Conventional and Advanced Water Treatment Processes for the Removal of Endocrine Disruptors and Pharmaceuticals

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Abstract

A suite of target endocrine disruptor compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) were evaluated for removal by several water treatment processes at bench-, pilot-, and full-scale. Over 60 different EDCs and PPCPs were chosen and simultaneously evaluated based on structure, occurrence, and potential health impacts. Treatment processes evaluated include physical (e.g., activated carbon, membrane filtration, softening, ion-exchange), oxidative (e.g. ozonation, chlorination, ultraviolet irradiation, chloramination), advanced oxidation (UV/peroxide, ozone/peroxide), and biological (e.g. biologically active filtration, soil aquifer treatment, membrane bioreactors, river bank filtration). Bench-scale evaluations were performed as static experiments in discrete conditions, generally as "jar-tests". Pilot-scale testing was conducted as dynamic, flow-through, experiments by either spiking a head tank or by feeding the spiking solution in-line. Full-scale testing was accomplished without spiking, thus limiting evaluations to compounds present in raw water. It was determined that bench-scale results adequately predicted removal trends observed at pilot and full scale. Summarily, the results show that ozone, chlorine, certain membranes, and powdered activated carbon are effective for removal of many EDCs and PPCPs. However, removal efficiency is compound specific and depends on operational parameters, such as oxidant dosage and contact time. For instance, UV irradiation was ineffective for removing target compounds at typical disinfectant doses of 40 mJ/cm^2 while doses of 1,000 mJ/cm^2 and peroxide addition were effective for many compounds. Molecular structure (e.g., pKa, Kow, molecular weight, UV absorbance) generally dictated whether a treatment process would or would not efficiently remove the compound. As a disinfection process, ozone was more effective for removing target compounds than was chlorine, UV, and chloramination. Removal by membranes was highly selective based on the membrane pore size, surface characteristics, and degree of fouling. Biological processes were effective for some compounds, and nearly ineffective for others. At full-scale, granular activated carbon and reverse osmosis were found to be the most effective treatment processes for removing a wide-variety of target compounds. Based on data obtained from this study, removal predictions are possible for new contaminants based on physico-chemical properties of the contaminant.

Introduction

Compounds that can alter the endocrine system of animals have been detected in water supplies around the world as the result of human activities. These substances are known as endocrine-disrupting compounds (EDCs) and have been linked to a variety of adverse effects in both humans and wildlife including hormone-dependent cancers, reproductive tract disorders, and reduction in reproductive fitness. Pharmaceutical compounds and personal care products have been collectively termed as PPCPs. Many EDCs and PPCPs have been detected in surface waters, a few of which have been detected in finished drinking water. The detection of EDCs and PPCPs in source waters is of great concern since these compounds have known physiological responses at low concentrations. The majority of EDCs and PPCPs are more polar than traditional contaminants, such as polychlorinated biphenyls, and several have acidic or basic moieties. These properties, coupled with trace quantities, create unique challenges for both removal processes and analytical detection. Reports of EDCs and PPCPs in water have raised substantial concern among the public and regulatory agencies; however, sparse data exist as to the fate of these compounds during drinking water treatment. This project sought to gather imperative data by evaluating the efficiencies of various conventional and advanced water treatment processes to remove EDCs and PPCPs. The first phase included the development of surrogate and characteristic compounds for specific classes of EDCs and PPCPs based on our past experiences and a thorough literature review. The second phase of the project involved testing of various conventional and advanced treatment processes to determine removal efficiencies of environmentally relevant concentrations of target EDC/PPCPs at bench-, pilot-, and full-scale. In the bench-scale experiments, waters of various qualities were fortified with a surrogate matrix comprised of various target EDC/PPCPs and tested in batches. Pilot studies maintained a constant influx of the surrogates to the raw waters in dynamic systems or utilized source waters with characterized EDC/PPCP contamination. Full-scale plants of various treatment processes have also been investigated by analyzing various EDCs and PPCPs in the raw and finished water, and between each unit process. Concentrations of selected EDCs and PPCPs in both natural and fortified water were determined using state of the art analytical instrumentation, such as liquid and gas chromatography coupled with mass spectrometric detectors. Quantitative structure activity relationship (QSAR) models have been generated to predict the fate of compounds not yet investigated.

