1 **Mineralizing Urban Net-Zero Water Treatment: Field Experience for**
2 **Energy-Positive Water Management**

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Abstract

An urban net-zero water treatment system, designed for energy-positive water management, 100% recycle of comingled black/grey water to drinking water standards, and mineralization of hormones and other organics, without production of concentrate, was constructed and operated for two years, serving an occupied four-bedroom, four-bath university residence hall apartment. The system comprised septic tank, denitrifying membrane bioreactor (MBR), iron-mediated aeration (IMA) reactor, vacuum ultrafilter, and peroxone or UV/H₂O₂ advanced oxidation, with 14% rainwater make-up and concomitant discharge of 14% of treated water (ultimately for reuse in irrigation). Chemical oxygen demand was reduced to 12.9 ± 3.7 mg/L by MBR and further decreased to below the detection limit (<0.7 mg/L) by IMA and advanced oxidation treatment. The process produced a mineral water meeting 115 of 115 Florida drinking water standards that, after 10 months of recycle operation with ~14% rainwater make-up, had a total dissolved solids of ~ 500 mg/L, pH 7.8 ± 0.4 , turbidity 0.12 ± 0.06 NTU, and NO₃-N concentration 3.0 ± 1.0 mg/L. None of 97 hormones, personal care products, and pharmaceuticals analyzed were detected in the product water. For a typical single-home system with full occupancy, sludge pumping is projected on a 12-24 month cycle. Operational aspects, including disinfection requirements, pH evolution through the process, mineral control, advanced oxidation by-products, and applicability of point-of-use filters, are discussed. A distributed, peroxone-based NZW management system is projected to save more energy than is consumed in treatment, due largely to retention of wastewater thermal energy. Recommendations regarding design and operation are offered.

Keywords: Net zero water treatment, Direct potable reuse, Advanced oxidation, Mineralization, energy

1. Introduction

Water reuse is now recognized as fundamental to addressing increasing water demand (Meneses et al., 2010; Schnoor, 2011), and is being implemented for non-potable, indirect potable reuse (IPR) (following passage through an environmental buffer), and direct potable reuse (DPR), employing various treatment technologies, both with and without black/grey water segregation. In particular, the term net-zero water (NZW) is used to refer to reuse systems not connected to external water and sewer grids, i.e., neither importing nor exporting significant water outside of the service area, which area may be a single property or an entire region (Englehardt et al., 2013). Though NZW DPR is not generally practical in rural areas due to cost and complexity (Guo and Englehardt 2015), well/septic systems may be considered NZW IPR, if off-site impacts of groundwater consumption and reuse are limited. In urban areas, on the other hand, treatment must be sufficient to avoid overloading environmental buffers. In either case, NZW systems utilize purified municipal wastewater as a stable, non-seasonal freshwater source.

In urban/suburban settings, NZW management may require DPR technology which, if high recycling rates are achieved, enables retention of not only water, but the thermal energy in wastewater as well. In fact, residential and commercial (non-industrial) hot water accounts for 3.62%, of total annual US primary energy consumption, whereas treatment of water and wastewater combined can be estimated to account for only ~0.3% (ICF, 2002; U.S. DOE, 2014). Therefore, direct reuse of this water presents the prospect of energy-positive water management, a term used to indicate a system that saves more energy (distinct from CO₂ emissions) than it uses. In addition, environmental releases of toxic chemicals and pesticides are eliminated as inputs to the municipal drinking water/wastewater cycle, and remaining organics can be

mineralized to provide high quality water and minimize environmental emissions (Wu and Englehardt 2015).

Several challenges must be addressed to achieve urban NZW management. First, treatment of water to high purity at low energy and cost remains a challenge. In fact, because DPR utilizes water source of potentially lower quality, public health criteria beyond those established for other drinking water have recently been proposed/developed (WRRF et al., 2015; SWRCB, 2015; NWRI, 2013; NRMMC et al., 2008). Example guidelines are summarized in Table S1 (Supplementary Information). In particular, 12-log and 10-log reduction in enteric virus and *Cryptosporidium*/*Giardia* concentrations, respectively, from the raw wastewater, are most conservatively and commonly proposed (NWRI 2013; SWRBC 2015). Moreover, environmental emissions must be minimal if all aqueous streams are to be retained on-site.

To address treatment challenges, urban NZW management requires advanced treatment, such as the reverse osmosis (RO) process typically employed in DPR systems. However, continual disposal of the RO concentrate stream, potentially containing microbes and endocrine-disrupting compounds, may necessitate additional treatment entailing further energy and cost. In addition, product water largely devoid of minerals may require blending or conditioning to control corrosion, potentially limiting the attainable recycling rate.

Advanced oxidation processes, involving the use of hydroxyl radical to mineralize organic contaminants while retaining dissolved minerals, have the potential to achieve high rates of recycling water and energy. However, unwanted byproducts can be generated in such highly oxidizing environments, and therefore advanced oxidation and other unit processes must be carefully selected and integrated. Also, experience with non-RO, advanced oxidation-based DPR is limited to the system in Windhoek, Namibia, which is not NZW but instead uses ca. 80%

surface water (Du Pisani 2014) for makeup and dilution, alleviating the need to control the accumulation of undesired constituents. Therefore, field experience with advanced oxidation-based NZW treatment, including control of total dissolved solids (TDS), oxidative byproducts, and pathogens, at high recycling rates, and with automated and remote process control for distributed treatment plants, is needed.

Previously we proposed an initial design for an advanced oxidation-based urban net-zero water treatment system, including potable treatment and mineralization of organics at ambient temperature and pressure and circum-neutral pH, without generation of concentrate or brine (Englehardt et al. 2013). A demonstration treatment plant was then constructed and operated at the University of Miami, FL, USA. The purpose of this paper is to report results, including the recycling rate achieved and associated energy projections; control of oxidative byproducts and minerals; compliance with existing drinking water standards including organics and nitrate/nitrite; mineralization of hormones, pharmaceuticals, and personal care products (HPPCP); fecal coliform regrowth; and (automated/remote) process control. Kinetic and operational analysis of the peroxone advanced oxidation process was presented previously (Wu and Englehardt, 2015). Further results, including rates of removal of emerging constituents by unit process, virus and protozoan inactivation, UV-hydrogen peroxide kinetics, and bromate and minerals control, are presented elsewhere (Gassie et al. 2016). Further study, including management of and energy recovery from process sludge, are beyond the current scope.

