OXIDATION OF EDCs AND PHARMACEUTICALS IN REUSE WATER

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ABSTRACT

Ozone is a proven technology for the oxidation of variety of organic contaminants in water. Advanced oxidation processes using hydroxyl radical chemistry also have been shown to oxidize a great diversity of contaminants. This study was initiated to determine the effectiveness of ozone and ozone/peroxide AOP for disinfection of tertiary treated wastewater. A desirable ancillary benefit of ozone processes is the oxidation of trace contaminants at disinfection doses. Ozone and ozone/peroxide were applied to tertiary treated wastewater during two seasons to determine the efficacy of disinfection and simultaneous contaminant oxidation. Results clearly demonstrate that ozone and ozone AOP are highly effective for the removal of a great number of organic contaminants. Moreover, estrogenicity as determined by an *in vitro* bioassay was also destroyed by ozone and advanced oxidation. Contaminant destruction was not significantly enhanced by the addition of peroxide for AOP as compared to ozone alone. Some microcontaminants were found to be resilient to oxidation. The contaminants include: TCEP (a flame-retardant), meprobamate (an anti-anxiety pharmaceutical), musk ketone (a synthetic fragrance), and iopromide (an x-ray contrast media).

KEYWORDS

Ozone, endocrine disruptors, pharmaceuticals, disinfection, oxidation

INTRODUCTION

The Clark County Water Reclamation District (CCWRD) has been serving the Las Vegas Valley since 1956. The Las Vegas valley has been experiencing phenomenal growth, with a growth rate of the past two years of around 6 percent. As a result, the flow increases at CCWRD have averaged about 5 mgd per year. CCWRD is now planning to expand its treatment capacity from 110 MGD to 150 MGD. In 1996, the US Geological Survey (USGS) reported that biomarkers for estrogenicity were elevated in fish from the Las Vegas Bay of Lake Mead (Bevans, Goodbred et al. 1996). By the end of 1997, research funded by the Southern Nevada Water Authority (SNWA) determined that trace estrogenic natural and synthetic steroids and alkylphenols were detectable in the Las Vegas Wash and Las Vegas Bay (Renner 1998; Snyder, Keith et al. 1999; Snyder 2000; Snyder, Snyder et al. 2000). Although estrogenic alkylphenols from surfactant

degradation also were present in the Las Vegas Bay (Snyder, Keith et al. 2001), an estrogencitity focused toxicity identification and evaluation (TIE) project demonstrated that natural and synthetic steroids were, by far, the most responsible compounds for observed *in vitro* estrogenicity (Snyder, Villeneuve et al. 2001). Additionally, the SNWA team also discovered a series of pharmaceuticals at ng/L concentrations (Snyder, Kelly et al. 2001; Vanderford, Pearson et al. 2003). Following the SNWA studies, the USGS also determined that trace pharmaceuticals were present in Lake Mead (Boyd and Furlong 2002). Table 1 shows the pharmaceuticals reported by USGS in Lake Mead. The SNWA also completed an endocrine disruptor evaluation of "laboratory" fish caged in various locations within Lake Mead and found only minor differences between fish caged in the Las Vegas Bay and control sites with the lake (Snyder, Snyder et al. 2004).

The detection of steroids and pharmaceuticals at ng/L levels is not unique to Lake Mead. Steroids and pharmaceuticals in wastewater effluents and surface waters were first discovered in the US in the 1960s and 1970s (Stumm-Zollinger and Fair 1965; Tabak and Bunch 1970; Garrison, Pope et al. 1975; Hignite and Azarnoff 1977). Later these trace contaminants were determined to be ubiquitous contaminants of wastewater effluents globally (Aherne, English et al. 1985; Eckel, Ross et al. 1993; Heberer and Stan 1996; Desbrow, Routledge et al. 1998; Halling-Sorensen, Nielsen et al. 1998; Ternes, Hirsch et al. 1998; Daughton and Ternes 1999; Snyder, Keith et al. 1999; Ternes, Stumpf et al. 1999; Metcalfe, Koenig et al. 2000). Treatment of these chemicals in wastewater effluent has become of great interest. Westerhoff et al. showed that ozone was much more effective for the oxidation of a diverse group of steroids, pharmaceuticals, and personal care products than was hypochlorite (Westerhoff, Yoon et al. 2005). Several reports have shown that ozone is effective for the oxidation of many microcontaminants (Zwiener and Frimmel 2000; Ternes, Meisenheimer et al. 2002; Balcioglu and Otker 2003; Huber, Canonica et al. 2003; Ternes, Stüber et al. 2003; Huber, Göbel et al. 2005; McDowell, Huber et al. 2005).

