

# **GROUNDWATER REPLENISHMENT PERFORMANCE AND OPERATIONS: LESSONS LEARNED DURING CLEARWATER'S ONE-YEAR PILOT**

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## **Executive Summary**

The City of Clearwater's yearlong groundwater replenishment pilot program demonstrated effective performance of a multiple barrier treatment train capable of meeting full treatment and disinfection requirements, meeting drinking water standards, removing infectious pathogens, removing mutagenic substances, removing microconstituents, and stabilizing the purified water for aquifer injection.

The experience gained through pilot testing provided several lessons learned.

- Taking source water from a chlorine contact chamber instead of a reclaimed water storage tank can help with control of total trihalomethanes in the purified water.
- Chemically enhanced backwash cycles for ultrafiltration should be repeated as necessary until the clean transmembrane pressure is restored, or no further pressure gains are achievable. This approach can extend the time between chemical cleans in place, and keep transmembrane pressures lower.
- Calcium phosphate scale formation is a potential concern for high recovery reverse osmosis in groundwater replenishment treatment trains. A two-stage RO system had less scale formation than a three-stage RO system at similar flux and recovery.
- When using both membrane contactors for dissolved oxygen removal and post treatment chemicals, a separate trace dissolved oxygen sensor should be provided before the post treatment chemicals, to avoid interference in the oxygen reading due to turbidity in the purified water.
- When adding lime to remineralize purified water, reducing the pH from 7.75 to 7.25 led to significant improvements in turbidity, and reductions in pipe scaling.
- Neutralization of peroxide with sodium bisulfide requires special attention from operators because sodium bisulfide feed stocks lose strength over weeks of air exposure, and peroxide neutralization can take nearly 30 minutes to complete.

- Dissolved oxygen removal appears to be a highly-effective approach to mitigation of arsenic mobilization in the target groundwater recharge aquifer. Both rock core column testing and water quality samples from aquifer recharge testing supported the tested approach, indicating that native arsenic levels decreased with decreasing dissolved oxygen concentration, and increasing sulfide content, supporting the selected treatment approach of dissolved oxygen removal and sulfide addition.

Lessons learned during pilot testing will be incorporated into full-scale design of the groundwater replenishment purification and aquifer recharge systems. In the next several years, several 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.

## **Introduction**

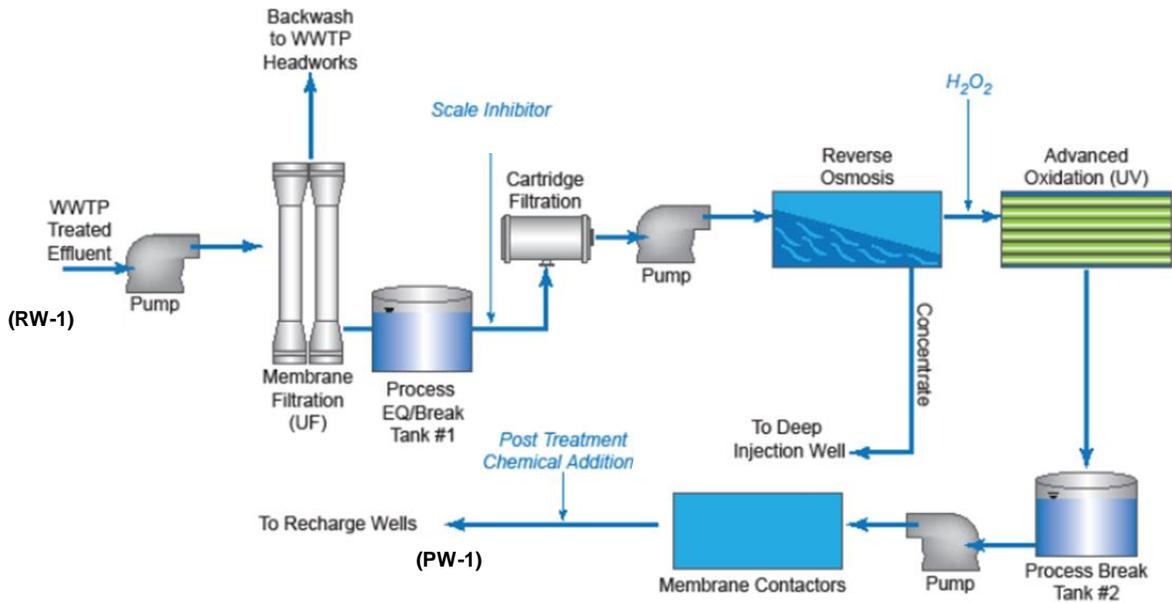
Challenged by the demand for affordable, safe drinking water and the need to reduce the impact of a high urban density on the coastal environment, the City of Clearwater investigated potable reuse through a pilot testing program for groundwater replenishment. Goals of this project include improving groundwater levels within the City of Clearwater 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 paper 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 UV, and membrane contactors to remove dissolved oxygen (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 a TDS between 800 and 3,000 mg/L TDS. 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.