2. Materials and Methods

The system was operated in this project phase over an 19-month period of apartment occupancy, January 2013 through July 2014, with routine sampling and analysis conducted three times daily,

five days per week, and research sampling and analysis conducted continuously, by a team ultimately comprising 73 undergraduate, graduate, independent study, volunteer, postdoctoral, and visiting students and scholars.

2.1. Site and System Description

The demonstration NZW system accepted all wastewater from sinks, toilets, showers, dishwasher, and washing machine from a 4-bedroom, 4-bath residence hall unit. As shown in Figure 1, the treatment process comprised septic tank, membrane bioreactor (MBR), iron-mediated aeration (IMA, to be described), flocculation, vacuum ultrafiltration, peroxone or UV-peroxide advanced oxidation, and granular activated carbon (GAC), with minor rainwater make-up and provision of H₂O₂/silver or chlorine disinfection residual. Similar to biological systems, minerals accumulate in the recycled water under ambient conditions, subject to precipitation by IMA, alkalinity consumption by denitrifying bacteria, salt-free treatment, and 14% dilution with rainwater. A detailed process flow diagram is available elsewhere (Englehardt et al., 2013). Design capacity of the system is 1514 L/day (400 gallon/day).

2.2. System Operation

The system was in operation for treatment of residence hall unit wastewater and disposal to city sewer for 6 months prior to placement into recycle mode in June 2013, returning treated water to the apartment for all uses except drinking and cooking. Major design/operation parameters and operational changes with their motivations are summarized in Table 1.

2.2.1. Septic tank and MBR

Wastewater from the apartment was collected in a below-grade 4.15 m³ septic tank, to provide anaerobic liquefaction of organic solids and flow equalization. Supernatant was pumped to the

MBR, controlled by water level floats and timer; when the timer was activated, the pump was ON for 30 sec every 3 hours, resulting in delivery of approximately 260 L water to the MBR.

The MBR (4.15 m³), (Membrane BioBarrier®, BioMicrobics Inc., Shawnee, KS) included anoxic and aerobic chambers separated by perforated baffle, to provide the major oxidation of organics (Figure S1). Oxidation-Reduction Potential (ORP) (Q45R/25R, ORP monitor/sensor, Analytical Technology, Inc., USA) in the anoxic chamber, pH (Q45R/25R, pH monitor/sensor, Analytical Technology, Inc., USA) and dissolved oxygen (DO) (Q45D/60, Analytical Technology, Inc., USA) in the aerobic chamber were monitored continuously. To provide nitrification/denitrification, 109 mg/L ethanol as external carbon source and 30~128 mg/L CaCO₃ (alkalinity) were metered to the anoxic chamber (for convenience, given the intermittent mixing of the chambers). Two blowers, one for mixing between the two chambers (ON for 1 min every 10 min) and one for aeration and membrane scouring in the aerobic chamber (ON during filtration/discharge and ON for 30 min every 90 min during relaxation, i.e. no discharge) were integral to the system. In order to prevent excess aeration, the MBR system master power was placed on a timer, to operate 12~18 hrs/day. The filtration pump was controlled by the water level floats, delivering approximately 800 L of filtered water to the dosing tank each time. The filtration rate was 5.6 LPM at system start-up, and no decrease was observed during the first 6 months; after the timer was installed in July 2013, the filtration rate decreased to 4.2 LPM over a 5-month period and to 2.8 LPM over the subsequent 5- month period.

2.2.2. Blended water

To provide a sink for excess minerals, 14% of the treated water was disposed and made up with rainwater. For this reason, and to allow the MBR to operate on an independent hydraulic

schedule, MBR effluent was stored in the dosing tank (4.5 m^3) and metered to the IMA reactor, along with 14% rainwater, collected from the roof ($\sim 930 \text{ m}^2$) of the residence hall building and stored in a 17.1 m^3 cistern, by electronic flow meter and continuous automatic valve control in each line. Flow rates were set at 0.79 LPM (DPL-1P05 G4, Kobold instruments Inc.) and 0.12 LPM (DPL-1P18 G4, Kobold instruments Inc.), respectively. Water levels in both tanks were monitored continuously (MBLT-2SC-IVPP-5-40, Dwyer Instruments, Inc.). Excess treated water, which by design would provide landscape irrigation, was disposed to city sewer for research purposes. Because backwash waters were returned to the septic tank, excess treated water was approximately 14% of total flow. In order to maintain the combination of low flow and high pump suction lift (0.5~ 0.9 m), a recirculation line with needle valve was installed around the water pump (gear pump) in each line, and adjusted manually to provide sustained flow.

2.2.3. IMA, flocculation tank, and ultrafiltration

The IMA process was described in detail previously (Englehardt et al. 2013; Deng et al. 2013). In this implementation, the process comprised aerated iron electrocoagulation/flocculation. While IMA can achieve organics oxidation and softening, in this research phase only the electrocoagulation unit was aerated, principally to maintain iron as Fe^{3+} and thereby prevent iron bleed-through during ultrafiltration. Phosphate was precipitated as well in this process, contributing to TDS control. [In subsequent work (Gassie et al. 2016) the dosing tank was aerated as well, providing additional residence time to precipitate excess calcium carbonate through equilibration with atmospheric CO_2].

The IMA reactor was a 57 L tank fitted with twelve 2.54 cm diameter iron rod anodes and cathodes. A constant current of 0.7A was supplied via a DC power supply (BK Precision 1902), ON when there was flow through the reactor, resulting in a dosage of 16 mg/L iron. 90

LPM air was supplied continuously by diaphragm air pump through a fine bubble disc diffuser with 30 cm diameter placed at the bottom of the reactor. A propeller mixer was used to further ensure coagulant suspension. Water flowed from the IMA reactor to the flocculation tank (114 L, FKC CO., Ltd., Port Angeles, WA) and then to the ultrafiltration unit by gravity. Approximately 700 mL sludge was wasted from bottom of the flocculation tank to the septic tank each day. The ultrafiltration unit included 16 ZW-10 membranes (GE Power & Water, Ontario). Filtration was controlled by water level sensor (MBLT-2SC-IVPP-5-40, Dwyer Instruments, Inc.), occurring intermittently with approximately 70 L transferred to the clearwell (625 L) each time. The membrane filters were backwashed for 30 sec every 20 min, during which time coarse-bubble aeration was provided at 900 LPM to enhance membrane cleaning. During power supply operation, prior to backwash, approximately 1.5 L of liquid was wasted from bottom of the unit to the septic tank.

