The UV-based AOP challenge testing provided additional data to inform potential changes to the UV-based AOP operating conditions, if a higher level of treatment is desired. Atenolol was the only nonregulated microconstituent identified in the purified water. Follow-up investigation of records found a temporary underfeed of peroxide on the day of sampling that was the likely cause of reduced atenolol destruction.

Compatibility with Native Groundwater in an Aquifer

After the treated water passes through the UVAOP process, additional treatment was applied to adjust its water quality to be compatible with the quality of the groundwater in lower zone A of the upper Floridan aquifer. The target aquifer injection zone includes limestone with traces of arsenopyrite (FeAsS) mineral. One goal of post-treatment was to increase the calcium carbonate stability of the treated water to mitigate the potential for dissolution of limestone in the aquifer. Another important goal of post-treatment was to reduce the oxidation reduction potential (ORP) of the treated water such that arsenic dissolution does not occur. Experience with aquifer storage recovery (ASR) in Florida has shown that oxygenated water can mobilize mineral-bound arsenic from the rock formation into groundwater. Therefore, post-treatment targets the removal or conversion of any residual oxidants in the treated water.

Calcium Carbonate Stability

Sampling results indicated that the post-treatment process improves the calcium carbonate stability of the water; however, dosing control was important to limit the precipitation of calcium carbonate scales in the purified water pipe. Before post-treatment, the process water was characteristic of RO permeate, with pH 5.5, calcium 5 mg/L as calcium carbonate, alkalinity 10 mg/L as calcium carbonate, and calcium carbonate precipitation potential (CCPP) of -110 mg/L as calcium carbonate. The negative CCPP indicates that this water would tend to dissolve calcium carbonate. While passing through the

membrane contactor, much of the dissolved carbon dioxide was removed from the water, increasing the pH to 6.5, while maintaining the same levels of calcium and alkalinity, and increasing the CCPP to -15 mg/L as calcium carbonate. After the membrane contactor, approximately 70 mg/L of carbon dioxide was injected into the solution under pressure, followed by 75 mg/L as calcium carbonate of lime, increasing the total calcium to 80 mg/L as calcium carbonate, the pH to 7.25, the alkalinity to 100 mg/L as calcium carbonate, and CCPP -10 mg/L as calcium carbonate.

Earlier in the pilot study, the pH was adjusted to 7.75, and closer to zero CCPP, by adding less carbon dioxide. However, at these targets, the pH was more difficult to control, and the purified water line would frequently grow a film of calcium carbonate scale and result in high turbidity above 10 nephelometric turbidity units (NTUs). It seems that the lime slurry did not have adequate time and driving force to completely dissolve into solution. Presumably, the instability in pH near 7.75 was due to some

combination of instability in carbon dioxide addition at low flow rates, and the lower pH buffering capacity of water near pH 8. Presumably, swings in pH could have led to the onset of calcium carbonate precipitation.

When the carbon dioxide dose was increased, and pH dropped to 7.25, pH stability improved, calcium carbonate scale formation diminished, and turbidity dropped below 10 NTUs. The CCPP should be maintained slightly negative in order to avoid clogging the purified water line and potentially scaling the aquifer, increasing well pressures. Similarly, the CCPP should be increased as much as possible beyond the negative starting point of -110 mg/L calcium carbonate to reduce the potential for limestone dissolution in the aquifer. One possible alternative that could avoid the turbidity issues and, potentially, the rapid scale formation, would be to substitute calcium chloride and caustic soda for lime. Preliminary desktop calculations indicate that a calcium chloride/caustic soda substitution

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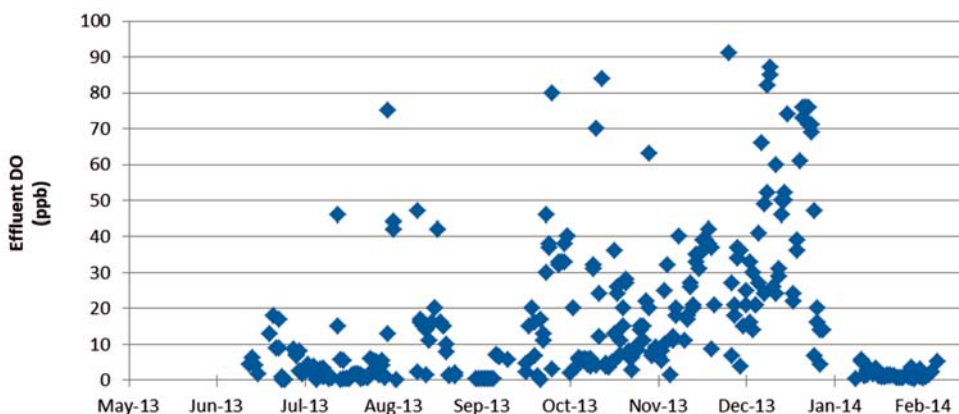


Figure 7. Trace Dissolved Oxygen Sensor Readings From the Post-Treated Purified Water and the Membrane Contactor Effluent

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could be up to six times more expensive than the current calcium carbonate addition approach.

