INVESTIGATING OZONE

The Southern Nevada Water Authority (SNWA) uses ozone disinfection to serve the drinking water needs of the Las Vegas valley. The Clark County Water Reclamation District partnered with SNWA to investigate the feasibility of using ozone to disinfect its filtered secondary effluent and oxidize organic contaminants.

A pilot-scale ozone treatment system shows promise in removing trace levels of pharmaceuticals, steroids, and personal care products from secondary effluent

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The Las Vegas Valley has experienced phenomenal growth in recent years, resulting in increased demand for wastewater treatment. To keep pace with this growth, the Clark County Water Reclamation District (CCWRD; Las Vegas) is planning to expand the capacity of its Central Wastewater Treatment Plant from 416,350 to 529,900 m^3/d (110 to 140 mgd) by 2010. As part of this expansion, CCWRD is increasing the capacity of the plant's advanced wastewater treatment processes by 113,550 m^3/d (30 mgd). CCWRD discharges its treated wastewater into the Las Vegas Wash, which, in turn, flows into the Las Vegas Bay of Lake Mead. The largest reservoir in the United States and the source of drinking water for the Las Vegas Valley, Lake Mead is formed by Hoover Dam, which is located on the Colorado River approximately 48 km (30 mi) southeast of Las Vegas.

In the face of a severe drought and increasing demand for water throughout the Colorado River's seven-state basin, the level of Lake Mead has dropped about 24 m (80 ft) during the last 5 years. The U.S. Bureau of Reclamation, which operates Hoover Dam, has forecasted that water levels in Lake Mead will continue to drop before recovering. The Nevada Department of Environmental Protection has indicated that it will evaluate the need for changing the water quality objectives pertaining to flows entering the lake and its tributaries as the lake's level lowers.

To ensure that its newly expanded treatment facility will not be obsolete soon after completion, CCWRD is planning to incorporate membrane technology and ozone disinfection. Along with removing bacteria and colloidal materials, membranes would improve disinfection by lowering the ozone demand of the water to be disinfected. Ozonation would deactivate viruses and destroy organic material present in minute amounts, an important consideration in light of recent findings that trace concentrations of pharmaceuticals, steroids, and personal care products reach Lake Mead via the Las Vegas Wash.

Ozone has been shown to be an effective means of oxidizing trace organic contaminants while providing exemplary disinfection. To investigate the feasibility of using ozone to disinfect its filtered secondary effluent and oxidize organic contaminants, CCWRD recently partnered with the Southern Nevada Water Authority (SNWA; Las Vegas), which uses ozone to disinfect the drinking water it provides to the Las Vegas Valley. For the study, samples of CCWRD's effluent were analyzed to determine the presence and concentrations of pharmaceuticals, steroids, and personal care products. To account for seasonal differences in water quality, pilot testing was conducted in June 2005 and January 2006, during which time effluent was treated with varying levels of ozone.

Although significant estrogenicity was observed in the filtered secondary effluent, even the lowest ozone doses evaluated were capable of removing estrogenicity to less than the detection level. Likewise, several pharmaceuticals also were detectable, and most were removed

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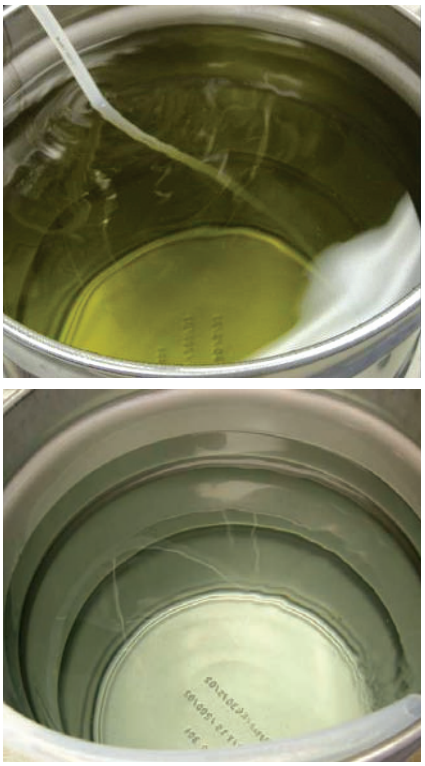


Effluent before (above) and after (below) ozonation.

readily by ozone. Ozone was found to be effective for disinfection even at the lowest ozone doses evaluated.

Detecting Endocrine Disruptors

In 1996, the U.S. Geological Survey reported symptoms of estrogen exposure in carp captured in Lake Mead's Las Vegas Bay. By the end of 1997, research funded by SNWA determined that trace levels of natural and synthetic estrogenic steroids and alkylphenols — a family of chemicals formed by the biodegradation of alkylphenolethoxylates, which are commonly used in personal care products — were detectable in the Las Vegas Wash and Las Vegas Bay. Although estrogenic alkylphenols resulting from the degradation of surfactants also were present in the Las Vegas Bay, a project that focused on identifying and evaluating estrogenicity demonstrated that natural and synthetic steroids were the compounds most responsible by far for observed *in vitro* estrogenicity.