2.2.4. Advanced oxidation (Peroxone/UV)

An advanced oxidation process (AOP), designed to reduce residual COD to below detection (0.7 mg/L) in the treated water, was operated in batch mode to facilitate kinetic study. One tank (3.79 m³) was treating continuously, while the other was filling intermittently from the clearwell. From January 2013 through May 2014 treatment was by the peroxone process, whereby water in treatment tank was recirculated between the tank and the ozone system (SPARTOX 60, Spartan Environmental Technologies, OH, USA) for treatment with ozone and H₂O₂. Process monitoring, and calculation of ozone transferred from gas phase to solution phase based on continuous ozone production and off-gas ozone data, are described in detail elsewhere (Wu and Englehardt, 2015). Typical transferred ozone dose was 5 mg/L·h, and the ozone/H₂O₂ molar ratio was maintained ≥2.4. Here O₃ was slightly overdosed to minimize residual H₂O₂, a known ·OH scavenger. AOP-

treated water was pumped to the treated water tank (5.12 m^3) when the filling tank filled, at which time treatment began on this full tank and the empty tank began filling. Working volume of each ozone tank was approximately 1500 L.

The system was converted from peroxone to UV/ H_2O_2 advanced oxidation in June, 2014 (to address bromate formation, as will be described). From June to August 2014, a 149 W UV reactor (Neotech D338, Spartan) with monitored light intensity varying from $8\sim 14 \text{ mW/cm}^2$ was used. H_2O_2 was added at the beginning of each batch run either by metering pump or direct addition into the tank, resulting in a total dose of $20\sim 30 \text{ mg/L}$. Due to low apartment occupancy during the summer (one person, June ~ August, 2014), treatment time varied from 4~8 days, at the end of which time H_2O_2 feed was terminated manually to minimize residual.

2.2.5. GAC, disinfection, and online monitoring

Dual GAC filters (CQE-CO-02051, Crystal Quest®, Marietta, GA) were mounted in series following advanced oxidation, to provide treatment redundancy and polishing. Media was recharged after 3 months, to control biological growth and maintain the physical adsorption process as designed. The filters were then replaced in September 2013 with point-of-use carbon filters on taps (Culligan FM-15A) and showers (Culligan ISH-100), to polish and remove residual chlorine in the finished water while greatly reducing the required carbon recharge volume.

In addition to primary disinfection by peroxone/UV, hydrogen peroxide solution (15% by weight) was added to the treated water to provide $35\sim 65 \text{ mg/L}$ residual. The injection point was moved from the top of the treated tank to the ozone treatment tank effluent pipe in Nov. 2013, to maintain disinfection residual in the pipe ($\sim 12 \text{ m}$) to the treated water tank. Beginning 10/2013,

30 µg/L of silver was also added to the treated water to provide synergetic disinfection. The system was switched to commercial calcium hypochlorite addition in December 2013.

The master control system was designed and built to operate all automatic valves needed for routine operation, including metering of 14% cistern water, and to provide real-time monitoring and control via online interface, and donated to the project by Engineered Control Systems (Miami, FL). Continuous data from water chemistry sensors, flow meters, and level sensors were recorded every 15 min to the project server, interfaced through the master control system. Principal operation and maintenance requirements for these instruments were regular calibration according to manufacturers' instructions. Sensors performed reliably with little maintenance, with the exceptions that one electronic flow transmitter on each ozone skid, and one water level sensor had to be replaced during the second year, and one ORP sensor never successfully communicated with the server.

2.4. Sampling and Analysis

Product water was sampled in 500 mL high-density polyethylene bottles three times daily, and monitored for pH, electrical conductivity (EC), dissolved oxygen (DO), turbidity, temperature and residual H₂O₂ concentration. TDS (mg/L) was estimated as 0.514·EC, determined as the average of five (consistent) ratios of gravimetric TDS analysis (SM 2540C) by external certified lab to in-house EC measurement over 18 months. Microbial analysis was conducted daily. City water samples were also analyzed for the initial 3-month period, for comparison. Samples including cistern water were also taken along the treatment train for selective analysis of COD, alkalinity, iron, nitrogen, phosphate and chloride. Details of sample analysis are available in Supplementary Information. Water temperature was measured on- site. All other analyses were conducted within 4 hrs, except for evening samples which were refrigerated at 4 °C and

measured the next morning. Sample bottles used for microbial analysis were sterilized by autoclave (STM-E, Market Forge, CO) at 121 °C and 14 psi for 15 min. Prior to sterilization, 0.5 mL of 10% sodium thiosulfate solution was added to the clean sample bottle, to quench any chlorine residual. Microbial samples were transported from site to lab in a cooler with ice packs, and analyzed within 6 hrs.

All chemicals used for sample analysis were analytical grade and used as received. Conductivity, pH, and DO were measured with Orion Star A3295 multimeter (Thermo Scientific, USA). Alkalinity measurements were performed using Standard Method 2320 (APHA et al. 2005). Phosphate, nitrate, ammonia, total nitrogen (TN), chlorine and COD were measured colorimetrically (UV-Vis spectrophotometer model DU720, Beckman Coulter, Brea, CA) using Hach phosphorus method 8048, 0.02-2.5 mg/L PO_4^{3-} , Hach nitrate method 8039, 0.3-10 mg/L NO_3^- -N, Hach ammonia method 8155, 0.01-0.50 mg/L NH_3 -N, Hach TN method 10071, 0.5-25 mg/L, Hach total chlorine method 8167, 0.02-2.00 mg/L Cl_2 , and Hach COD method 8000, 3-150 mg/L and 0.7-40 mg/L (Hach Co., Loveland, CO) respectively. Samples were diluted with Milli-Q water (18.2 M Ω -cm) as necessary to fall within the appropriate measurement range. Hydrogen peroxide was measured by iodometric titration (Gordon et al. 1992). Fecal coliform was measured by EPA Method 1103.1 for *E. Coli*, using mTEC agar to select for gram-negative, lactose-fermenting bacteria, but omitting the in situ urease test (generally used to further differentiate *E. Coli* from other thermotolerant, lactose-positive organisms), as recommended by Pagel et al. (1982) for selective enumeration of fecal coliforms.