Methods and Materials

Conventional and advanced drinking water treatment processes were evaluated under typical water treatment plant conditions to determine their effectiveness in the removal of target EDC/PPCP compounds. In these experiments, six common water treatment processes, alum/iron coagulation, lime softening, powdered activated carbon adsorption, membrane filtration, chlorination, and ozonation, were evaluated. Table 1 identifies the conventional and advanced treatment processes that were applied to the different water matrices used in this study. Experiments were conducted using two model waters in the presence/absence of NOM (DI water and SRW) and three different natural waters (CRW, ORW, and PVW) prepared by spiking the studied compounds. Powdered activated carbon (PAC), ozonation, and NF were all shown to be effective in removing most of the studied compounds while chlorination and UF were less effective. Conversely, alum and iron coagulation and excess lime/soda ash softening were all relatively ineffective techniques of EDC/PPCP removal. It is critical to note that bench-scale membrane experiments were conducted only with virgin membrane materials where compound adsorption was likely the dominant removal mechanism, which is unlikely to be significant in full-scale applications.

Table 1: Matrix for bench-scale testing of conventional and advanced treatment processes

Process	DI	CRW	SR-NOM	ORW	PVW
Coagulation	10 mg/L (alum), 2.3 mg/L (iron), pH 5.5 and 8.5 (alum), pH 8.5 (iron)	25 mg/L (alum), 5.9 mg/L (iron), pH 5.5 and ambient (alum*), ambient pH (iron)	40 mg/L (alum), 9.4 mg/L (iron), pH 5.5 and 8.5 (alum), pH 8.5 (iron)	35 mg/L (alum), 8.8 mg/L (iron), pH 5.5 and ambient* (alum), ambient pH (iron)	40 mg/L (alum), 38 mg/L (iron), ambient pH
Lime softening (as $CaCO_3$)	52 mg/L (lime), 0 mg/L (soda ash), pH 9 and 11.3	213 mg/L (lime), 87 mg/L (soda ash), pH 9	52 mg/L (lime), 0 mg/L (soda ash), pH 9 and 11.3	135 mg/L (lime), 41 mg/L (soda ash), pH 11.3	133 mg/L (lime), 32 mg/L (soda ash), pH 11.3
Powered activated carbon	5 mg/L (AC800 and WPM**), pH 5.8	5 mg/L (AC800 and WPM), pH 6.0 and ambient (AC800), ambient pH (WPM*)	5 mg/L (AC800), 1*, 5*, and 20* mg/L (WPM), pH 7.5	5 mg/L (AC800* and WPM*), ambient pH	5 mg/L (WPM)*, ambient pH
Membranes	NF and UF, pH 5.8	NF* and UF*, ambient pH	NF and UF, pH 7.5	NF and UF, ambient pH	NF and UF, ambient pH
Chlorination (as Cl_2)	1.5 mg/L (quenched with ammonium chloride), pH 5.5 and 8.5	3.0 mg/L (quenched with ammonium chloride** and sodium thiosulfate), pH 5.5 and ambient	6.75 mg/L (no quenching), pH 5.5 and 8.5	2.8 mg/L (no quenching), pH 5.5 and ambient	3.8 mg/L(no quenching), pH 5.5 and ambient
Ozonation (as O_3)	1.5 mg/L (quenched with ammonium chloride) w/ and w/o H_2O_2, pH 5.5	3.1 mg/L (no quenching) w/ and w/o H_2O_2, ambient pH	4.0 and 8.0 mg/L(no quenching) w/ and w/o H_2O_2, pH 7.5	3.5* mg/L (no quenching) w/ and w/o H_2O_2, ambient pH	3.0* mg/L (no quenching) w/ and w/o H_2O_2, ambient pH

Literature reviews were completed for both analytical methods (1) and for treatment processes (2) available for EDCs and PPCPs. From these literature reviews and previous experience by the research team, a target compound list was created (Table 2) (3). Both gas chromatography and liquid chromatography methods were developed, both using tandem mass spectrometric detection (4). These methods were capable of ng/L reporting limits all target compounds.

All water treatment standards and chemicals were at least reagent grade and/or of the highest purity commercially available. All glassware and supplies are solvent rinsed 3 times each using acetone, hexane, and methanol obtained from Burdick & Jackson (Muskegon, MI, USA) or Sigma-Aldrich (Milwaukee, WI, USA). Cocktail-stock solutions of EDC/PPCP target compounds were initially prepared in methanol at 10 to 250 mg/L. Compounds were spiked in waters at concentrations generally between 100 – 200 ng/L by spiking a minimum volume of the concentrated stock solution into in a stainless steel container containing source water of 25 L.