Additionally, the SNWA team discovered a series of pharmaceuticals present in concentrations on the order of nanograms per liter. Following the SNWA studies, the U.S. Geological Survey also determined that trace pharmaceuticals were present in Lake Mead. SNWA also completed an evaluation of endocrine disrupting compounds in "laboratory" fish caged in various locations within Lake Mead. The study found only minor differences between fish caged in the Las Vegas Bay and control sites within the lake.

The detection of steroids and pharmaceuticals at the level of nanograms per liter is not unique to Lake Mead. Steroids and pharmaceuticals were discovered in wastewater effluent and surface waters in the United States as long ago as the 1960s and 1970s. Later studies determined that trace levels of these contaminants were ubiquitous in wastewater effluent globally. Treatment of these chemicals in wastewater effluent has become a matter of great interest.

Because of the reports indicating that compounds transported by the Las Vegas Wash may affect fish in Lake Mead, CCWRD has a keen interest in removing estrogenic chemicals from its wastewater discharges. Previous research has shown that ozone is much more effective than hypochlorite in oxidating a diverse group of steroids, pharmaceuticals, and personal care products. Several reports have shown that ozone is effective for the oxidation of many microcontaminants.

Table 1. Ozone Oxidation During June 2005 Pilot Test

Note: All units are ng/L. Compound	Class	Raw influent	Filtered secondary	After ozone dose of 4.9 mg/L	After ozone dose of 7.3 mg/L	After ozone dose of 8.7 mg/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

Identifying and Quantifying Target Compounds

Target pharmaceuticals, steroids, and personal care products were chosen in conjunction with a previous SNWA study funded by the American Water Works Association Research Foundation (Denver). Briefly, the analytical method used to identify and quantify target analytes involved preserving 1-L (0.26-gal) samples using sodium azide and refrigerating them until samples were extracted. Stable isotope surrogates were added to the samples before extraction. Stable isotope internal standards were added to the resulting extraction before analysis by liquid chromatography with tandem mass spectrometry using electrospray ionization and atmospheric pressure chemical ionization. Detection limits ranged from 1 to 10 ng/L.

Estrogenicity of the extracted samples was measured by means of an *in vitro* bioassay using human breast cancer cells, which are extremely sensitive to endogenous estrogens and estrogenic chemicals. Cell cultures were dosed with a small amount of extract. The cell line used for

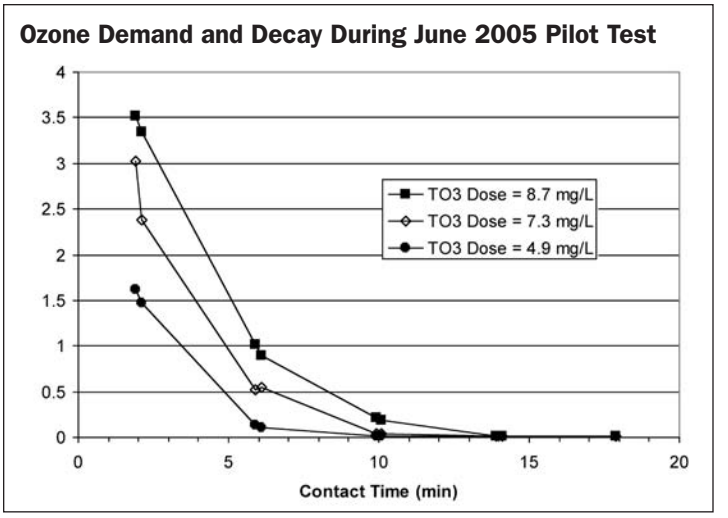
the study is responsive to estrogen agonists, which induce cellular replication. Estrogenicity is determined by comparing the number of cells in cultures exposed to the extract to that of control cells. Specifically, estrogenicity is measured in terms of estrogen equivalent units — that is, nanograms of estrogen per milliliter of extract. Such units equate roughly to nanograms per liter in the water sample, since 1-L (0.26-gal) samples were used throughout the study.