A full set of NZW samples was collected (17:00 10/15/2013 and 9:00 07/03/2014, respectively), and sent for complete drinking water analysis to certified external laboratory (Florida-Spectrum Environmental Services, Inc., Ft. Lauderdale, FL, USA). Samples were

collected in containers provided by Florida Spectrum, refrigerated at 4 °C, and transferred to the external lab within 24 hrs. In addition, samples were taken along the treatment train and sent to the same lab for bromide/bromate analysis on 01/31/2014. Finally, a sample of the treated (UV-H₂O₂) water, drawn and frozen on 12/19/2014 and defrosted for preservation and analysis on 11/03/15, was analyzed for 98 hormones, pharmaceuticals, and personal care products (HPPCPs) (Table 2) by certified laboratory (Eurofins Eaton Analytical, Inc., Monrovia, CA, USA) using LC-MS-MS.

3. Results

Results of system operation from July 1, 2013 through July 31, 2014 are reported in this section. Examples (September, 2013) of water usage and water levels in the two system holding tanks are plotted in Figure 2. Actual water demand was approximately 50% of design capacity, with an average flow of 32.5 LPH. As expected for an onsite water treatment system, significant fluctuations in flow were observed, with a peak flow of 610.3 LPH and hourly peaking factor of 19.

3.1. Water Chemistry and Salinity

Comparison of the principal NZW and city water chemistry parameters is shown in Figure 3. As seen, pH (Figure 3a) was circum-neutral, and turbidity (Figure 3b) was lower than that of (lime-softened) county water, at 0.12 ± 0.06 . The temperature of NZW (Figure 3e) ranged from 20~35 °C depending on season, as pipes and tanks were uninsulated. Product water was supersaturated with dissolved oxygen (Figure 3c) during the sampling period because (a) during peroxone treatment, ozone and oxygen were continuously injected, and (b) hydrogen peroxide residual decomposed to water and oxygen, particularly when added as the secondary disinfectant. At the

time of conversion to recycling mode, approximately 60% of system water was replaced with rainwater. The resulting initial concentration of ~120 mg/L TDS then increased gradually, reaching ~500 mg/L after 19 months. The dip in TDS seen in the figure was due to the addition of supplemental cistern water, necessary for emergency booster pump maintenance in October 2013.

The evolution of pH through the NZW process over the period July 2013 to April 2014 is shown in Figure 4. As shown, the unit processes were pH-integrated, with neutral-basic chemistry through the system (including successful iron coagulation). In particular, pH presumably fell somewhat in the septic tank due to fermentative organic acid production, increasing with alkalinity addition in the MBR aerobic zone, and dropping slightly during advanced oxidation.

3.2. Organics

Total organics remaining following treatment were measured as COD, for convenience. Although some chlorinated organic byproducts of electrochemical treatment may not be detected as COD (Bagastyo et al., 2013), the present work did not employ such treatment and the method is free of bicarbonate interference. COD reduction along the treatment train is shown in Figure 5. As shown, COD of the septic tank effluent varied from less than 200 mg/L to more than 400 mg/L. More than 90% of this COD was removed by MBR treatment, resulting in 12.9 ± 3.7 mg/L COD in dosing tank water. Following dilution by rainwater and additional removal by IMA, COD in the clearwell was 7.9 ± 1.2 mg/L. Residual organics were then mineralized to below detection (< 0.7 mg/L) in terms of COD by advanced oxidation. Importantly, none of the 98 analyzed HPPCPs were detected in the finished water.

3.3. Nutrients

As seen in Figure 6, total nitrogen in the septic tank effluent was around 60 mg/L, most present as ammonia. MBR effluent (dosing tank water) contained 6.1 ± 3.0 mg/L TN, principally nitrate, indicating effective nitrification/denitrification. The IMA unit provided additional reduction, resulting in 3.0 ± 1.0 mg/L NO_3^- -N in the final NZW, below the 10 mg/L NO_3^- -N US EPA drinking water standard. Reduction of phosphate along the treatment train is illustrated in Figure 7. In September 2013, phosphate in dosing tank samples was 10~15 mg/L, and typically < 5 mg/L in the clearwell. These concentrations then increased to 30~40 mg/L and 15~25 mg/L respectively in December 2013 (at which time phosphate in septic tank effluent was measured at ~40 mg/L). High phosphate values were expected due to progressive accumulation to steady-state, through recycle starting July 2013 involving 50~60% removal by IMA.

3.4. Microbiological Testing

Initially hydrogen peroxide was tested at bench scale as an alternative disinfectant to minimize salt input, and further minimize any possible chlorinated byproducts, in a closed-loop system. Briefly, 15 one-liter samples of GAC effluent were prepared with 0, 2, 8, 16 and 32 mg/L of hydrogen peroxide residual. The sample bottles were covered with mylar to prevent the light-stimulating growth, and stored near the treated water tank at the plant site. After 5 days fecal coliform was measured in each sample. No fecal coliform was detected in the samples having hydrogen peroxide concentration ≥ 16 mg/L.

Based on bench-scale results, 20~30 mg/L hydrogen peroxide residual was metered to the treated water tank during filling to prevent regrowth. To address occasional positive FC analyses, residual hydrogen peroxide in the treated water storage tank was gradually increased to 40~60 mg/L during September ~ December 2013, and this concentration was then reduced at the point-

of-use via GAC filters on all taps and showers. In addition, beginning October 2013, 30 µg/L silver was added to the treated water, due to its reported synergistic effect on disinfection when used with hydrogen peroxide (Pedahzur et al., 1997), and as approved for use in drinking water in several European countries (Batterman et al., 2000). However, positive FC readings still occurred several times during daily monitoring. In addition, the booster pump periodically lost prime due to oxygen outgassing in the pump head. Therefore, the system was switched to chlorine as the secondary disinfectant in December, 2013. Even then, reliable control of microbiological regrowth required a chlorine residual of 2-4 mg/L.