Four waters were initially investigated. Namely, Suwannee River (natural organic matter) water (SR-NOM), Colorado River water (CRW) collected from Lake Mead, Nevada, Ohio River water (ORW) collected in Louisville, Kentucky, and Passaic River Water (PVW) collected in Passaic Valley, New Jersey. Dissolved organic carbon (DOC) of 4 mg/L was added in the waters for SR-NOM experiments. Unfiltered CRW, ORW, and PVW were used for coagulation and chemical softening experiments. The CRW, ORW, and PVW were also prefiltered with a 0.7 mm glass fiber filter prior to spiking target compounds and the prefiltered CRW, ORW, and PVW were used for chlorination, ozonation, PAC, and membrane experiments. The raw water samples were analyzed for various water quality parameters including DOC, ultraviolet absorbance at 254 nm, pH, alkalinity, hardness, and conductivity.

Treatment Processes

(a) Coagulation

Two coagulants, aluminum sulfate (alum) and ferric chloride (iron), were used in jar tests using a six-place gang stirrer and 2-L glass beakers filled with a 1.5-L source water for reactors. Stock solutions of alum and iron were initially prepared in DI at 10,000 mg/L. Coagulant dosages were 40 mg/L (SR-NOM), 25 mg/L (CRW), 35 mg/L (ORW), 40 mg/L (PVW) of alum and 9.4 mg/L (SR-NOM), 5.9 mg/L (CRW), 8.8 mg/L (ORW), 38 mg/L (PVW) of iron. Experiments were performed at pH 5.5 and 8.5 (SR-NOM), pH 5.5 and ambient pH (CRW, ORW, and PVW) for alum and pH 8.5 (SR-NOM), ambient pH (CRW, ORW, and PVW) for iron. Mixing conditions involved 1 min of rapid mixing at 100 rpm and 20 min at 30 rpm followed by 60 min of settling time. All experiments were conducted at a room temperature of approximately 20° C. Samples were carefully collected and filtered through a 0.7-mm (GF/F) glass-fiber filter prior to LC/MS/MS and GC/MS/MS analysis.

(b) Chemical Softening

In the chemical softening experiments using calcium hydroxide and soda ash, the total, calcium, and magnesium of hardness of the CRW was determined to be 307, 76.8, and 27.9 mg/L as CaCO3, respectively. The total hardness of the ORW was 128 mg/L as CaCO3, respectively. The pH and alkalinity of the CRW/ORW were 8.2/7.9 mg/L and 140/79 mg/L as CaCO3. All the SR-NOM, CRW, ORW, and PVW were examined at pH 9 ± 0.2 and/or 11.3 ± 0.2 in the chemical softening experiments although SR-NOM water did not include calcium and magnesium. Stock solutions of lime and soda ash were initially prepared in DI at 50,000 mg/L. Softening dosages were 52 mg/L (SR-NOM), 213 and 320 mg/L (CRW), 135 mg/L (ORW), and 180 mg/L (PVW) as CaCO3 of lime and 0 mg/L (SR-NOM), 87 and 170 mg/L (CRW), 41 mg/L (ORW), 30 mg/L (PVW) as CaCO3 of soda ash, respectively. The applied/theoretical lime and soda ash dosages were calculated based upon initial pH, alkalinity, and carbonic acid concentration for excess-lime softening conditions.

Jar tests were conducted to simulate conventional chemical softening processes by using a six-place gang stirrer and 2 L glass beakers filled with a 1.5 L source water for reactors. Chemicals were rapidly added during a rapid mix stage (100 rpm) for 1 min and a 20 min slow-mixing aggregation stage (30 rpm) followed by a 60 min sedimentation stage (no mixing). After lime and soda ash addition, the pH was adjusted to 11.3 ± 0.2 by adding a sodium hydroxide solution for removal of magnesium and calcium. The similar sampling and analysis processes were conducted as described for the coagulation tests.

(c) Powered Activated Carbon Adsorption

Activated carbon adsorption studies were conducted in the laboratory with two commercially available brands of PAC, AC800 (AC800, Acticarb, Dunnellon, FL, USA) and WPM (PAC form of F400, Calgon Carbon Corp., Pittsburgh, PA, USA). The PACs were hydrated for 24 hours in distilled water prior to use, and added as a slurry to the samples. PAC dosages were 5 mg/L of AC800 and 1, 5, and 20 mg/L of WPM at pH 7.5 buffered with 1 mM phosphate for SR-NOM, and 5 mg/L of AC800 at ambient pH and/or pH 6.0 buffered 1 mM phosphate and 5 mg/L of WPM at ambient pH for CRW, ORW, and PVW. The experiments were performed in a six-place gang stirrer and 2-L glass beakers filled with a 1.5-L source water for reactors with a contact time of 4 hours prior to sampling to simulate common PAC treatment processes in water treatment plants (WTPs). The dosages and contact time were applied since many full-scale WTPs that use PAC have contact times of 1 to 5 hours and apply PAC dosages of 5 to 50 mg/L. Similarly, sampling and filtration procedures were followed as described for the coagulation and chemical softening. AC800 and WPM were selected after PAC brand screening experiments by the investigators with six different PAC brands tested for the removal of bisphenol A (common plasticizer), 17b-estradiol (natural estrogen), and 17a-ethynyl estradiol (synthetic estrogen – oral birth control pharmaceutical).

