Urban Net-Zero Water Treatment: Phase II Field Results and Design

Recommendations

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Abstract

Net-zero water (NZW) systems, or water management systems achieving high recycling rates and low residuals generation so as to avoid water import and export, can also conserve energy used to heat and convey water, while economically protecting local eco-hydrology. The objective of this paper is to present the results of the second phase of operation of an advanced oxidation-based NZW pilot system designed, constructed, and operated for a period of two years, serving an occupied four-person apartment. System water was monitored, either continuously or thrice daily, for routine water quality parameters, minerals, and MicroTox® in-vitro toxicity, and intermittently for somatic and male-specific coliphage, adenovirus, *Cryptosporidium*, *Giardia*, emerging organic constituents (non-quantitative), and the Florida drinking water standards. All 115 drinking water standards with the exception of bromate were met in this phase. Neither virus nor protozoa were detected in the treated water, with the exception of measurement of adenovirus genome copies attributed to accumulation of inactive genetic material in hydraulic dead zones. All but six of 1006 emerging organic constituents analyzed were either undetected or removed >90% in treatment. Total dissolved solids were maintained at ~500 mg/L at steady state, partially through aerated aluminum electrocoagulation. Bromate accumulation is projected to be controlled by aluminum electrocoagulation with separate disposal of backwash water. Further development of such systems and their automated/remote process control systems is recommended.

Keywords: Advanced oxidation, potable water reuse, net-zero

1. Introduction

A net-zero water (NZW) system has been defined as (a) a municipal water management system that neither imports nor exports significant water to/from the service area, which may range in scale from a single property to a large urban water district (Englehardt et al., 2013), and (b) a military system installation that “... limits the consumption of freshwater resources and returns water back to the same watershed so not to deplete the groundwater and surface water resources of that region in quantity and quality over the course of a year” (U.S. Army, 2015). Such systems can conserve water and conveyance energy, while restoring local hydrology in terms of water quality and quantity. One approach suitable in areas of adequate rainfall is to employ rainwater harvesting for building water supply, and treatment of wastewater for irrigation reuse, as is designed into the Bullitt Center in Seattle (Cowan et al., 2014). Another approach may involve indirect potable reuse, in which wastewater passes through an environmental buffer before being withdrawn for possible further treatment and potable use, and some septic tank/well systems in rural areas may be considered to fall into this category.

An approach to NZW that may be appropriate in urban areas and areas of limited water supply is direct potable reuse (DPR), or potable reuse without an environmental buffer. Typically, existing systems employ reverse osmosis (RO) to remove pathogens, residual organics, and constituents including salts and nitrate. However, the process also removes natural minerals that reduce the corrosivity of the treated water, and generates a concentrate stream, potentially containing pharmaceuticals and other emerging constituents, that requires continual disposal on-site or off-site. As a result, recycle rate may be limited by process recovery rates and the need to blend treated water with another source water to reduce corrosivity. Also, chemical additives may be needed to control membrane fouling (Wu and Englehardt, 2015).

Recently, an advanced oxidation-based, urban NZW, DPR system was operated for a period of two years serving an occupied, four-bedroom, four-bath residence hall apartment at the University of Miami(UM) (Englehardt et al., 2013; Wu and Englehardt, 2016, 2015). Advanced oxidation processes generate hydroxyl radical, capable of mineralizing organic constituents to below detection in terms of chemical oxygen demand (COD). The system was able to produce potable mineral water from 85% recycled wastewater, with 15% rainwater added to achieve reasonable steady-state concentrations of total dissolved solids, while generating no routinely-disposed residual other than 15% of the treated potable reuse water suitable for irrigation (Wu and Englehardt, 2016).

The UM system is termed NZW because it supports water independence for a building or a region, due to its (a) 85% water recovery rate, and (b) lack of residuals requiring routine disposal. The remaining 15% of municipal demand is typically available as rainfall in urban watersheds. In addition, pharmaceuticals and other emerging organic constituents are mineralized, allowing excess treated water to be released onsite. Currently, the approach is projected to be comparable in total capital, operation, and maintenance cost to conventional municipal water and wastewater management, for plants serving 100-10,000 households (Guo and Englehardt, 2015; Guo et al. 2016). However, the long-term safety of the advanced oxidation based NZW approach must be demonstrated, including adequate disinfection and the avoidance of long-term accumulation of byproducts of advanced oxidation, such as bromate.

The purpose of this paper is to report results of the second phase of testing of the UM urban NZW system, including compliance with Florida drinking water standards (F.A.C. 62-550), mineral composition of the treated water, total dissolved solids (TDS) removal across individual treatment processes, kinetics of the UV/hydrogen peroxide advanced oxidation

process, and bromate control. Although quantitative analysis of unregulated microbiological and chemical constituents was outside of the scope of this project, results of the analysis of viable phage, adenovirus, *Giardia*, and *Cryptosporidium*, and rates of removal of emerging constituents such as pharmaceuticals, are also presented. Design and operating recommendations and principles are offered. Additional results, including system operation and control, water quality and chemistry, energetic analysis, daily fecal coliform, and quantitative analysis of 83 pharmaceuticals, hormones and personal care products are reported elsewhere (Wu and Englehardt, 2016).

2. Materials and Methods

Previously results were presented for the first 13 months of operation of the UM urban NZW system (Wu and Englehardt, 2016). In this paper, results are presented for the subsequent five months of operation, during which time process changes were made as described in the next section.

2.1. Site and System Description

A diagram of the net-zero water treatment facility is shown in Figure 1. Unit processes over the reported period consisted of septic tank, membrane bioreactor (MBR), aluminum electrocoagulation (EC), flocculation, vacuum ultrafiltration, peroxone or UV-hydrogen peroxide advanced oxidation, chlorine disinfection, and point-of-use granular activated carbon (GAC) filtration. The system design capacity is 1514 L/day (400 GPD), whereas actual average flow was 984 L/day (260 GPD) over the period of operation.