3.5. Drinking Water Analysis

Partial results of the external certified analysis of 115 contaminants, showing all detected analytes and representing all F.A.C. 62-550 Florida drinking water standards (equal or stricter than US EPA federal standards) including inorganic contaminants, synthetic organics, secondary contaminants, disinfection byproducts, radionuclides, volatile organics and total coliform, are presented in Table 3. In the sample set of 10/15/2013, the only compound exceeding the MCL (Maximum Contaminant Level) was bromate at 86.3 µg/L. Results of subsequent bromide and bromate analysis indicate that cistern and county water contained 70 µg/L and 120 µg/L bromide, respectively. No bromate was detected in samples from the treatment units preceding the peroxone process. To avoid bromate formation, peroxone advanced oxidation was replaced with UV/H₂O₂ treatment in May 2014. As a result, no bromate was detected in the 07/03/2014 sample, and all 115 drinking water standards were met.

4. Discussion

In this demonstration, TDS appeared to stabilize at approximately 500 mg/L, more than 75% of which comprised Na^+ , Cl^- , SO_4^{2-} , and NO_3^- . Other major constituents, not tested in this phase of the work, include Ca^{2+} , Mg^{2+} , K^+ , and HCO_3^- . The concentration of Na^+ increased ~67% between the 07/03/2014 and 10/15/2013 sampling events, similar to the increase in TDS, whereas Cl^- increased by 125%, presumably due to the switch to chlorine addition. Because no significant change in the trend of TDS versus time was observed between the two groups of four residents to occupy the apartment during the project, and because results agree with those predicted previously by mass balance based on typical mineral increase from domestic water use (Englehardt et al. 2013), we feel that the ~15% rate of rainwater makeup demonstrated here is a reasonable design goal. Further, this level of TDS was not observed to inhibit the kinetics of either biological or chemical treatment. Also, while nitrogen management has been recognized as one of the challenges for urban NZW treatment, nitrate compliance was reliably maintained via MBR nitrification-denitrification with external alkalinity and carbon addition.

4.1. Disinfection

In the present system there are four barriers to microbiological growth, including: MBR membrane, nominal pore size 0.04~0.06 μm ; vacuum ultrafiltration, membrane pore size of 0.04 μm effectively reduced with metal coagulant; and advanced oxidation comprising either peroxone, with typical $\text{Ct} > 100 \text{ mg O}_3 \cdot \text{min/L}$ as estimated based on the dissolved ozone concentration monitored online, or UV- H_2O_2 having total UV dose 6.6 ~ 11.6 J/cm^2 based on continuously-monitored UV intensity and internal reactor dimensions, either of which provides primary disinfection to the treated water. Finally, disinfectant residual is maintained in the treated water to prevent microbial regrowth. Estimates of overall log-removal of microbes through the proposed treatment train, assuming worst-case performance and based on published

coefficients of lethality, are summarized in Table 4 and described in detail in the Supplementary Information. Of note, these log-removals, which are far beyond reuse guidelines, require extrapolation far beyond the range of the original observed data, and therefore should be interpreted only qualitatively.

Despite the four pathogenic barriers just described, 8 of 136 daily fecal coliform measurements over the period were positive (Figure S3). This finding may be due to the high water temperature, which accelerated both chlorine decay and microbial growth in the small diameter influent piping with low, intermittent flowrates, and a treated water tank with residence time ~2 days and high DO. In addition, relatively frequent access to the tank was required for research purposes, representing opportunities for contamination. These factors were compounded in the trial of H₂O₂/silver as a secondary disinfectant, by the facts that (a) hydrogen peroxide is more effective against Gram-positive than Gram-negative bacteria such as fecal coliform (Wagner et al., 2002; Alasri et al., 1992), (b) pH of the treated water was consistently above neutral and high in ORP, favoring H₂O₂ oxidation ($\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$; H₂O₂ decay was observed up to 10~20 mg/L per day); and biofilm growth (Kim et al., 2000) was suspected in the treated water tank influent pipe preceding disinfectant dosing.

4.2. Advanced Oxidation and Disinfection Byproducts

The present system is designed to avoid the introduction of pesticides and other toxic environmental chemicals to municipal water, to avoid disinfection byproduct formation through efficient mineralization of organic precursors, and to destroy pharmaceuticals, personal care products, and other emerging organics permanently. In general the design was successful as indicated by the results shown in Figure 5 and Table 2, although the increase of dichloroacetic acid and trichloroacetic acid (albeit remaining below regulated levels) after the system was

converted to chlorine disinfection should be noted. However, bromide may occur in rainwater at concentrations up to 110 $\mu\text{g/L}$ (Neal et al. 2007)], and in human diets at levels on the order of 16.6 $\text{mg Br}^-/(\text{cap}\cdot\text{d})$ (Zhang et al. 2001; Flury and Papritz 1993). In that case, either source may typically result in bromate non-compliance in a NZW system following oxidation by ozone. Additionally, while on each cycle the bromate may be reduced to bromide in the septic tank and denitrification steps, it accumulates in a NZW system and is re-oxidized in the peroxone process.

The possible fate of bromide/bromate in the treatment process along with the bromide/bromate test results of 01/31/2014 is illustrated in Figure 8. The bromate removal capacity of GAC has been reported to vary from 12.7 $\mu\text{g BrO}_3^-/\text{g carbon}$ to 94.8 $\text{mg BrO}_3^-/\text{g carbon}$ (Siddiqui et al., 1996; Asami et al., 1999; Kirisits et al., 2000; Huang and Cheng, 2008), depending on the physical/chemical properties of the GAC and the presence of natural organic matter and competing anions. However, based on a system mass balance assuming 15% rainwater makeup with 70 $\mu\text{g/L}$ bromide, 15% treated water discharge, and additional bromide input from residential and commercial water use, adsorptive removal would likely need to be consistently above 60% to maintain a compliant steady-state bromate concentration, whereas the removal mechanism is known to be significantly reductive (Siddiqui 1996).