Expanding the CCWRD wastewater treatment plant provided an opportunity to utilize "state of the art technology" to address the EDCs and pharmaceuticals in the wastewater. In the plant expansion, ozone could provide efficient disinfection with simultaneous contaminant destruction. Since previous reports have indicated that the Las Vegas Wash may impact fish in Lake Mead, CCWRD was keenly interested in the removal of estrogenic chemicals.

Table 1. 2001-2002 USGS Monitoring of Lake Mead. Adapted from USGS Report 02-385, *Boyd & Furlong – 2002*.

Acetaminophen	Analgesic; anti-inflammatory
Amoxicillin	Antibiotic
Azithromycin	Antibiotic
Caffeine	Stimulant
Carbamazepine	Antiepileptic; analgesic

Cephalexin	Antibiotic
Cimetidine	Antiulcerant; stomach-acid reducer
Clarithromycin	Antibiotic
Codeine	Narcotic; analgesic
Cotinine	Metabolite of nicotine
Dehydronifedipine	Metabolite of Procardia (vasodilator)
Digoxigenin	Metabolite of Digoxin (antianginal)
Digoxin	Antianginal (cardiac stimulant)
Diltiazem	Antianginal
1,7-dimethylxanthine	Metabolite of caffeine
Diphenhydramine	Antihistamine
Enalaprilat	Antihypertensive
Erythromycin	Antibiotic
Fluoxetine	Antidepressant
Furosemide	Edema medication; diuretic
Gemfibrozil	Cholesterol regulator
Ibuprofen	Analgesic; anti-inflammatory
Lisinopril	Antihypertensive
Metformin	Antiglycemic
Miconazole	Antifungal
Paroxetine metabolite	Metabolite of Paroxetine (antianxiety)
Ranitidine	Antiulcerant; antacid
Salbutamol (albuterol)	Anti-inflammatory; bronchodilator
Sulfamethoxazole	Antibiotic
Thiabendazole	Anthelmintic (intestinal wormer)
Trimethoprim	Antibiotic
Urobilin	Metabolite of human excrement
Warfarin	Anticoagulant

METHODS

Target EDCs and pharmaceuticals were chosen in conjunction with a previous SNWA study funding by AwwaRF (Project #2758). The analytical method used to identify and quantify target analytes was described previously (Vanderford, Pearson et al. 2003). Briefly, 1-L samples were preserved using sodium azide and refrigerated until sample extraction. Stable isotope surrogates were added to the samples before extraction using automated solid-phase extraction (ASPE). Stable isotope internal standards were added

to the resulting extraction before analysis by liquid chromatography with tandem mass spectrometry (LC-MS/MS) using both electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI).

An *in vitro* bioassay using human breast cancer cells was used to evaluate the estrogenicity of extracts resulting from aqueous samples (Zacharewski 1997; Snyder, Snyder et al. 2000). Cell cultures as dosed with a small amount of extract. This cell line is responses to estrogen agonists, which induce cellular replication. Estrogenicity is determined by comparing the cell number of exposed cells to that of control cells. Units are provide as estrogen equivalent units (EEQs) as ng estrogen per mL of extract, which equates roughly to ng/L in the water sample since 1-L samples were used throughout this study.