Figure 1. Schematic overview of the net-zero water facility at the University of Miami. Ozone and H₂O₂ injection points were changed depending on treatment process. Aeration in the dosing tank and EC could be switched on/off for experiments.

Complete details on system design and operation are described elsewhere (Wu and Englehardt, 2016). Briefly, wastewater enters a septic tank from the apartment, where it undergoes primary settling and anaerobic decomposition with a 2-4 day retention time. From there the liquid passes to a 500 gpd BioMicrobics BioBarrier MBR providing aerobic biological decomposition of organics and denitrification. The MBR discharges to the dosing tank, which serves as a flow equalizer and can be aerated to provide aeration softening (Chao and Westerhoff, 2002; Deng et al., 2013). The water then passes through electrocoagulation and flocculation, followed by vacuum ultrafiltration through 16 Zenon ZW-10 ZeeWeed filter modules (GE Power & Water, Ontario). Following filtration, the water undergoes hydrogen peroxide injection followed by UV irradiation before being sent to the final treated water tank and dosed with 2-4 mg/L chlorine. Point of use GAC filters on showers and sinks provide final

polishing, prior to use for all purposes except drinking and cooking. Mass flow rates for input chemicals and rainwater are shown in Table 1.

Table 1. Mass Flow Rates for Chemical Inputs, Water, and Residuals

Input	Mass flow rate (per cubic meter of treated water)
CaCO ₃	128 g ¹
Ethanol	109 g
Aluminum	15 g
H ₂ O ₂	34 g
NaOCl	3.5 g
Rainwater	150 L
Treated Water Disposed	150 L
Biosolids Disposed	5.3 g

¹16 g/m³ would have been adequate (Perera et al., 2016)

At the start of this reporting period, UV power was increased from one to two 149 W reactors (NeoTech D338, NeoTech Aqua Solutions, San Diego, CA) on August 19, 2014, due to return of the apartment to full occupancy. Subsequently, two principal changes were made to the system. First, iron electrodes in the 57 L EC reactor were replaced with twelve 2.5 cm x 72 cm aluminum electrodes on October 10, 2014, to determine the efficiency of bromide co-precipitation and minimization of subsequent bromate formation in the advanced oxidation process. Second, one additional 298 W UV reactor (NeoTech D438) was added to the system on October 6, 2014, to allow continued use of the UV-hydrogen peroxide advanced oxidation process, which was implemented during summer 2014 but which was found to have insufficient capacity to service four-person occupancy as needed during Fall 2014. UV power was thus provided by four 149 W lamps housed in three parallel reactors.

2.3. Sampling and Analysis

Throughout the project, routine and non-routine samples were taken to analyze system performance.

2.3.1. Routine Sampling

Water was sampled at various points throughout the system three times daily in 500 mL high-density polyethylene wide mouth laboratory bottles, and analyzed for pH, conductivity, dissolved oxygen (DO), turbidity, temperature, and residual chlorine. In addition, analysis for COD was added to these samples from September 5, 2014 through December 17, 2014. Some additional samples were collected twice to three times per week for measurement of COD, alkalinity, nitrogen species, and minerals as part of the daily monitor to measure performance of the MBR.

2.3.2. Non-Routine Sampling

Non-routine research sampling was conducted as follows. First, samples were taken from the dosing tank, clearwell, and treated water tank in 1 L high-density polyethylene wide mouth laboratory bottles. One set of samples was taken on July 30, 2014, and two additional sets, replicates of the first, were taken on December 22, 2014. These samples were delivered to Florida International University for qualitative screening analysis of organic constituents including pesticides, pharmaceuticals, and hormones. Second, samples were taken from the dosing tank and clearwell in 500 mL high-density polyethylene wide mouth laboratory bottles from December 2014 to January 2015, while the aeration in the dosing tank and EC was enabled. These samples were acidified with HNO_3 to a pH of less than 2 and stored for 14-28 days at 4°C with no headspace and analyzed for minerals to determine the extent of co-precipitation through aeration and electrocoagulation. Third, samples were taken October through December 2014 from the dosing tank, clearwell, advanced oxidation tank, and treated tank, for coliphage and adenovirus analysis. These samples were filtered through Rexeed 25S ultrafilters using a peristaltic pump. Tubing was disinfected prior to each sample using

concentrated chlorine solution (12,800 mg/L free chlorine) and then rinsed for 10 minutes with sample water before attaching to the filter. Flow rate was maintained at less than 2 LPM and recorded using a stopwatch and 5 L beaker. Water was filtered until a total of 100 L passed through the ultrafilters. Filters were placed in a ziploc bag in a cooler with ice packs and shipped overnight express to the U.S. Environmental Protection Agency (USEPA) lab in Cincinnati, OH for analysis.

Additional research sampling was conducted as follows. First, samples for UV/peroxide kinetic analysis were taken from November through December 2014 in 500 mL high-density polyethylene wide mouth laboratory bottles. Samples were taken at specific time intervals during each batch treatment, to support kinetic modeling of the process. Samples were taken to the lab and analyzed immediately for COD and residual hydrogen peroxide. Second, four samples were collected (two on December 3, 2014 and two on December 17, 2014) for full drinking water standards analysis by certified external laboratory (Florida Spectrum Environmental Services, Inc., Fort Lauderdale, FL, USA). These samples were collected and preserved according to their respective standard methods, and maintained at 4°C until analyzed. Finally, weekly samples for bromide, to determine removal in the EC, were collected in polyethylene sample bottles and maintained at 4°C until analysis.