(d) Nanofiltration and Ultrafiltration

EDCs and PPCPs rejection experiments were done on commercially available nanofiltration (NF) and ultrafiltration (UF) membranes. The NF (ESNA, Hydranautics, U.S.A.) and UF (GM, Desal/Osmonics, U.S.A.) membranes are thin film composites (TFC) made of aromatic polyamide (ESNA) and made of sulfonated polyethersulfone (PES) coated with an ultrathin polyimide (GM) (according to the manufacture), respectively. The membranes have also different pore sizes based upon their nominal molecular weight cut-offs (MWCOs), 200 Daltons for ESNA and 8,000 Daltons for GM, respectively. Those membranes have ionizable functional groups such as carboxylic acids based upon their zeta potential values, -11.1 mV (ESNA) and -32.2 mV (GM) at pH 7.5 and conductivity of 300 mS/cm with a NaCl solution. Membrane filtration experiments were

performed at pH 5.8 (DI), 7.5 buffered with 1 mM phosphate (SR-NOM), and ambient pH (CRW, ORW, and PVW).

A commercial bench-scale dead-end stirred-cell membrane unit (SEPA® ST, Osmonics, Minnetonka, MN, U.S.A.) was used to evaluate flat-sheet membrane specimens. The membrane filtration unit made of stainless steel was employed to minimize adsorption of the compounds onto the cell. All of the experiments were performed at a constant initial pure water flux, 1.2 m/day, a pressure of 677 ± 39 kPa for ESNA and 421 ± 40 kPa for GM, and a room temperature of 20 oC. The membranes were precompacted for 5 to 7 hours at the same pressures with NaCl solutions. When the flux remained constant, the feed water was exchanged. In these experiments, an initial volume of 300 mL of a given sample was passed through the membrane until 200 mL of permeate was obtained, and the corresponding retentate was also collected. The experiments were repeated until a total volume of 1,000 mL of permeate was obtained. Removal of each compound was calculated and flux-decline was monitored.

(e) Chlorination
Samples were chlorinated with sodium hypochlorite (NaOCl, Fisher Scientific, USA) in 1-L glass bottles using DI unbuffered at pH 5.5 and 8.5, SN-NOM (buffered with 1 mM phosphate) at pH 5.5 and 8.5, and CRW/ORW/PVW at ambient pH (8.2/7.9/6.8) and pH 5.5. Residual chlorine was quenched with ammonium chloride for DI, ammonium chloride, sodium thiosulfate, or ascorbic acid for CRW and PVW at a concentration of 25 to100 mg/L. One CRW sample was not quenched. All SR-NOM and ORW samples were not quenched. The residual chlorine in the water samples unquenched was stripped off to the air while samples were being collected for analysis. All of the chlorination experiments were performed at a contact time of 24 hours. Stock solutions of chlorine were initially prepared in DI at 1,200 mg/L. Applied chlorine dosages were 1.5 mg/L (DI), 6.75 mg/L (SR-NOM), 3.0 mg/L (CRW), 2.8 mg/L (ORW), and 3.8 mg/L (PVW) as Cl2.

(f) Ozonation

Ozone experiments were conducted in 1-L glass bottles by placing DI unbuffered at pH 5.5, SN-NOM (buffered with 1 mM phosphate) at pH 7.5, and CRW/ORW/PVW at ambient pH in the presence/absence of H2O2 (0.025 mgH2O2/mgO3). Applied ozone dosages were 1.5 mg/L (DI), 4.0 and 8.0 mg/L (SR-NOM), 3.1 mg/L (CRW), 3.5 mg/L (ORW), and 3.0 mg/L as O3. The residual ozone in the water samples was quenched with ammonium chloride for DI or stripped off using pure helium after samples (SR-NOM, CRW, and ORW) and collected after a 3 to 5 min contact time.