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

## 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*

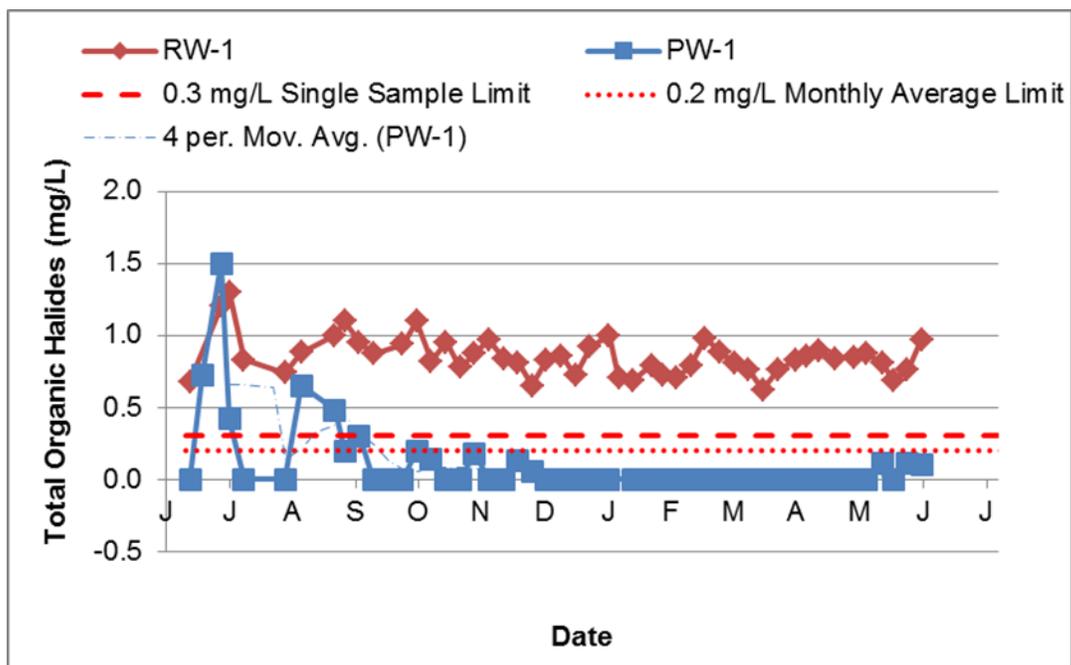
Sampling results indicated that the treatment train provided effective treatment for removal of total organic carbon (TOC). Typically, the treatment train reduced TOC by more than 99% from about 10 mg/L in the reclaimed water (RW-1) to below a detection limit of 0.06 mg/L in the purified water (PW-1). 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.

#### *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 then

flushing the sample tap, may have introduced some TOX that were not naturally present in the purified water, increasing the observed value.

Total organic halides (TOX) is 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.