2.3.3. Analytical Methods

All chemicals used for sample analysis were analytical grade and used as received. pH, conductivity, and dissolved oxygen were measured with an Orion Star A3295 probe unit (Thermo Scientific, USA). Turbidity was measured by nephelometer (Monitek Nephelometer TA1, Galvanic Applied Sciences USA, Inc). Alkalinity measurements were performed using Standard Method 2320. Chloride was measured using Standard Method 9253. Calcium,

magnesium, potassium, and sodium were measured by atomic absorption spectroscopy (AAAnalyst 800, Perkin Elmer, USA) using Standard Method 3111 (American Public Health Association et al., 2012). Samples were prepared within 48 hours by filtration through Millipore 0.45 μm filter membranes, which were treated with 1:1 HNO_3 , rinsed with deionized (DI) water, and air dried. Full drinking water analyses for 115 analytes were performed by certified external lab according to their respective standard methods.

Phosphate, nitrate, sulfate, COD, and chlorine were measured colorimetrically (UV-Vis spectrophotometer model DU720, Beckman Coulter, Brea, CA) using Hach phosphorus method 8048, Hach nitrate method 8039, Hach sulfate method 8051, Hach COD method 8000 (ultra low range), and Hach free chlorine method 8021 (Hach Co., Loveland, CO). Samples were diluted appropriately with DI water to fall within the range of the test. COD measurements were corrected as appropriate by measuring H_2O_2 residual concentration in the samples and assuming a ratio of 16 mg/L COD:1 mM H_2O_2 (Wu and Englehardt, 2012). In addition, because COD data were often near the detection limit (0.7 mg/L) of the low-range COD test, all original COD data < 5 mg/L were corrected for absorbance-concentration non-linearity with the regression equation found in the Supplementary Information. Hydrogen peroxide was measured by iodometric titration (Gordon et al., 1992). TDS was estimated as 0.514 times the specific electrical conductivity in $\mu\text{S}/\text{cm}$, and compared with gravimetric analysis by certified external laboratory. MicroTox® acute chemical toxicity screen was conducted using a Microtox® M500 analyzer (Modern Water Inc., New Castle, Delaware).

Analysis of relative concentrations of emerging constituents across the treatment train was conducted on sets of dosing tank, clearwell, treated water samples collected as described in the previous section. Samples were simply filtered, fortified with reference standards and

analyzed. The pre-concentration and analytical separation of analytes were performed using a Thermo EQuan Max on-line SPE liquid chromatographic system (Waltham, MA, USA) equipped with a Hypersil GOLD aQ (20 x 2.1 mm, 12 μ m particle size) and Hypersil Gold aQ (50 $\times$ 2.1mm, 1.9 μ m particle size) columns from Thermo Scientific (Bellefonte, PA), respectively. The total sample volume injected was 5 mL resulting in approximate concentration factors of about 2000 times. Two sets of mobile phases were used for sample loading and chromatography separation and the gradients are shown in the Supplementary Information.

All water samples were analyzed by a Q Exactive benchtop Orbitrap mass spectrometer (Thermo Scientific, San Jose, CA) equipped with a heated electrospray ion source (HESI-II) operated in positive mode. As a part of routine maintenance, the instrument was calibrated weekly using Pierce LTQ Velos ESI Positive Ion and Negative Ion Calibration Solutions (Thermo Scientific, Rockford, IL) for positive and negative modes, respectively. Mass accuracy less than 0.6 ppm was always achieved from the external calibration that was performed prior to analysis or every 24 hours. Ultra-pure nitrogen and argon were used as ion source gas and collision gas, respectively. Mass spectrometry parameters were set as follows: Sheath gas, Aux gas and Sweep gas were at 35, 35 and 5 arbitrary units, respectively. Spray voltage was at 4 kV. Capillary temperature and Vaporizer temperature were at 300 $^{\circ}$ C. The high-resolution mass spectrometer was operated at a resolving power of 35,000 with a scan range from 150-600 m/z.

The high-resolution full scan data obtained were screened using the TraceFinder 2.2 Environmental and Food Safety (EFS) database (Thermo Scientific, San Jose, CA) which includes a total of 1006 individual compounds ranging from common pesticides, pharmaceuticals, personal care products, additives, industrial chemicals, and hormones to search for potential matches. Positive identification of analytes was based on the accurate mass of the

analytes with less than 5 ppm mass error, and isotopic distribution match between the measured and expected patterns of the calculated elemental composition ($\geq 90\%$ fit threshold, $\leq \pm 5$ ppm). Relative concentrations were calculated by comparing peak areas of samples at different treatment stages. Only compounds that had peaks in all three replicate samples, and having peak area $> 500,000$, peak time < 15 seconds, and signal to noise ratio > 10 were considered to have been identified.

Filtration/immunogenic separation/immunofluorescence assay analysis of *Cryptosporidium* and *Giardia* was conducted by certified external lab using EPA method 1623.1 (US EPA, 2005). Somatic and male-specific coliphage and adenovirus were measured after concentration of 100 L samples of system water by passage through Rexeed® 25 hollow fiber ultrafilters (Dial Medical Supply, Chester Springs, PA) and dead-end ultrafiltration. Upon receipt, the ultrafilters were eluted with 400 ml of a solution containing 0.01% (w/v) sodium polyphosphate (Sigma-Aldrich), 0.01% (v/v) Tween-80 (Sigma-Aldrich) and 0.001% (v/v) Antifoam Y-30 Emulsion (Sigma-Aldrich) by 2 cycles of clockwise and counterclockwise circulation for 1 minute each. Ten ml of the eluate was used to enumerate somatic and male-specific coliphage in samples using Standard Methods 9224B and 9224C (American Public Health Association, Standard Methods for the Examination of Water and Wastewater, Washington, DC). Quantities were then back-calculated to the original sample volume and normalized per liter of original sample. For enumeration of adenovirus, the remaining eluate (approximately 400 ml) was filtered through a 0.22 μm membrane filter and viral DNA was extracted from 0.2 ml of concentrated sample using the QIAamp DNA Blood Mini Kit (Qiagen, Valencia, CA) as described (Cashdollar et al., 2013). Adenovirus genomes in extracted concentrated samples were enumerated using qPCR as described (Brinkman et al., 2013) in a StepOne Plus (Life

Technologies, Carlsbad, CA) instrument. Adenovirus quantities were determined following a most probable number (MPN) analysis of 5-fold dilutions of samples, using 5 replicate reactions per dilution. Quantities were then back calculated to the original sample volume and normalized per liter of original sample.