Many known bromate control approaches rely on chemical reduction, and therefore do not address long-term accumulation of bromide as a bromate precursor in a closed-loop advanced-oxidation-based NZW system. Therefore, peroxone advanced oxidation was replaced with the UV/ H_2O_2 process, in which excess H_2O_2 can react with intermediates such as OBr^- and thus disable the oxidation pathway for bromate formation.

4.3. Analysis of Energy Impact

While the current peroxone and UV-H₂O₂ systems were designed to develop NZW design principles based on water quality and economic goals, the data collected suggest that a moderately-sized distributed NZW system can save more energy than it uses in treatment. As an example, energy costs for a 3790 m³/d (1 MGD) peroxone-based NZW management system with aluminum electrocoagulation for bromate control (Ge et al., 2007; Selcuk et al., 2005; Gassie et al. 2016) are shown in Table 5, neglecting the embodied energy of alkalinity and/or external carbon potentially needed for nitrification/denitrification. Calculations assume the proposed NZW process is essentially equivalent to an advanced wastewater treatment process, followed by conventional water treatment, with replacement of granular filtration by membrane filtration and the addition of peroxone organics mineralization. Because both ultrafiltration stages of the proposed NZW process operate continuously at <5 psi, energy differences beyond peroxone treatment were neglected. Calculations are based on a tap water temperature at steady-state (heat loss equal to heat input), found as 27°C. Typical US water conveyance energy was assumed as reported at 82.5% of total water treatment plant energy (EPRI, 2000).

As shown in Table 5, savings in hot water heating energy exceed treatment energy significantly, even assuming mineralization of COD below 0.7 mg/L, and further exceed the total of treatment and typical US conveyance cost. With less stringent treatment, improvements in AOP energy-efficiency, and/or recovery of energy from biosolids, the potential for energy-positive water management is further raised. Note that while energy recovery from biological sludge was not considered in this project, a 24-month sludge pumping schedule was adequate for the septic tank and MBR of the onsite system described in this work. Also note that energy requirements for COD mineralization in secondary effluent by the UV-H₂O₂ process are

reportedly 3.3 times higher than those of the peroxone process (Gassie et al. 2016), so that a UV-
H₂O₂ –based NZW management system would not currently be energy positive.

5. Conclusions and Recommendations

An advanced oxidation-based direct potable reuse NZW system, designed for urban/suburban
NZW treatment and potentially energy-positive operation, is preliminarily demonstrated in this
work. The advanced oxidation approach effects permanent destruction of emerging constituents,
and offers an alternative to RO when for concentrate treatment and disposal options are too
energy/cost-intensive. Further, by potentially increasing recovery and eliminating the need for
blending of RO water with other local water to control corrosivity, a higher degree of reuse may
be achieved, potentially allowing energy-positive water management. Thus NZW energy
recovery goals exceed current goals for net-zero energy wastewater treatment, in that saved
energy may cover water treatment and, in typical US settings, conveyance as well. This result is
due to the magnitude of hot water energy demand relative to that of treatment and conveyance in
distributed systems, and to direct retention of this energy, avoiding losses in heat exchange, heat
pumping, and energy conversion.

It should be noted that achieving 85% recycling may require landscape irrigation to be
accomplished with a flow equaling 15% of the indoor service demand plus any additional onsite
water; otherwise the recycle rate must be reduced to provide the additional single-pass irrigation
water. Conversely, adequate rainwater collection area and storage volume must be accessible to
the treatment plant to provide 15% of demand. Subject to these conditions, NZW management
can be decentralized to minimize cost and/or energy.

The NZW process produced a mineral water meeting 115 of 115 Florida drinking water standards that, after 10 months of operation in recycle mode with 14% rainwater make-up, had a TDS concentration of ~500 mg/L as indicated by gravimetric analysis. At this mineral concentration, the water was judged excellent in flavor by the authors, and equivalent to tap water by the apartment residents, though aesthetic aspects have not otherwise been evaluated. Organics were mineralized to below detection in terms of COD, addressing the accumulation of endocrine-disrupting compounds in environmental waters. The energy for such peroxone mineralization represents a cost of only \$0.25/m³ (\$0.96/1000 gal) [assuming 2.11 kWh/m³ for mineralization of COD in secondary effluent (Wu and Englehardt 2015) and US average \$0.12/kWh electricity (US Energy Information Administration, 2013)]. Because other factors may dominate utility expenses, total capital and operating cost for ~2 MGD peroxone-based NZW plants, after hot water energy savings, has been projected lower than combined water/wastewater rates reported for several major U.S. cities (Guo et al., 2016). Presumably, operation of such moderately-sized distributed plants can be facilitated by remote automated process monitoring and control, allowing off-site and mobile technical support.

Specific conclusions regarding the design and operation of such NZW treatment systems include:

1. Results over the period indicate that the proposed advanced oxidation-based urban NZW systems can be operated with approximately 15% rainwater make-up for control of mineral content, and discharge of a similar flow of treated water for irrigation reuse, consistent with previous mass balance modeling;
2. Distributed peroxone NZW implementations are projected capable of saving more thermal energy for domestic water heating than they consume in treatment;

3. The onsite enhanced MBR employed is a low-maintenance unit process for efficient COD reduction and nitrification/denitrification following primary solids digestion;
 4. When iron is used for coagulation, pH must be maintained above neutral to avoid formation of $\text{Fe}^{(\text{II})}$ and consequent passage through filtration. Iron mediated aeration employing electrocoagulation can be a holistic approach to avoiding salt addition, maintaining $\text{Fe}^{(\text{III})}$ iron, providing aeration softening, and co-precipitating organics and multivalent inorganic ions such as phosphate;
 5. The peroxone and $\text{UV}/\text{H}_2\text{O}_2$ processes were demonstrated to provide efficient organics mineralization of COD to below 0.7 mg/L. While peroxone is more energy-efficient, both systems can be cost-effective;
 6. With the exception of bromate, regulated disinfection byproducts, pesticides, metals, and other constituents, as well as unregulated hormones, personal care products, and pharmaceuticals were maintained in compliance and generally below detection limits;
 7. No inhibition of biological or chemical kinetics by the high TDS content was observed; and
 8. Activated carbon was effective as a polishing treatment for turbidity, chlorine, hydrogen peroxide, bromate, and other trace constituents, preceding or following chlorine residual. In onsite implementations, point-of-use GAC filters may be more economical and easy to maintain, if permitted by regulation.
- Based on the results presented, the following recommendations are made:
1. Additional longer-term research is needed to demonstrate the ability of such NZW systems to avoid the accumulation of any undesirable constituents;