**Figure 2** Total Organic Halides in the Reclaimed Water and Purified Water

### *Drinking Water Standards*

#### *Disinfection Byproducts*

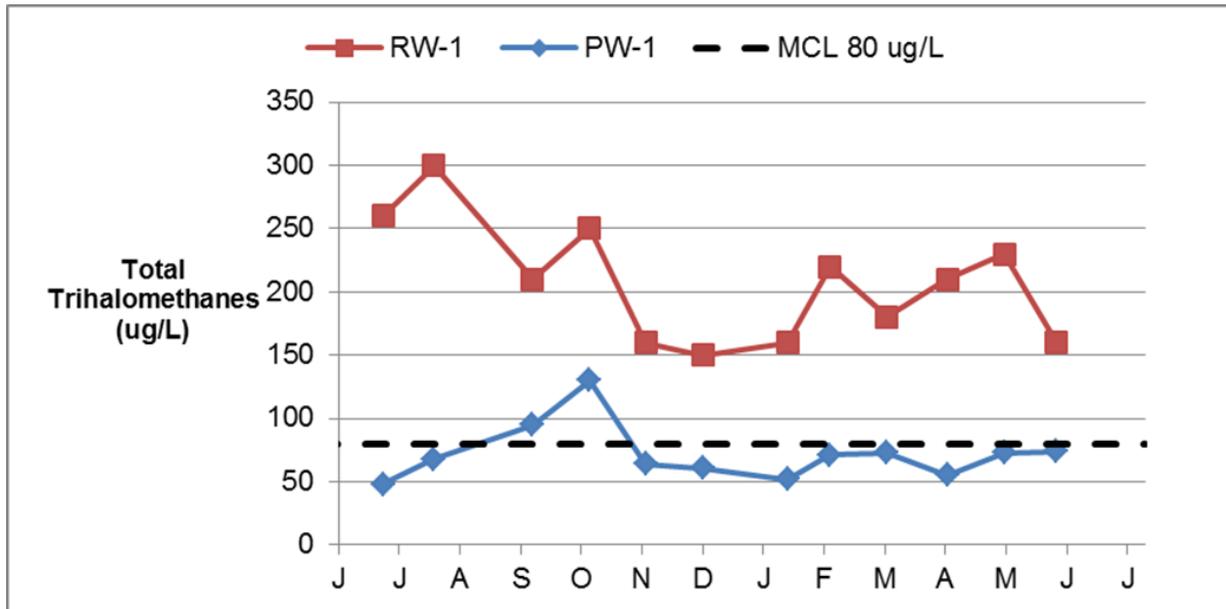
Sampling results indicated that the treatment train provided effective removal of disinfection byproducts. Disinfection byproducts, including total trihalomethanes (TTHMs) and haloacetic acids (HAA5), are regulated to the levels listed in the Primary Drinking Water Standards. The maximum contaminant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

#### Haloacetic Acids

The treatment train consistently reduced HAA5s below the 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. HAA5 is the sum of five regulated haloacetic acids: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid.