The concentration procedure just described provides a recovery efficiency of 66 (± 20)% for somatic coliphage and 94 (± 17)% for male-specific coliphage in MBR effluent ($n=5$) (Leow et al., 2016). This approach provides a 250-fold concentration and allows for the equivalent of 250 ml of the original sample to be represented by each 1 ml used in the plaque assay. Given the concentration factor and fraction of the sample assayed, the theoretical detection limit is 0.016 PFU/L.

To assess the recovery efficiency of adenovirus using the procedures described above, 9 liters of MBR effluent was spiked with 1 liter of raw wastewater and processed as described above. The recovery efficiency of adenovirus through these steps was 98 ($\pm 49\%$, $n=5$). This approach provides a 500-fold concentration and allows for the equivalent of 250 μ l of the original sample to be represented in each qPCR reaction. The theoretical detection limit of the procedures used is 0.8 equivalent genomic copies per liter.

3. Results

3.1. Minerals and Bromide Removal in the EC

Following biological wastewater treatment, performance of which is reported elsewhere (Wu and Englehardt, 2016), aeration softening was investigated for its ability to precipitate calcium carbonate (Deng et al., 2013), and co-precipitate other minerals (Deng et al., 2013) from the MBR effluent/10-15% rainwater blend. Full results are shown in the Supplementary Information. Of the analyzed dissolved minerals, TDS, calcium, magnesium, and nitrate showed

significant ($p < 0.001$, $p = 0.017$, $p = 0.002$, and $p < 0.001$, respectively) reduction in passing from dosing tank to clearwell, after aeration was introduced in the dosing tank and EC, compared to clearwell samples prior to aeration in the dosing tank and EC. Phosphate experienced significant reduction from the dosing tank to clearwell ($p < 0.001$), but unlike the four previously mentioned, an increase in reduction was not significant once aeration was introduced ($p = 0.102$). All other minerals analyzed did not experience significant reduction from the dosing tank to clearwell, either before or after aeration was introduced in the dosing tank and EC ($p > 0.05$). These results are shown in Figure 2, pointing to the potential utility of such coagulant-mediated aeration, as reported previously for iron-mediated aeration (Deng et al., 2013), albeit at a cost in terms of blower energy.

Figure 2. Dissolved mineral reduction through electrocoagulation/flocculation/vacuum ultrafiltration, with and without preceding aeration. [Conditions: pH = 7.4, temp. = 29°C, alkalinity = 95 mg/L]

Aluminum was effective in co-precipitating bromide, the precursor from which bromate is formed in ozone-based oxidation processes, with removal apparently following aluminum concentration up to approximately 15 mg/L as reported previously (Ge et al., 2007). Bromide concentrations in the dosing tank and clearwell at varying aluminum doses are shown in Figure 3. As shown, bromide concentrations in the dosing tank and clearwell prior to conversion to aluminum electrocoagulation were hundreds of micrograms per liter. After conversion, at a

308 starting dose of 15 mg/L aluminum, bromide concentrations in both the clearwell and dosing
 309 tank were reduced below the 69 µg/L detection limit of the analysis. Subsequently, the
 310 aluminum dose was increased to 30 mg/L, then decreased to ~12 mg/L and then 8 mg/L, at
 311 which point bromide was again detected in the samples once the system reached steady state.
 312 The aluminum was then set back to 15 mg/L, and bromide again dropped below detection.

313 Bromate measurements were performed on the finished water on December 3, 2014 and
 314 December 17, 2014 as part of the complete external drinking water analyses. Of note, the switch
 315 from UV/peroxide to peroxone also occurred on December 3, 2014, immediately after the first
 316 set of water samples were taken. Bromate concentrations were significantly lower following
 317 UV/peroxide treatment in comparison with peroxone treatment (~15 µg/L vs. ~60 µg/L),
 318 though both exceeded the drinking water standard of 10 µg/L.

Figure 3. Bromide and aluminum concentrations over time. [Conditions: pH = 7.4, temp. = 29°C, TDS (Dosing tank) = 770 mg/L, TDS (Clearwell) = 735mg/L, alkalinity (Dosing tank) = 100 mg/L, alkalinity (clearwell) = 90 mg/L]

3.2. UV/Hydrogen Peroxide Organics Mineralization

Kinetic data were collected on COD mineralization by the UV-hydrogen peroxide process, using the batch treatment tank with 596 W UV power, and a constant H₂O₂ feed rate resulting in total dosages of 41, 35, and 25 mg/L treated water in the first, second, and third experiments, respectively. Total treatment volume was 795 gallons. In general, noise in the data

was attributed to H₂O₂ interference with the measurement of COD values near the detection limit. In fact, correction of COD values for measured H₂O₂ averaged 24% after three hours of treatment, and > 300% after 48 hours of treatment. In addition, COD measurements of 25.0 mg/L at 30 h, and 9.61 mg/L at 27 h, in the second and third experiments, respectively, were significantly higher than initial COD, and were eliminated due to suspected sample contamination.