2. In particular, and for development of energy-positive NZW technology, further study of bromate control in ozone-based systems is needed;
3. Further study of requirements for preventing microbial re-growth in treated NZW having high-temperature (due to wastewater thermal energy retention) and high DO (e.g. due to reaction of H₂O₂ with chlorine), including required chlorine residual level and methods to monitor and maintain such consistently, is needed; and
4. Further research is needed regarding the fate of pharmaceuticals and personal care products, and microbial inactivation, through the treatment train.

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Figure 2. Water usage and storage in September, 2013.

Figure 3. Water chemistry (NZW vs. City water) and salinity changes of net-zero product water. [Sampled 07/01/2013 ~ 09/27/2013 for city water; 07/01/2013 ~ 07/31/2014 for NZW; TDS concentrations were calculated based on: $\text{TDS (mg/L)} = 0.514 \times \text{Cond. (}\mu\text{s/cm)}$]

Figure 4. pH evolution through the NZW process

Figure 5. Reduction of chemical oxygen demand (COD) along net-zero water treatment train. [BDL: below detection limit, 0.7 mg/L; sampled between Jul., 2013 and Dec. 2013]

Figure 6. Reduction of nitrogen species along net-zero water treatment train. [Sampled between Jul., 2013 and Dec., 2013]

Figure 7. Reduction of phosphate along net-zero water treatment train. [Grey box: sampled in Dec., 2013; Blank box: sampled in Sep., 2013]

Figure 8. Fate and transformation of bromide/bromate through net-zero water treatment. [ND: Not Detected (MDL: 2.5 $\mu\text{g/L}$); sampled on 01/31/2014.]

Table 1. Summary of Design/Operation Parameters and Major Changes in System Operation

Unit	Design/Operation Parameters	Changes
Septic tank	<u>Design capacity:</u> 500 GPD <u>Operation:</u> 2~3 retention time	
MBR	<u>Design capacity:</u> 500 GPD <u>Operation:</u> powered 12~18 hrs/day; Chemical dose: 109 mg/L ethanol, 30~128 mg/L CaCO ₃	<ul style="list-style-type: none"> • Installed timer in MBR to reduce duration of aeration (07/25/2013)
IMA	<u>Design:</u> 57 L IMA tank with 12 iron rods (2.54 cm OD); 117 L floc tank <u>Operation:</u> 16 mg/L Fe dose at current of 0.7 A	
UF	<u>Design:</u> <5 psi; 16 ZW-10 modules <u>Operation:</u> backwash for 30 S every 20 min; 900 LPM aeration during backwash; ~1.5 L liquid waste to septic tank before backwash	
Peroxone	<u>Design:</u> 2×3.79 m ³ tank; 2×30g/h ozonator <u>Operation:</u> batch mode (one tank filling and one for treatment); retention time: 2~3 days; typical treatment condition: 24 hrs with 5 mg/L O ₃ ; O ₃ /H ₂ O ₂ molar ratio ≥2.4	<ul style="list-style-type: none"> • Replaced peroxone with UV/H₂O₂ advanced oxidation to address bromate formation (05/31/2014); • Added one additional 149 W UV reactor to provide advanced oxidation capacity for full four-person occupancy (08/19/2014)
Other changes		<ul style="list-style-type: none"> • Replaced in-line GAC filters with point-of-use carbon filters on showers and sinks to minimize cost and energy of carbon replacement (09/19/2013) • Moved disinfectant injection point from the top of the treated tank to the ozone treatment tank effluent pipe to maintain disinfection residual in the pipe (11/07/2013) • Switched from hydrogen peroxide/silver to chlorine as the secondary disinfectant to improve disinfection reliability (12/12/2013)

668 **Table 2. List of HPPCPs Analyzed (none detected; MDL: method detection limit)**

Analyte	MDL (ng/L)	Analyte	MDL (ng/L)	Analyte	MDL (ng/L)	Analyte	MDL (ng/L)
OUST (Sulfameturon,methyl)	5	Albuterol	5	Cimetidine	5	Sulfadiazine	5
DIA	5	Atrazine	5	TCEP	10	Salicylic Acid	100
Triclocarban	5	Cyanazine	5	Estrone	5	Sulfathiazole	5
Acetaminophen	5	Nifedipine	20	Fluoxetine	10	Sulfamethoxazole	5
4-nonylphenol - semi quantitative	100	Ketoprofen	5	Acesulfame-K	20	Iopromide	5
Erythromycin	10	Naproxen	10	Sucralose	100	Bendroflumethiazide	5
Ethylparaben	20	Gemfibrozil	5	Chloramphenicol	10	Trimethoprim	5
Sulfadimethoxine	5	Amoxicillin (semi- quantitative)	20	Dilantin	20	Ethinyl Estradiol - 17 alpha	5
Simazine	5	4-tert-Octylphenol	50	Meprobamate	5	Butalbital	5
Primidone	5	Atenolol	5	Sulfamethazine	5	Ketorolac	
Sulfamerazine	5	Carbamazepine	5	Progesterone	5	Carisoprodol	5
DEET	10	Bromacil	5	Caffeine	5	BPA	10
TCPP	100	Diuron	5	Testosterone	5	Sulfachloropyridazine	5
TDCPP	100	Linuron	5	Theophylline	20	Warfarin	5
Lidocaine	5	DACT	5	Phenazone	5	Theobromine	10
Propazine	5	Isoproturon	100	1,7-Dimethylxanthine	10	Azithromycin	20
Sulfamethizole	5	Bezafibrate	5	DEA	5	Clofibric Acid	5
Oxolinic acid	10	Diltiazem	5	Androstenedione	5	Quinoline	5
Thiabendazole	5	Isobutylparaben	5	Meclofenamic Acid	5	Propylparaben	5
Diazepam	5	Flumequine	10	Pentoxifylline	5	Butylparaben	5
Diclofenac	5	Cotinine	10	Ioexal	10	2,4-D	5
Lincomycin	10	Estriol	5	Dehydronifedipine	5	Methylparaben	20
Chlorotoluron	5	Estradiol	5	Metazachlor	5		
Ibuprofen	10	Metolachlor	5	Carbadox	5		
Chloridazon	5	Lopressor	20	Norethisterone	5		