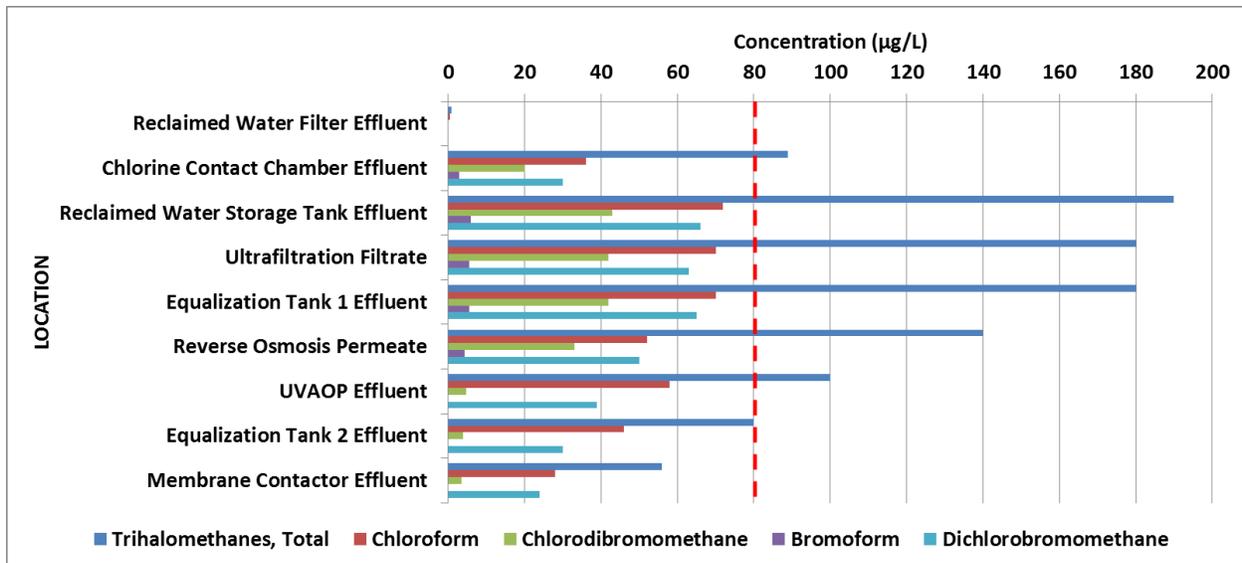
### Total Trihalomethanes

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). TTHM is the sum of four regulated trihalomethanes: chloroform, bromodichloromethane, dibromochloromethane, and bromoform. TTHM levels were above and below the 80 µg/L MCL.



**Figure 3** Total Trihalomethanes in the Reclaimed Water and Purified Water

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 the TTHMs. 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 post chlorine contact chamber. The sampling location MF-F-1 represents reclaimed water that has passed through the reclaimed water storage tank and is before the membrane filtration step with ultrafiltration membranes.



**Figure 4** Profile of Trihalomethanes through the Treatment Process

The total trihalomethanes 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%. Assuming a corresponding 50% 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%. This reduction was not attributable to one single process but rather several processes working in series. Reverse osmosis removed about 25% of TTHMs, with no significant difference by type of THM. The ultraviolet and hydrogen peroxide advanced oxidation process (UVAOP ) removed about 30% of TTHMs, with chlorodibromomethane being much higher (85% removal) than the other species, and no significant 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% of all TTHMs. The membrane contactor removed about 30% of TTHMs. These differences in removal by trihalomethane (THM) type provide insight into the specific role of each unit process in removing THMs. Nevertheless, relocating 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 (Table 1) 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, 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.

**Table 1** Pathogen Counts for the 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	IU <sup>(1)</sup> / 100L	BDL	BDL	BDL	BDL	BDL	BDL
Giardia	Oocysts / 100L	2.8	12.5	7.0	22.6	<1.4	BDL
Helminth Ova	Total <sup>(2)</sup> 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 <sup>(3)</sup>	12/3/13 <sup>(3)</sup>	02/04/14 <sup>(3)</sup>	04/03/14 <sup>(3)</sup>	05/27/14 <sup>(3)</sup>
Cryptosporidium	Oocysts / 100L	N/A <sup>(4)</sup>	BDL	BDL	BDL	BDL	BDL
Enteroviruses	IU <sup>(1)</sup> / 100L	BDL	BDL	BDL	BDL	BDL	BDL
Giardia	Oocysts / 100L	BDL	BDL	BDL	BDL	BDL	BDL
Helminth Ova	Total <sup>(4,5)</sup> ova/L	BDL	0.07	0.16	0.07	0.10	0.16
	Viable ova/L	BDL	BDL	BDL	BDL	BDL	BDL

Notes:

<sup>1</sup> IU - Infectious Units

<sup>2</sup> None of the ova were found to be viable, and therefore do not pose any infection risk.

<sup>3</sup> Sampled from membrane contactor effluent (MC-E-1) to avoid turbidity interference from lime addition.

<sup>4</sup> Turbidity interference from lime addition in the purified water interfered with pathogen counts for 7/19/13.

<sup>5</sup> 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.