Bench scale tests were performed to provide estimates of ozone demand and decay rates to be used in subsequent pilot plant testing. A sample of purified water was placed inside a water-jacketed flask and chilled to 2°C. Once chilled, gaseous ozone was diffused into the water using an ozone generator producing 11 percent ozone (model CFS-1A, Ozonia North America Inc., Elmwood Park, NJ USA). Ozone stock solution concentrations and dissolved ozone residuals were measured according to Standard Methods 4500-O3 (Bader and Hoigne 1982; APHA, AWWA et al. 1998). Ozone dosages of 2, 5, and 10 mg/L were achieved by injecting an aliquot of ozone stock solution into a 1-L amber glass dispenser containing the tertiary treated wastewater at room temperature (20°C). Dissolved ozone residual was measured until it decayed to less than 0.05 mg/L or until a contact time of 24 minutes was achieved.

A 55-gallon drum filled with tertiary treated wastewater provided the influent to a 1 L/min bench-top pilot plant (BTPP). The BTPP consists of a continuous-flow ozone contactor constructed using inert materials such as glass, fluorocarbon polymers, and stainless steel. A peristaltic pump was used to control the flow rate at 1L/min. The ozone contactor consisted of 12 glass chambers each providing 2 minutes of contact time for a total of 24 minutes. The bottom of each glass chamber was equipped with a sample port. Ozone feed gas was produced from oxygen with a laboratory-scale ozone generator (model LAB2B, Ozonia North America Inc., Elmwood Park, NJ USA). Ozone was added in the first contactor chamber with counter-current flow through a glass-fritted diffuser with bubble size of 0.1 um. A mass flow controller calibrated for oxygen gas (model AFC2600D, Aalborg Instruments and Controls, Inc., Orangeburg, NY USA) and a feed gas concentration analyzer (model H1-S, IN USA Inc., Needham, MA USA) were used to calculate and control the ozone dosage. The off gas was collected from the top of each cell into a central manifold and sent to an ozone destruction unit containing manganese dioxide destruct catalyst. The process effluent was discharged to the sanitary sewer.

Pilot plant testing was conducted during June 2005 and January 2006 to capture seasonal changes in TOC, which could impact ozone demand and decay rates. During the June 2005 pilot testing, three O3 dosages of 4.9, 7.3, 8.7 mg/L were evaluated. During the January 2006 pilot study, ozone dosages of 2.1, 3.6, and 7.0 mg/L were selected based

upon bench-scale demand/decay data. During each test, the tertiary wastewater was maintained at room temperature (20°C). Dissolved O3 measurements were collected from each chamber to examine ozone demand and decay rates. Water quality samples were collected for assimilable organic carbon (AOC), carboxylic acids, aldehydes, bromate, total coliforms and fecal coliforms.

RESULTS

Bench top batch reactors were used to determine the ozone demand and decay. The demand/decay curves for June 2005 are shown in Figure 1. Contaminant removal results for June 2005 and January 2006 are provided in Tables 2 and 3, respectively. Estrogenicity as determined by the *in vitro* bioassay is shown in Table 4.