Oxidation Reduction Potential

The membrane contactors and sodium bisulfide chemical feed work together to reduce the oxidation reduction potential of the water by removing DO or converting oxidizing species (chlorine, peroxide) from the water, which could potentially cause undesirable mobilization of arsenic or other metals in the aquifer.

Oxidants

The membrane contactors routinely removed most of the DO from the purified water. The DO entered the membrane contactors at near 100 percent saturation (6-9 mg/L), and was removed down to 100 parts per billion (ppb) or less of DO, with the capability of operating near 1 ppb of DO. Figure 7 shows the trace DO levels in ppb over time. Proper air calibration and zeroing of trace DO meters were essential to the measurement of DO at ppb levels. While operating the membrane contactor, in order to maximize performance, it was important to maintain adequate sweep gas flow rate and adequate vacuum on the sweep gas line (less than approximately -27 inHg).

The DO readings were lower and more repeatable when they were taken before post-treatment chemical addition. Before January 2014, the trace DO sensor was drawing off of the purified water line, after lime addition and bisulfide addition. After January, the DO sensor membrane was replaced and set to run only on water received immediately after the membrane contactor and before chemical addition. When the old sensor membrane was removed, it appeared to have a yellow hue and some precipitate, indicating that some of the post-treatment chemicals may have interfered with the sensor. Therefore, two trace DO sensors should be installed on a full-scale system: one before post-treatment chemical addition (and potential chemical interference) and one after chemical addition.

After sodium bisulfide addition, the chlorine residual was consumed within seconds to below the detection limit of field instrumentation. Approximately 1.2 mg/L of chloramines carry through the membrane contactors until the point of sodium bisulfide addition.

Hydrogen peroxide reacted slowly with sodium bisulfide, typically requiring about 30 minutes to reach completion. If insufficient sodium bisulfide was added, it was used up and residual peroxide remained. Underfeeding of sodium bisulfide and incomplete quenching of peroxide appeared to impact early mutagenicity tests. Hydrogen peroxide was added upstream at a residual of about 2 mg/L, as a part of the UVAOP. During the advanced oxidation process, only about half of the added peroxide was consumed, and the remaining 1 mg/L of peroxide passed downstream through the membrane contactors until sodium bisulfide was added.

Sodium bisulfide addition is important for quenching remaining oxidants in the water and reducing the overall ORP before injection into the aquifer. The feed rate of bisulfide needed to be monitored throughout the usage of each barrel of

chemical. As the barrel of chemical aged, it turned from a yellow color to a red color, and a higher chemical feed rate was needed to neutralize peroxide completely. After initial mutagenicity tests indicated that more sulfide feed was required to quench peroxide, the sulfide dose was increased such that, after 30 minutes, peroxide would be quenched and a 0.5 mg/L sulfide residual would remain.

Rock Core Testing and Aquifer Recharge Testing

Rock core and aquifer recharge testing were being studied concurrently with the pilot purification process. Rock core testing consisted of running purified water through native rock core samples with varying amounts of post-treatment. Arsenic release data indicated a direct correlation between DO removal and arsenic mobilization, supporting DO removal as a control strategy for arsenic mitigation. Water quality samples collected from lower zone A of the Floridan aquifer during the recharge test indicated that native arsenic levels decreased with decreasing DO concentration and increasing sulfide content, supporting the selected treatment approach of DO removal and sulfide addition.

Summary

Results from the City's groundwater replenishment show that the facility produced purified water that reliably met drinking water quality standards. The water also consistently met all water quality requirements from the 2012 Full Treatment and Disinfection Requirements [Florida Administrative Code (FAC) Chapter 62-610.563(3)].

Important lessons learned affecting the operations of the groundwater replenishment treatment train will be incorporated into full-scale design of the groundwater replenishment water purification and aquifer recharge systems. In the next several years, multiple Florida utilities are anticipated to implement full-scale groundwater replenishment programs. Sharing of best practices and operational lessons learned will help Florida utilities move confidently together into a future of sustainable, abundant water supplies.

References

- ¹ Trussell, R.R. et al., 2013. "Potable Reuse: State of the Science Report and Equivalency Criteria for Treatment Trains." WateReuse Research Foundation. Alexandria, Va. ◊

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