A small amount of nonviable helminth ova were observed in the purified water on 10/8/13 and 12/3/13; however, since these helminth ova were nonviable, they would not present any risk of infection.

### *Coliform Bacteria*

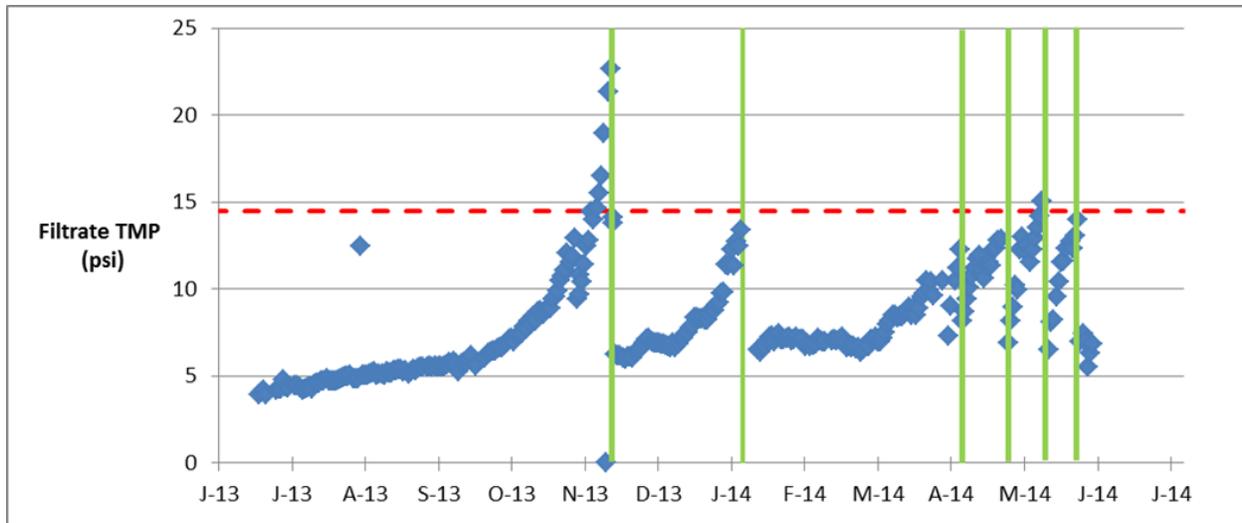
Sampling results indicated that the treatment train provided effective treatment for removal of coliform bacteria. The purified water and reclaimed water were sampled for total coliforms and *Escherichia* coliform bacteria on a weekly basis using a presence/absence method. In the purified water, neither total coliform bacteria nor *E.coli* were detected after 51 weekly samples. In the reclaimed water *E.coli* were present in 1 out of 51 weekly samples and total coliform present in 11 out of 51 weekly samples.

### *Maintaining Ultrafiltration Performance*

Ultrafiltration was the primary filtration process for physical removal of pathogens in the treatment train. 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 ultrafiltration membranes accumulated moderate fouling as shown by the increase in transmembrane pressure (Figure 5). The pilot ran for approximately five months before requiring the first clean in place (CIP). High pH cleaning was effective for removing total organic carbon from the membranes. Low pH cleaning was effective in removing iron fouling.

Towards 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, procedure of repeated chemically enhanced backwashes (CEBs) over a few hours, led to significant drops in TMP by more than 7 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 CEB may have removed large masses of accumulated iron fouling. With more frequent low pH CEBs, it is anticipated that fewer cleans in place would be required. An autopsy of the UF module by Dow 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 transmembrane pressure (i.e. >1 psi), the CEB cycle should be repeated until the decrease in transmembrane pressure diminishes with each test. If the transmembrane pressure is still well above the clean startup pressure, another CEB solution should be tried. Otherwise, if the transmembrane pressure drops to near the clean startup pressure, chemical backwashing should be discontinued, and normal production resumed