Figure 1. Ozone Demand/Decay – June 2005

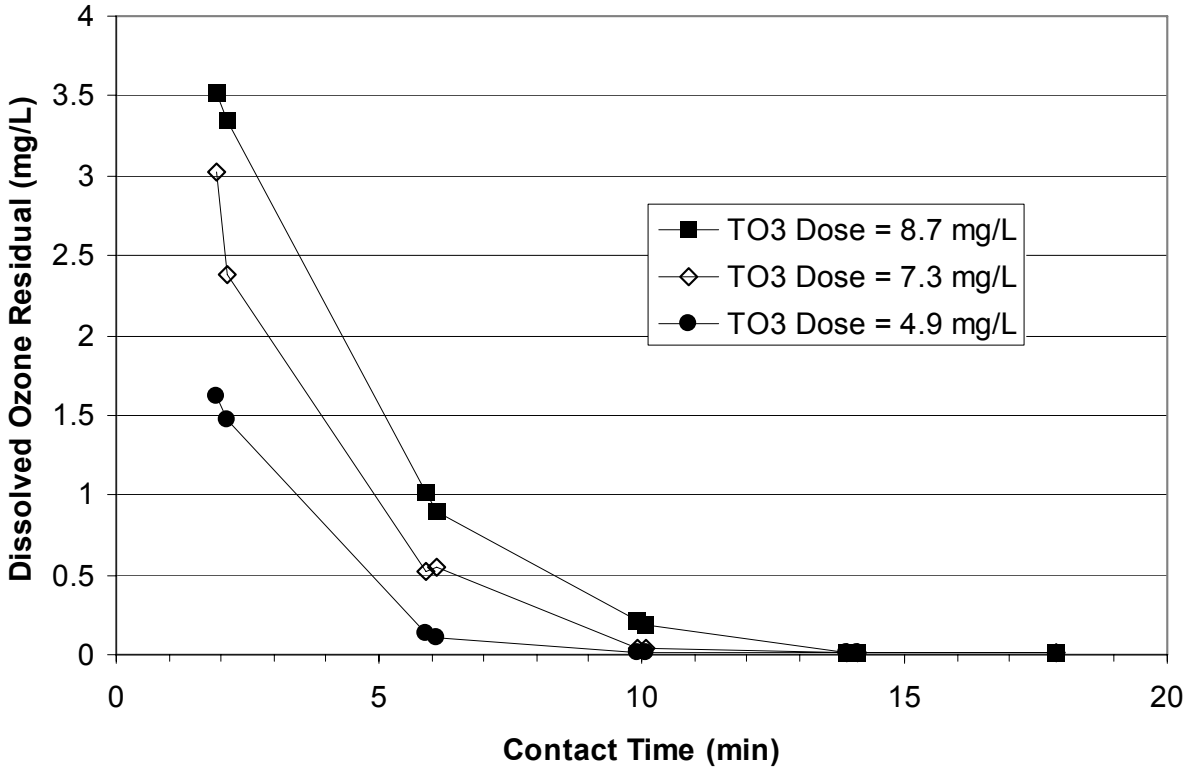

Table 2. Ozone Oxidation – June 2005

Compound	Class	Raw Influent	Filtered Secondary	4.9 mg O_3/L	7.3 mg O_3/L	8.7 mg O_3/L
Androstenedione	Hormone	684	<1.0	<1.0	<1.0	<1.0
Estradiol	Hormone	49	<1.0	<1.0	<1.0	<1.0
Estriol	Hormone	240	<5.0	<5.0	<5.0	<5.0
Estrone	Hormone	<25	<1.0	<1.0	1.1	<1.0
Ethynylestradiol	Hormone	<25	<1.0	<1.0	<1.0	<1.0
Progesterone	Hormone	103	<1.0	<1.0	<1.0	<1.0
Testosterone	Hormone	110	<1.0	<1.0	<1.0	<1.0
Acetaminophen	Pharmaceutical	43750	<1.0	<1.0	<1.0	<1.0
Carbamazepine	Pharmaceutical	99	210	<1.0	<1.0	<1.0
Diazepam	Pharmaceutical	<25	<1.0	<1.0	<1.0	<1.0
Diclofenac	Pharmaceutical	28	54	<1.0	<1.0	<1.0
Dilantin	Pharmaceutical	94	154	17	3.4	<1.0
Erythromycin	Pharmaceutical	285	133	<1.0	<1.0	<1.0
Fluoxetine	Pharmaceutical	<25	18	<1.0	<1.0	<1.0
Gemfibrozil	Pharmaceutical	1105	<1.0	<1.0	<1.0	<1.0
Hydrocodone	Pharmaceutical	218	240	<1.0	<1.0	<1.0
Ibuprofen	Pharmaceutical	11950	19	1.1	<1.0	<1.0
Iopromide	Pharmaceutical	37	22	6.2	2.0	<1.0
Meprobamate	Pharmaceutical	739	332	140	63	42
Naproxen	Pharmaceutical	13200	13	<1.0	<1.0	<1.0
Pentoxifylline	Pharmaceutical	46	<1.0	<1.0	<1.0	<1.0
Sulfamethoxazole	Pharmaceutical	590	841	3.1	<1.0	<1.0
Trimethoprim	Pharmaceutical	319	35	<1.0	<1.0	<1.0
Triclosan	Antimicrobial	1590	85	112	50	72
Caffeine	Stimulant	97800	51	<10	<10	<10
TCEP	Flame Retardant	453	373	427	352	334
DEET	Personal Care	413	188	39	10	3.4
Oxybenzone	Personal Care	2925	6	8.2	<1.0	1.5
Atrazine	Pesticide	251	<1.0	<1.0	<1.0	<1.0