669

670 **Table 3. Partial Results of Product Water Analyzed by Certified External Laboratory**
671 **(sampled on 10/15/2013 and 07/03/2014, respectively)**

Analyte	Units	Sample dates				MCL
		10/15/2013	MDL	07/03/2014	MDL	
Chloride	mg/L	80.7	0.11	182	1.22	250
Fluoride	mg/L	ND	0.0420	0.0800	0.0420	4.0
Nitrate as N	mg/L	8.72	0.038	4.24	0.174	10
Threshold Odor Number	T.O.N.	1.00	1.00	1.00	1.00	3
Sulfate	mg/L	57.7	0.107	52.0	0.670	250
Total Dissolved Solids	mg/L	374	10.0	488	10.0	500
Antimony	mg/L	ND	0.000100	0.00172	0.000100	0.006
Chromium	mg/L	0.00116	0.000130	0.000650	0.000130	0.1
Aluminum	mg/L	ND	0.0007	0.0090	0.0007	0.2
Iron	mg/L	ND	0.000800	0.00300	0.000800	0.3
Sodium	mg/L	72.9	0.0028	122	0.00280	160
Coliform-Total	---	Absent	---	Absent	---	
Radium-226	pCi/L	0.2U ± 0.1	0.200	0.3 ± 0.2	0.200	5
Dichloroacetic Acid	µg/L	ND	0.45	15.7	0.45	---
Trichloroacetic Acid	µg/L	ND	0.36	1.62	0.36	---
Total Haloacetic Acids	µg/L	0	---	17.32	---	60
Chloroform	µg/L	8.7	0.11	ND	0.11	---
Total Trihalomethanes	µg/L	8.7	---	0	---	80
Bromate	µg/L	86.3	1.22	ND	2.5	10

672 MDL: method detection limit

673 MCL: maximum contaminant level

674 ND: analyte not detected at or above the detection limit

Table 4. Pathogen Log Reduction for the Proposed Treatment Train, Assuming (Unrealistically) Linear Increase in Reduction with Dose

Treatment process		Log removal		
		Enteric virus	Giardia cyst	Cryptosporidium
MBR & UF		2 ^a	4 ^b	4 ^b
AOPs	Peroxone	36 ^c	82 ^c	36 ^c
	UV/H ₂ O ₂	156 ^d	25 ^d	26 ^d
Residual Cl ₂		6 ^b	3 ^b	0 ^b
Total	Peroxone	44	89	40
	UV/H ₂ O ₂	164	32	30

^a Davis, M., 2010; ^b WRRF, 2015;

^cCt: 100 mg·min /L; kinetic parameters taken from Table 13-3, Crittenden et al., 2012;^d Dose: 6.6 J/cm²; kinetic parameters extrapolated from Table 13-11, Crittenden et al., 2012.

Table 5. Energy Used and Saved by a 3790 m³/d (1 MGD) NZW Management System (Steady-State Tap Water Temperature 27°C)

	Electrical Energy (kWh/m ³)	Primary (Fuel) Energy Equivalent (kWh/m ³)
Treatment Energy		
Advanced wastewater treatment ¹	-0.78	-2.39
Water treatment ²	-0.0686	-2.10
Peroxone mineralization ³	-2.11	-6.46
H ₂ O ₂ embodied energy ⁴	-0.0205	-0.0627
Subtotal: energy for treatment		-11.01
Hot Water Energy		
Hot water energy available to save ⁵	15.64	23.81
Aeration heat loss ⁶	-2.62	-3.97
Piping and tank heat losses ⁷	-1.59	-2.41
Heat lost in use (shower) ⁸	-0.50	-0.76
Heat lost in 15% irrigation water ⁹	-2.26	-3.42
Subtotal: hot water energy saved	8.68	13.25
Net Energy Saved		2.24
Energy for Treated Water Conveyance	0.323	0.990

¹Pumping to treatment, bar screen, aerated grit chamber, diffused air aeration, nitrification, denitrification, chemical feed/mixing, filtration, primary sludge gravity thickening, secondary sludge flotation thickening, anaerobic digestion, belt press dewatering (EPRI, 2000)

²Pumping to treatment, alum/polymer chemical feed, rapid mix, flocculation, sedimentation, filtration, chlorination, sludge drying beds, waste backwash water lagoon with pump to headworks (ICF Consulting, 2002)

³Electrical energy per order of magnitude COD mineralization in secondary effluent (EEO): 1.73~2.49 kWh/m³/log (Wu and Englehardt 2015)

⁴Gibbs Free Energy H₂O + 0.5 O₂ → H₂O₂ plus electricity-related losses, H₂O₂ dose 21.5 mg/L (Wu and Englehardt 2015)

⁵2013 US average primary energy (fuel) use for residential and commercial, gas and electric hot water, assuming 39.6 L/cap·d (150 GPCD) average municipal water use for new system with 15% outdoor use (Tchobanoglous et al. 2014; U. S. Department of Energy, 2015)

⁶Method of Talati and Stenstrom (1990) assuming 99.3 m³ air/m³ water for diffused air aeration

⁷Includes mains, laterals, and treatment tanks, as detailed in Supplementary Information

⁸Based on 5°F decrease, showerhead to drain, 11.7 GPCD average US shower use

⁹Projected 81°F and 92°F water entering and leaving home at steady state, respectively, assuming 54°F ambient outdoor temperature (Supplementary Information)