**Figure 5** Ultrafiltration Transmembrane Pressure

### *Maintaining Reverse Osmosis Performance*

Reverse osmosis 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 cleans in place. The RO process was converted from 3-stage to 2-stage during the testing and successful testing results supporting use of 2-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, it is relatively easy to carry out, and is partly quantitative. A standard commercial test kit (MUTA-CHROMOPLATE™ manufactured by EBPI) was used for all mutagenicity testing. Each test kit incorporated standard, 96-well microplates and five (5) different strains of salmonella bacteria. Each sample was exposed to five (5) 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 5 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 (8/22/2013, 10/8/2013) it was observed that sodium bisulfide was under-dosed, therefore allowing peroxide, an oxidant added to support the UVAOP process and known mutagenic agent, 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 (11/19/2013 and 1/24/2014).

**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	White	Green	Green	Green	Green	White

*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
- Yellow: Moderate-weak mutagenic effects observed.
- Red: Strong mutagenic effects observed
- White: Not available

**Microconstituents**

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

*Microconstituent Sampling*

Sampling results (Table 3) indicated that the treatment train effectively reduced nearly all microconstituents tested to below minimum reporting levels. Only one compound, atenolol, was detected in the purified water during one of five sampling events (January 2014). 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. 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 was the only microconstituent that was detected in the purified water. Atenolol is a beta blocker medication used to treat high blood pressure. Atenolol is a relatively polar, hydrophilic compound, with molecular weight of 266 daltons, known to survive normal wastewater treatment processes. In January 2014, it was detected in the reclaimed water at a concentration of 75 ng/L. The concentration in the purified water was 16 ng/L. This concentration was above the analytical laboratory's minimum reporting limit of 5 ng/L.

Review of operational records found that underfeeding of peroxide on 1/14/2014 resulted in decreased atenolol destruction by the UVAOP treatment barrier. The peroxide residual was actually 0.3 mg/L instead of the target dose of 2.0 mg/L. Even with this reduced feed of peroxide, the pilot treatment train removed 79% (0.67 log) of atenolol from the water. This rate of removal exceeds the California draft regulation of 68% (0.5 log) for atenolol as a Group D indicator compound.

Currently, there is no regulatory limit set for atenolol in drinking water. Without a regulatory limit for atenolol, some other point of reference is needed in order to understand the significance of low-level concentrations of atenolol. 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/L<sup>1</sup> 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. Follow-up UVAOP challenge testing with atenolol demonstrated affirmatively that peroxide addition is key for effective removal of atenolol, when present.

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<sup>1</sup> Trussell, R.R. et al. 2013. "Potable Reuse: State of the Science Report and Equivalency Criteria for Treatment Trains." WateReuse Research Foundation. Alexandria, VA.

**Table 3. Microconstituent Concentrations**

Item	Reporting Limit (PQL) (ng/L)	Reclaimed Water <sup>(1)</sup> (ng/L)		Purified Water (ng/L)	
		Average <sup>(2)</sup>	Maximum	Average <sup>(2)</sup>	Maximum
Sucralose	100	47,400	56,000	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 <sup>(4)</sup>	16 <sup>(4)</sup>
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	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

**Notes:**

1“Reclaimed water” prior to purification process.

2 Average calculated with observed concentrations, and observations below reporting limit counted as half the reporting limit.