Estimating Rates of Ozone Demand and Decay

Bench-scale tests were performed to provide estimates of ozone demand and decay rates for use in subsequent pilot testing. A sample of purified water was placed inside a water-jacketed flask and chilled to 2°C (36°F). Once the sample had been chilled, gaseous ozone was diffused into the water by means of an ozone generator to produce 11% ozone. Ozone stock solution concentrations and dissolved ozone residuals were measured according to method 4500-O3 of *Standard Methods for the Examination of Water and Wastewater*. Ozone dosages of 2, 5, and 10 mg/L were achieved by injecting an aliquot of ozone stock solution into a 1-L (0.26-gal) amber glass dispenser containing the tertiary treated wastewater at room temperature (20°C [68°F]). 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 0.2-m^3 (55-gal) drum filled with tertiary treated wastewater provided the influent to a bench-top pilot plant that consisted 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 1 L/min (0.26 gal/min). The ozone contactor comprised 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. Ozone with a bubble size of 0.1 µm was added in the first contactor chamber with counter-current flow through a glass-fritted diffuser. A mass-flow controller calibrated for oxygen gas and a feed-gas concentration analyzer were used to calculate and control ozone dosage. Off-gas was collected from the top of each cell into a central manifold and sent to an ozone-destruction unit containing manganese dioxide as the catalyst. Process effluent was discharged to the sanitary sewer.



Conducting the Pilot Tests

Pilot testing was conducted during June 2005 and January 2006 to capture seasonal changes in total organic carbon (TOC) that could affect ozone demand and decay rates. During the June 2005 pilot testing, three ozone dosages — 4.9, 7.3, and 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 on bench-scale data regarding ozone demand and decay.

During each test, the tertiary wastewater was maintained at room temperature (20°C [68°F]). Dissolved ozone measurements were collected from each chamber to examine rates of ozone demand and decay. Water quality samples were collected to determine concentrations of assimi-

Table 2. Ozone Oxidation During January 2006 Pilot Test

Note: All units are ng/L.

Compound	Class	Filtered secondary	After ozone dose of 2.1 mg/L	After ozone dose of 3.6 mg/L	After ozone dose of 7.0 mg/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

The ozone advanced oxidation process was shown to greatly reduce estrogenicity, remove pharmaceuticals, and disinfect effectively.

lable organic carbon, carboxylic acids, aldehydes, bromate, total coliforms, and fecal coliforms.

Bench-top batch reactors were used to determine ozone demand and decay. The demand–decay curves for June 2005 are shown in the figure on p. 59. Contaminant removal results for June 2005 and January 2006 are provided in tables 1 and 2, respectively (see p. 58 and p. 59). Estrogenicity as determined by the *in vitro* bioassay is shown in Table 3 (see below).

Analyzing the Results

During full-scale operation, the proposed strategy for controlling the ozone-disinfection process would be to feed enough ozone to meet the demand. Ozone would have to decay completely before the wastewater is discharged. Much of the ozone demand results from TOC. During the study, TOC levels in CCWRD's secondary effluent ranged from 5.4 to 8.5 mg/L, with the lower concentrations occurring in summer and the higher concentrations occurring in winter. Ozone demand and decay occurred at expected levels, considering the effluent's TOC concentrations. Complete decay of ozone required 10 to 20 minutes.

Data from the bench-scale testing in June 2005 indicated that some compounds — for example, carbamazepine and diclofenac — occurred in greater concentrations in the secondary effluent than in the raw wastewater. Although these results seem counterintuitive, this finding may result from deviations in influent concentration over time or the deconjugation of metabolites to reform the active pharmaceutical. More research is required to determine the factors causing this observation.

During the January 2006 bench-scale testing, the concentration of estriol seemed to increase during ozonation, contradicting all previous findings. However, it is unlikely that estriol concentrations increased during ozonation. This unexpected result may have occurred because of analytical variability near the method detection limit. Meanwhile, the increase in estrone concentration is not significant within the method's analytical variability.

Ozonation greatly reduced estrogenicity, as measured by cellular bioassay. It is interesting to note that estrogenicity and steroid levels in CCWRD's secondary effluent are quite small. These data suggest that CCWRD's treatment process generally removes estrogenicity and steroids well, even without ozone oxidation.

Overall, the bench-scale testing indicated that ozonation reduced about 90% of the organic contaminants by approximately 90%. Some chemicals were more resistant to ozone oxidation, such as the pharmaceutical meprobamate and the chloro-phosphate flame-retardant tris-chloroethylphosphate. Ozone was found to be effective for disinfection even at the lowest ozone doses evaluated.

As part of a separate evaluation, CCWRD determined that capital costs for the proposed membrane technology and ozonation would be about 31% higher than what it would cost to expand the facility's existing sand filters and ultraviolet disinfection system. However, CCWRD's evaluation of disinfection processes determined that ozonation would be more cost-effective to operate and maintain, compared to ultraviolet disinfection. In February, the district accepted bids from vendors seeking to install the membrane technology and ozone disinfection system. Construction is expected to begin by the end of the year.

Table 3. Estrogenicity Results From In Vitro Bioassay

All units are estrogen equivalent units (nanograms of estrogen per milliliter of extract).

	Raw influent	Filtered secondary	Low ozone dose	Medium ozone dose	High ozone dose
June-05	54	0.66	<0.06	<0.06	<0.06
January-06	Not measured	1.00	0.82	0.10	0.08

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