The data were fitted with a pseudo-first order model, with rate coefficients shown in Table 3. In addition, a non-pseudo-steady state version of the model of Glaze et al., (1995), simplified in terms of radical species considered, but accounting for absorption of UV radiation by organics, was also fitted as follows:

$$-\frac{d[COD]}{dt} = k_{COD, \bullet OH}[OH \bullet][COD] + \Phi_{COD}f_{COD}I_0(1 - e^{-A_t}) \quad (1)$$

In Equation 1, $k_{COD, \bullet OH}$ is the rate constant for the reaction of COD with hydroxyl radical, OH•; Φ_{COD} is the quantum yield for the photolysis of COD; f_{COD} is the fraction of radiation absorbed by COD; I_0 is the intensity of UV radiation; and A_t is the total absorbance of the solution at wavelength λ . The second term on the right-hand side accounts for COD oxidation by direct photolysis, here assumed negligible compared with oxidation by hydroxyl radical. [OH•] at each time increment is calculated as:

$$[OH \bullet] = \frac{2\Phi_{H_2O_2}I_0f_{H_2O_2}(1 - e^{-A_t})}{k_1[H_2O_2] + k_2[HCO_3^-] + k_{OH}[COD]} \quad (2)$$

in which $\Phi_{H_2O_2} = 0.5$ mol/Einsteins is the quantum yield for photolysis of H₂O₂ (Volman and Chen, 1959; Zellner et al., 1990), I_0 is the total intensity of UV radiation available for absorption in Einstein/L-s, $f_{H_2O_2}$ is the fraction of radiation absorbed by H₂O₂ assuming that H₂O₂ and COD are the only UV absorbers, and k_1 and k_2 are 2.7×10^7 M⁻¹s⁻¹ and 8.5×10^6 M⁻¹s⁻¹,

respectively (Glaze et al. 1995). Due to the design of the UV reactors used, designed to efficiently reflect low pressure mercury lamp UV radiation, UV light was assumed efficiently absorbed by hydrogen peroxide and organic constituents, such that $1 - e^{-A_t} \approx 1$ (Glaze et al., 1995). The model was computed numerically, finding $[OH\bullet]$ at each time step based on the continuous hydrogen peroxide feed, the COD remaining at that time, and assuming a constant 49 mg/L HCO_3^- based on an average measured 90 mg/L total alkalinity and $\text{pH} = 8.0$. UV power ranged from $15\text{-}36 \text{ mW/cm}^2$, increasing as the treatment progressed.

In Equation 2, the product $I_0 f_{\text{H}_2\text{O}_2}$ was found directly from intensity measurements, observed to increase from 15 mW/cm^2 to 36 mW/cm^2 over the course of treatment. That is, all UV radiation was assumed absorbed by H_2O_2 and COD, due to the highly reflective walls of the UV reactor employed. Then, because hydrogen peroxide dosage was maintained constant through treatment, the product $I_0 f_{\text{H}_2\text{O}_2}$ was assumed to increase from 15 to 36 mW/cm^2 in inverse proportion to the computed decay in COD concentration during treatment, with $f_{\text{H}_2\text{O}_2}$ approaching 1, according to:

$$f_{\text{H}_2\text{O}_2} = \frac{I}{I_0} = \frac{\epsilon_{\text{H}_2\text{O}_2} c_{\text{H}_2\text{O}_2}}{\epsilon_{\text{H}_2\text{O}_2} c_{\text{H}_2\text{O}_2} + \epsilon_{\text{COD}} c_{\text{COD}}} \quad (3)$$

In Equation 3, $\epsilon_{\text{H}_2\text{O}_2}$ and ϵ_{COD} are the extinction coefficients for H_2O_2 and COD, respectively, and $c_{\text{H}_2\text{O}_2}$ and c_{COD} are concentrations of H_2O_2 and COD, respectively, in the UV reactors.

To find $f_{\text{H}_2\text{O}_2}$ for use in Equation 2, ϵ_{COD} was computed for the complex mixture of biologically recalcitrant organics in secondary effluent. First, for use in Equation 2, observed intensities can be converted to Einsteins/L-sec based on Equations 4:

$$E_p = hf = h\left(\frac{c}{\lambda}\right)$$

$$\begin{aligned}
 N_p &= \frac{I}{E_p} = I \left(\frac{\lambda}{ch} \right) \\
 I_E &= \frac{N_p}{N_A} = \frac{\lambda}{c \cdot h \cdot N_A} \\
 I_0 &= I_E \cdot \frac{A_R}{V_R}
 \end{aligned}
 \tag{4}$$

371 in which E_p is the energy of a photon, N_p is the number of photons, I is intensity [W/m²], h is
 372 Planck's constant (6.63×10^{-34} Js), c is the speed of light (3×10^8 m/s), λ is the operative UV
 373 wavelength [254×10^{-9} m], f is frequency [s⁻¹], I_E is UV intensity in Einsteins/m²·s, N_A is
 374 Avogadro's number, A_R is the reactor surface area [0.604 m²], and V_R is the reactor volume
 375 [15.82 L]. The initial value $f_{H_2O_2} = 0.417$ at the start of treatment was found from the intensity
 376 measured at the start of treatment, $I_i = 5.08 \times 10^{-5}$ Einsteins/L-sec, and $I_0 = 1.22 \times 10^{-4}$
 377 Einsteins/L-sec. The extinction coefficient $\epsilon_{COD} = 0.164 \pm 0.032$ L/mg(O₂)-cm for coagulated,
 378 ultrafiltered, secondary effluent organics was then calculated from Equation 3 using the H₂O₂
 379 dosage and initial COD concentration for each of three runs, assuming $\epsilon_{H_2O_2} = 0.526$ L/mg-cm
 380 (Glaze et al., 1995) and averaging across runs.