3 Atenolol was below the reporting limit of 5 ng/L four times and measured at 16 ng/L on one occasion.

### *UVAOP Challenge Testing*

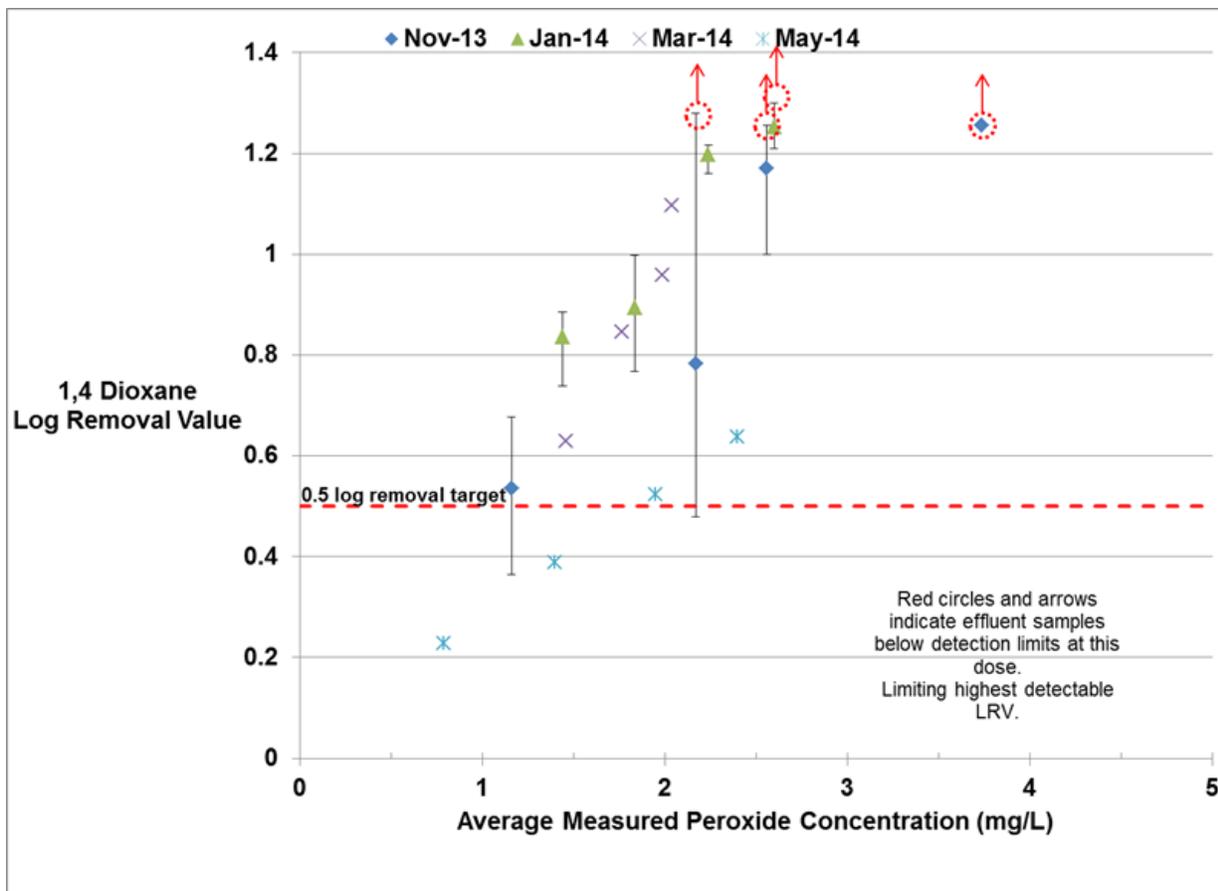
The UVAOP process is intended to reduce concentrations of microconstituents that remain after reverse osmosis. Concentrations of microconstituents are very low and often variable due to changes in community use of products and treatment plant performance. Consequently, it can be difficult to show that 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 nitrosodimethylamine (NDMA) (1.4 log removal) and 1,4-dioxane (0.5 log removal). These goals and target contaminants, were based on the California Department of Public Health's draft criteria for groundwater recharge with reclaimed water, and are widely used as a benchmark for measuring UVAOP performance in groundwater recharge applications.

NDMA was removed below detection limits at all peroxide doses tested except for one sample which 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. 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 dependent 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 ( $\text{OH}\cdot$ ) that are formed when UV light splits hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) 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, thus becoming the only microconstituent measured above reporting limits in the purified water during the pilot testing phase. 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. 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.