Table 3. Ozone Oxidation – January 2006

Compound	Class	Filtered Secondary	2.1 mg O_3/L	3.6 mg O_3/L	7.0 mg O_3/L
Androstenedione	Hormone	2	<1.0	<1.0	<1.0
Estradiol	Hormone	<1.0	<1.0	<1.0	<1.0
Estriol	Hormone	6	7.7	9.3	<5.0
Estrone	Hormone	5	6.6	<1.0	1.0
Ethynylestradiol	Hormone	<1.0	<1.0	<1.0	<1.0
Progesterone	Hormone	<1.0	<1.0	<1.0	<1.0
Testosterone	Hormone	2	<1.0	<1.0	<1.0
Acetaminophen	Pharmaceutical	<1.0	<1.0	<1.0	<1.0
Carbamazepine	Pharmaceutical	139	<1.0	<1.0	<1.0
Diazepam	Pharmaceutical	1	<1.0	<1.0	<1.0
Diclofenac	Pharmaceutical	73	<1.0	<1.0	<1.0
Dilantin	Pharmaceutical	143	81	40	1.9
Erythromycin-H_2O	Pharmaceutical	162	2.6	<1.0	<1.0
Fluoxetine	Pharmaceutical	14	<1.0	<1.0	<1.0
Gemfibrozil	Pharmaceutical	16	<1.0	<1.0	<1.0
Hydrocodone	Pharmaceutical	199	1.8	<1.0	<1.0
Ibuprofen	Pharmaceutical	6	12	<1.0	<1.0
Iopromide	Pharmaceutical	139	119	83	25
Meprobamate	Pharmaceutical	796	552	472	137
Naproxen	Pharmaceutical	25	<1.0	<1.0	<1.0
Pentoxifylline	Pharmaceutical	<1.0	<1.0	<1.0	<1.0
Sulfamethoxazole	Pharmaceutical	669	50	3.2	<1.0
Trimethoprim	Pharmaceutical	191	<1.0	<1.0	<1.0
Triclosan	Antimicrobial	35	1.7	1.4	<1.0
Caffeine	Stiumlant	21	14	<10	<10
TCEP	Flame Retardant	235	192	269	221
DEET	Personal Care	133	77	44	4.9
Oxybenzone	Personal Care	<1.0	<1.0	<1.0	<1.0
Atrazine	Pesticide	<1.0	<1.0	<1.0	<1.0

Table 4. Estrogenicity Results

	Raw Influent	Filtered Secondary	Low	Medium	High
June-05	54	0.66	<0.06	<0.06	<0.06
January-06	NM	1.00	0.82	0.10	0.08

NM=Not Measured

DISCUSSION

Ozone was determined to be effective for the oxidation of the vast number of contaminants present in CCWRD filtered secondary effluent. Ozone demand and decay was as expected considering the TOC present in this water. Date from the June 2005 indicate that some compounds (i.e., carbamazepine & diclofenac) were of greater concentration in the secondary effluent than were present in the raw sewage. While these results are contra intuitive, this may be the result of deviations in influent concentration over time or the result of deconjugation of metabolites to the reform the active pharmaceutical. More research is required to determine the factors causing this observation. In the January 2006 experiment, the concentration of estriol appears to rise during ozonation, which contradicts all previous finding. Estriol has poorer chromatography and quantitation may have suffered due to the challenging matrix at concentrations approaching the analytical detection limit (5 ng/L). It is unlikely that estriol concentrations increased during ozonation. The rise in estrone concentration is not significant within the analytical variability of the method. Estrogenicity, as measured by cellular bioassay, was greatly reduced by ozonation. It is interesting to note that estrogenicity and steroid levels at CCWRD are quite small. These data suggest that CCWRD has good removal of steroids and estrogenicity in general, even without the addition of ozone oxidation.

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