381 Results, assuming that UV light is absorbed completely by H₂O₂ and COD, and $\Phi_{COD} =$
 382 0, meaning COD degradation by UV irradiation is negligible in comparison with oxidative
 383 decomposition by OH• (Glaze et al., 1995), are shown in Figure 4. The two models produced
 384 similar goodness of fit in terms of COD, as seen in Table 2. However, in order to predict H₂O₂
 385 concentration versus time it was necessary to use the model of Equations 1 – 3, and the fitted
 386 value of ϵ_{COD} for secondary effluent organics. The mean second order rate constant for OH•
 387 oxidation of secondary effluent organics, $6.37 \times 10^7 \pm 4.19 \times 10^7$ M⁻¹s⁻¹, obtained by fitting the
 388 model to the three kinetic runs (by minimizing $S_{k_{OH}}$, the standard error of regression) and
 389 averaging, is on the same order as the value $k_{OH} = 1.24 \times 10^7 \pm 0.64 \times 10^7$ M⁻¹s⁻¹ reported

previously (Wu and Englehardt, 2015). Results suggest that 40 mg/L hydrogen peroxide may have been an overdose in this application such that H_2O_2 is scavenging $\text{OH}^\bullet$. Also of note, ORP was not found useful as an indicator of the degree of mineralization by the UV-hydrogen peroxide process, as it was for the peroxone process in this project (Wu and Englehardt, 2016).

Using $k = 0.0646$ at a dose of 35 mg/L (Run 2), the electrical energy per order of magnitude reduction (EE/O) of COD is $(4 \times 0.149 \text{ kW}) \times 35.6 \text{ h} / (795 \text{ gal} / 264 \text{ gal/m}^3) = 7.0 \text{ kW/m}^3$. As expected, this value is higher than the 1.73-2.49 kW h/m^3 reported previously for the peroxone process. Also, the value is high relative to many reported for oxidation of trace organic constituents in natural water matrices by the UV- H_2O_2 process (Water Research Institute, 2011), as may be expected of biologically-recalcitrant organics.

Figure 4. Measured COD, first order fit, and adapted Glaze et al. (1995) model results versus time of UV/ H_2O_2 treatment, in which (a) $\text{COD}_i = 5.29 \text{ mg/L}$, total H_2O_2 dose = 41 mg/L, (b) $\text{COD}_i = 7.26 \text{ mg/L}$, total H_2O_2 dose = 35 mg/L, and (c) $\text{COD}_i = 7.64 \text{ mg/L}$, total H_2O_2 dose = 25 mg/L. [Conditions: pH = 8, alkalinity = 90 mg/L, temp. = 29-36°C, UV intensity = 15-36 mW/cm^2 . COD measurements of 25.0 mg/L at 30 h, and 9.61 mg/L at 27 h, in the second and third experiments, respectively were eliminated due to suspected sample contamination. Run (a): H_2O_2 dosing discontinued after 48 hours.]

Table 2. Experimental Results for First Order Rate Constants (k) and Second Order Rate Constants (k_{OH}) for Oxidation of Secondary Effluent Organics (as COD in mol O_2/L)

Run	COD _i (mg/L)	k (h ⁻¹)	S_k	k_{OH} ($\times 10^7 \text{ M}^{-1}\text{s}^{-1}$)	$S_{k_{\text{OH}}}$
1	5.29	0.0411	0.202	4.04	0.357
2	7.26	0.0646	0.334	11.2	0.596
3	7.64	0.0355	1.611	3.86	1.516
Mean		0.0471		6.37	
Std. Dev.		0.0154		4.19	

3.3. Drinking Water Quality

As discussed elsewhere (Englehardt and Wu 2016) and shown further in the Supplementary Information, water quality was generally similar to County water, with the exception of TDS, which at an 85% recycle rate appeared to stabilize at ~500 mg/L. The concentrations of all regulated drinking water quality parameters are shown in the Supplementary Information. While treated water met all 115 Florida primary (mandatory, health-based) and secondary (optional, aesthetic) drinking water standards (at least as strict as US federal standards) on July 3, 2014, the two sets of samples collected in December 2014 met only 114 of 115 primary drinking water standards and all secondary standards. The exception was bromate, which was exceeded in both December samples including the set collected prior to re-conversion to peroxone advanced oxidation on December 3, 2014, for reasons to be discussed. For comparison, samples were also collected prior to GAC filtration, and analyzed. In those samples, 114 of 115 primary standards were met as well, and all secondary drinking water standards were met except aluminum and TDS. Overall, the principal effect of the GAC in terms of drinking water standards was further reduction of haloacetic acids and trihalomethanes.

3.4. Emerging Constituents

Results of the MicroTox® screen for toxicity (Supplementary Information) indicate that inhibition of *V. fischeri* by the test was generally lower in the net-zero treated water than in County water. In addition, of 1006 compounds (Supplementary Information) qualitatively screened by high-resolution LC-MS, only 56 were detected in the dosing tank, the earliest treatment stage sampled. Of these 56, 50 were removed > 90% (peak area reduction across the treatment train), three were removed < 90%, and three apparently increased in concentration. The reduction of emerging constituents by each unit process, in passage from the dosing tank (secondary effluent) to the final treated water, as interpreted from LC-MS scans is shown in Figures 5 and 6. In general, highest removals occurred during advanced oxidation. Also of note, Imazalil, 3,4-dichloroaniline, and Coumachlor were removed >70% in the coagulation/membrane filtration process, and Tralkoxydim and Disulfiram were removed >60% during GAC filtration.

Figure 5. Percent reduction of emerging constituents in the (a) metals mediated aeration coagulation and flocculation process, (b) advanced oxidation process, and (c) granular activated carbon process. Percent reduction is relative to initial concentration in the dosing tank.