**Figure 6** Log Removal of 1,4-Dioxane versus Peroxide Dose for the UVAOP Process

### *Compatibility with Native Groundwater in 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 CaCO<sub>3</sub>, alkalinity 10 mg/L as CaCO<sub>3</sub>, and calcium

carbonate precipitation potential (CCPP) of -110 mg/L as CaCO<sub>3</sub>. 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 CaCO<sub>3</sub>. After the membrane contactor, approximately 70 mg/L of carbon dioxide was injected into the solution under pressure, followed by 75 mg/L as CaCO<sub>3</sub> of lime, increasing the total calcium to 80 mg/L as CaCO<sub>3</sub>, the pH to 7.25, the alkalinity to 100 mg/L as CaCO<sub>3</sub>, and CCPP -10 mg/L as CaCO<sub>3</sub>.

Earlier in the pilot study, the pH was adjusted to 7.75, and closer to zero CCPP, by adding less CO<sub>2</sub>. 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 NTUs (nephelometric turbidity units). 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 NTU. 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 CaCO<sub>3</sub> 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 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 (dissolved oxygen) or converting oxidizing species (chlorine, peroxide) from the water, which could potentially cause undesirable mobilization of arsenic or other metals in the aquifer.

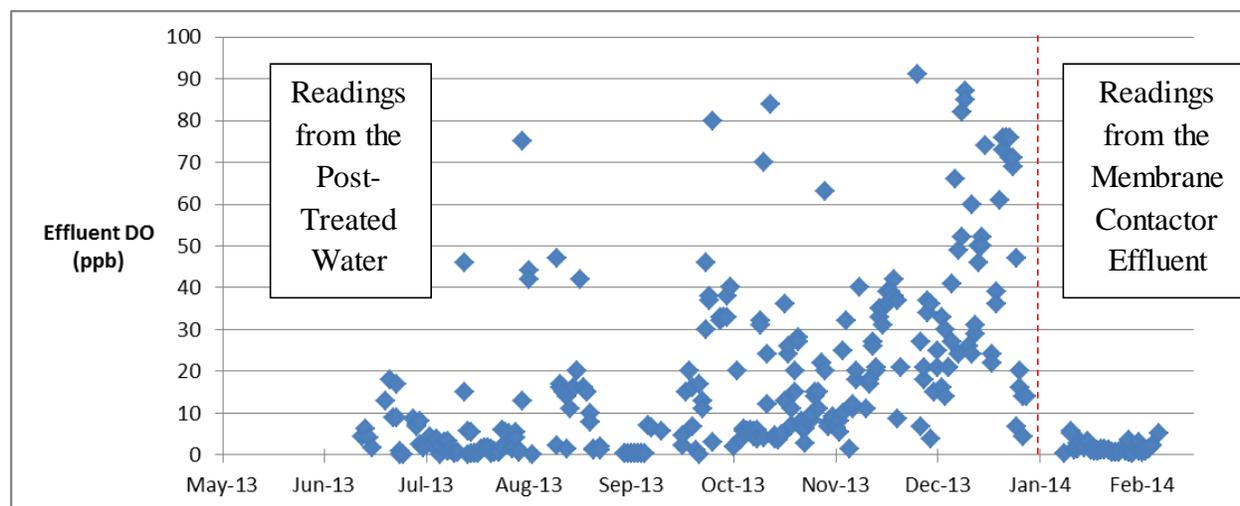
### Oxidants

The membrane contactors routinely removed most of the dissolved oxygen from the purified water. Dissolved oxygen (DO) entered the membrane contactors at near 100% saturation (6-9 mg/L), and was removed down to 100 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 was essential to 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).

Dissolved oxygen readings were lower and more repeatable when they were taken before post treatment chemical addition. Before January, the trace DO sensor was drawing off of the purified water line, after lime addition and bisulfide addition. After January, the dissolved oxygen 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, the sodium bisulfide 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.



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

Sodium bisulfide addition is important for quenching remaining oxidants in the water, and reducing the overall oxidation reduction potential (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 dissolved oxygen removal and arsenic mobilization, supporting dissolved oxygen 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 dissolved oxygen concentration, and increasing sulfide content, supporting the selected treatment approach of dissolved oxygen removal and sulfide addition.

## **Summary**

Results from the City of Clearwater'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.