Figure 6. Overall reduction of emerging constituents throughout the treatment processes.

3.5. Phage/Virus Removal

The results of culture analysis for somatic and male-specific coliphage in plaque forming units (PFU, coliphages) per liter, qPCR analysis of adenovirus in equivalent genomic copies (egc) per liter, and immunofluorescence assay of *Cryptosporidium*, and *Giardia* in oocysts/cysts per liter are shown in Figure 7. No *Cryptosporidium*, *Giardia*, or coliphage were detected in any treated samples. However, the treated water sample on Oct. 28, 2014, and on Dec. 1, 2014, tested positive for adenovirus as indicated by qPCR analysis. Across the treatment train, no somatic coliphage were detected. Male-specific coliphage were detected in two clearwell samples, however none were detected downstream, indicating AOP inactivation. Adenovirus was detected in 3 highly treated samples and ranged in concentration from 7-21 equivalent genomic copies/L. Given the level of treatment performed and that PCR is unable to distinguish infectious and non-infectious virions, it is likely that these positive detections resulted from the presence of non-infectious adenovirus particles or remnants of inactivated genomes. In fact, light-colored residue was detected visually in the bottom of the ozone treatment tank, below discharge piping, suggesting accumulation of such organic material in this highly-oxidizing, hydraulically isolated reactor zone.

(a)

(b)

(c)

(d)

(e)

Figure 7. Concentrations over time of (a) male specific coliphage, (b) somatic coliphage, and (c) adenovirus in different stages of treatment, and (d) *Cryptosporidium* and (e) *Giardia* in the treated water.

4. Discussion

Regarding compounds that apparently increased or were removed < 90% in advanced oxidation, Cyprodinil, Trichlorfon, and Chinomethionate are food crop pesticides which may have entered through the food of apartment residents. Dichlorprop-p is a weedkiller with no obvious source. However, leaves did routinely enter the worksite from landscaped areas, and landscaping debris entered the cistern on Aug. 2 and 9, 2013, raising TDS from 30 to 400 mg/L. (Nevertheless, on Aug. 10 the cistern was evacuated, and advanced oxidation was increased to address the issue.) Oxibendazole is a veterinary medicine, also unexplained in occurrence because pets were never observed in the apartment. The observed increase in DEET concentration through advanced oxidation may potentially be attributed to use of insect repellent by project staff prior to the reporting period, though DEET was not used regularly during the period, and DEET is not generally recalcitrant to advanced oxidation (Song et al., 2009). Because these results are only qualitative in nature, it is possible that some results reported are actually due to the presence of another compound, having the same chemical formula but different structure and properties (isomer), not present in the EFS database.

The principal challenge observed in the work presented in this paper was avoidance of bromate formation from bromide during advanced oxidation. In fact, Br^- was found at 112 $\mu\text{g/L}$ as BrO_3^- in the cistern water on Jan. 31, 2014. Although this concentration is extremely high, likely due to the proximity of the site to the ocean, Br^- concentrations of 32 $\mu\text{g/L}$ as BrO_3^- , i.e. three times the 10 $\mu\text{g/L}$ drinking water standard for bromate, are common in rainwater (Yamada, 1997). Thus, even at 15% rainwater blending, and even though bromate may be reduced to bromide in the MBR, bromate can accumulate in an advanced oxidation-based system employing ozone without RO.

As noted previously, bromate was not detected at 2.5 µg/L or above on July 3, 2014, but was present at 15 µg/L on December 3, 2014, although during that time the system had been running with UV/peroxide to alleviate bromate formation. This unexpected result suggests the formation of some ozone in the UV reactor. That is, because 80% of system water was replaced with cistern water upon conversion to UV-hydrogen peroxide operation in May 2014, and system water tested below 2.5 µg/L bromate on July 3, 2014, any residual bromate would have had to have been contained in septic tank biosolids and ZeeWeed filter sludge. However, only Br⁻, not BrO₃⁻, was detected in the dosing tank and clearwell on Jan 31, 2014, suggesting that bromate was biochemically reduced to bromide in the septic tank and MBR anoxic zone. In that case, some bromide would have had to have been oxidized to bromate subsequent to May 2014, in order for additional bromate to accumulate in the system.

We postulate that accumulation of bromine species occurred as follows. First, ZeeWeed filter backwash water was continually disposed to the septic tank, which presumably had already accumulated significant bromide in the decomposing septage. The additional bromide load may have accumulated to the point where bromide discharged to electrocoagulation was not adequately co-precipitated. Aggravating this accumulation may have been the increase in recycling rate from 85% to 90%, and flowrate from ~60 GPD to 240 GPD, in August 2014. Then, while ca. 35% of the UV lamp power is output at 254 nm, another 7% is output at 185 nm. Typically, most 185 nm radiation is absorbed by water, producing OH•, but enough may have produced ozone from dissolved oxygen introduced in the MBR and ZeeWeed filter to produce some bromate from the accumulated bromide. Otherwise, there would have had to have been bromate stored in the generally anoxic septic tank/MBR solids, and perhaps some of this

bromate was solubilized and released when system flow increased due to return to full occupancy, August 2014.

We feel that one additional process modification, in addition to conversion to UV-hydrogen peroxide advanced oxidation and conversion to aluminum electrocoagulation, would solve the bromate issue, particularly for sites without such extreme rainwater bromide concentrations and without a history of ozone treatment. That is, ZeeWeed backwash water, representing only 2-3% of the flow, can be routed to a separate settling tank for effluent disinfection and e.g. discharge for irrigation as appropriate. Other alternative systems are discussed elsewhere (Wu and Englehardt, 2016).

In terms of virus, if 1, 1, 4, and 6-log reduction are assumed for ultrafiltration (MBR), ultrafiltration (ZeeWeed), advanced oxidation ($UV \geq 186 \text{ mJ/cm}^2$), and engineered storage buffer with free chlorine $Ct \geq 900 \text{ mg}\cdot\text{min/L}$, a minimum of 12-log virus inactivation would be expected, meeting a 12-log virus inactivation standard as proposed in current reuse guidelines (WateReuse Research Foundation et al., 2015). In fact, log-removals were calculated to be much higher (Wu and Englehardt, 2016). For example, at a 7 mW/cm^2 minimum transmittance, 12.8 gal UV reactor volume, 500 gal recirculation treatment tank volume, and 48 h treatment time, the UV process provides a dose of at least $30,970 \text{ mJ/cm}^2$, 166 times the level required for 4-log reduction. In addition, at 48 h storage time and 2 mg/L minimum free chlorine, the chlorine Ct was at least $5760 \text{ mg}\cdot\text{min/L}$, 6.4 times the level required for 6-log reduction. Partly for this reason, the adenovirus genomic copies detected were attributed to possible accumulation of DNA in dead zones of the ozone treatment tank and the treated water tank, where floc was occasionally observed at depths below the tank outlet. It should further be noted that adenovirus shedding rates are high in feces ($4 \times 10^2 - 6 \times 10^5 \text{ gc/gram}$ of feces in health

individuals, Vetter et al., 2015), and concentrations are consistently high in raw wastewater (3.25-8.62 log₁₀ genome copies/L; 1.00-4.08 log₁₀ infectious units/L), varying more widely in small treatment systems (Hewitt et al., 2011; Kuo et al., 2010).

To prevent microbial re-growth in the warm treated water, maintenance of consistent chlorine residual was critical in this work (Wu and Englehardt, 2016). This design task may be challenging in onsite UV-H₂O₂ systems, because substantial variation in influent organics causes variation in H₂O₂ residual in the UV-H₂O₂ process effluent, and this variation presents variable chlorine demand. However, several process refinements may stabilize hydrogen peroxide residual in the AOP effluent. First, H₂O₂ decomposition can be abated by minimizing solution temperature and exposure to light, and by feeding directly from the chemical drum or diluting with metal-free water, allowing for better dosage control. A catalytic GAC filter may be employed to remove any remaining H₂O₂ residual.

5. Conclusion and Recommendations

This paper is the third presenting operating experience with the municipal NZW treatment system described. The system generates less than 15% of the treated potable water for discharge, e.g. as irrigation water. Over two years of operation the septic tank/MBR did not need pumping, and we project < 2 m³ biosolids per household-year, to be pumped every one to two years. Moreover, when implemented with peroxone advanced oxidation and bromate control, and an 85% recycle rate, the system is projected to be capable of energy-positive operation. That is, because the thermal energy imparted by municipal water heaters is retained in the recycled water, the resulting tap water requires little re-heating, thus saving more energy than is used for treatment by a peroxone-based NZW system (Wu and Englehardt, 2016). In terms of

overall system mass balance, the system passes human-derived mineral input and converts total organics largely to CO₂ and biosolids, similar to conventional technology. Uniquely, the system:

- Largely retains and recycles water;
- Largely retains and recycles wastewater thermal energy;
- Avoids geologic mineral input; and
- Converts dissolved emerging trace organics to CO₂.

Based on work to date, the following conclusions are drawn:

- A system comprising septic tank, denitrifying MBR, subsequent 15% rainwater dosing, aluminum electrocoagulation, flocculation, vacuum ultrafiltration, UV-hydrogen peroxide organics mineralization, catalytic GAC, and chlorine disinfection can achieve 85% municipal wastewater recycling, economically producing a potable mineral water having TDS concentration of ~500 mg/L;
- The aluminum-mediated aeration/filtration process provided significant reduction of dissolved minerals including calcium, magnesium, phosphate, and nitrate, when compared with electro-coagulation/filtration, and effectively co-precipitated bromide;
- The UV-H₂O₂ process mineralized organics to below the COD detection limit (0.7 mg/L) and provided >1-log removal of 50 emerging constituents screened for in MBR effluent (950 analyzed compounds were undetected), while minimizing bromate formation. Compounds screened for and apparently removed <1-log were cyprodinil, trichlorfon, chinomethionate, dichlorprop-p, oxibendazole, and DEET; and

The following design and operational recommendations are made:

- While COD reduction by UV- H_2O_2 followed a pseudo-first order rate, a more sophisticated model was needed to characterize H_2O_2 concentration over time, suggesting broader applicability of the more detailed model for design;
- Provision of control over the duration of MBR aeration is suggested to control denitrification;
- While virus disinfection Ct values for the system are estimated based on the literature to be well above proposed 12 log virus inactivation guidelines, further study of requirements for long term microbiological control is suggested
- Aluminum electrocoagulation (15 mg Al/L) is recommended to maintain low bromide concentrations in the influent to advanced oxidation;
- Backwash waters from the flocculation tank, ZeeWeed filter, and granular activated carbon filter should be delivered to a separate tank for sedimentation and discharged together with ~12% of the treated water (e.g. for irrigation as appropriate), to prevent accumulation of bromide and other undesired constituents;
- Catalytic carbon is suggested to precede chlorination, if necessary to catalyze decay of H_2O_2 residual for maintenance of consistent chlorine residual in the treated water; and
- Automation of process control should be considered for remote operation of distributed NZW systems.

Further development of NZW management systems should include a focus on disinfection beyond drinking water standards, e.g. through controlled and monitored pilot studies in new residential or commercial developments, including log-removal achieved across the full treatment train beginning at the septic tank. Research regarding automated monitoring of

organics mineralization by the UV-hydrogen peroxide process, such as by UV₂₅₄ absorbance measurement, is also needed.

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