Dissolved ozone stock solution was made by dissolving a high concentration of gaseous ozone into chilled deionized water. Gaseous ozone was generated by OREC™ (Model V5-0, Phoenix, AZ, USA) ozone generator from pure oxygen. Dissolved ozone concentrations were measured spectrophtometrically (258 nm; e: 3150 m-1s-1) after a 2:1 dilution with a few drops of 1.0 N phosphoric acid. The stock ozone solution of approximately 40 mg/L was produced routinely after an hour. The ozone stock solution was directly added into the water samples in bottles.

Results and Discussion

Summaries of each treatment process investigated are provided in the following sections. Results are grouped separately into GC/MS and LC/MS compounds.

In general, very low removals (<25%) were observed for coagulation and softening processes. However, compounds with relatively high log Kow's (>4) were often removed at >25% due to binding to particles. In DI water no compounds were well removed by coagulation and softening.

A summary of results from chlorination experiments is provided in Tables 1 and 2. In general, chlorination at a suppressed pH achieved greater removal than did chlorination at ambient pH. This observation is logical considering that hypochlorous acid is the dominate chlorine species at suppressed pH and is a stronger oxidant than hypochlorite, which is the dominant species at most ambient pH's. A particularly interesting finding was the efficient removal of phenolic steroids (i.e., estradiol, ethynylestradio, and estrone) by chlorination, while steroids lacking the phenolic moiety were not (i.e., androstenedione and testosterone) (Table 1).

Ozone results are summarized in Tables 3 and 4. Ozone, as expected, proved to be a more powerful oxidant than did chlorine (Tables 5 and 6). In contrast to chlorination, ozone displayed excellent removal for all steroids regardless of the phenolic moiety (Table 5).

Table 1: Summary of Percent Removal by Chlorination (LC/MS Compounds)

Source Water	**PVW**	**CRW**	**ORW**	**PVW**	**CRW**	**ORW**
pH	**5.5**	**5.5**	**5.5**	**6.8**	**8.2**	**7.9**
Chlorine Dose [mg/L]	**3.8**	**3.5**	**2.8**	**3.8**	**3.5**	**2.8**
Reaction Time [hours]	**24**	**24**		**24**	**24**	
Ascorbic Acid Dose [mg/L]	**25**	**25**	**0**	**25**	**25**	**0**
Ethynylestradiol	>99	>99	>99	>99	>99	>99
Estrone	>99	>98	>99	>99	>98	>99
Estriol	>99	>99		>99	>99	
Estradiol	>99	>98		>99	>98	
Trimethoprim	>98	>98	>98	>98	>98	>98
Hydrocodone	>98	>98		>98	>98	
Gemfibrozil	>98	>98	>98	58.1	70.1	>98
Acetaminophen	97.3	>96	>96	>97	>96	>96
Triclosan	>97	>97	>97	>97	>97	>97
Oxybenzone	>96	>97	>96	>96	>97	>96
Erythromycin-H_2O	>96	>96	81.7	>96	>96	>97
Carbamazepine	92.1	>98	>98	33.2	22.3	19.6
Naproxen	>91	>94	>95	>91	>94	>95
Diclofenac	>86	>96	>97	>86	>96	>97
Sulfamethoxazole	>78	>97	>95	>78	>97	>95
Octylphenol			>94			>94
Diazepam	79.0	80.6	83.1	27.4	12.7	25.0
Ibuprofen	78.0	44.7	37.2	58.6	37.2	23.3
Pentoxifylline	74.2	86.1	>98	27.4	20.3	30.4
Progesterone	61.8	50.0	93.3	50.6	29.3	31.4
Testosterone	60.8	52.2	95.2	47.9	26.1	28.1
Caffeine	60.0	67.9	>98	27.9	17.3	10.7
Androstenedione	57.0	40.4	86.3	44.0	23.4	25.0
Dilantin	53.5	32.6	21.9	34.9	18.5	0.0
Fluoxetine	45.7	20.0	12.5	42.4	19.0	0.0
DEET	32.5	16.5	1.9	30.7	14.1	0.0
Iopromide	26.6	6.9	5.2	26.6	28.4	20.7
Atrazine	24.4	15.3	0.0	11.1	1.7	0.0
TCEP	22.0	4.4	0.0	12.2	0.0	0.0
Meprobamate	21.7	15.5	18.0	21.7	17.6	0.0

Table 2: Summary of Percent Removal by Chlorination (GC/MS Compounds)

Source Water	**PVW**	**CRW**	**ORW**	**PVW**	**CRW**	**ORW**
pH	**5.5**	**5.5**	**5.5**	**6.8**	**8.2**	**7.9**
Chlorine Dose [mg/L]	**3.8**	**3.5**	**2.8**	**3.8**	**3.5**	**2.8**
Reaction Time [hours]	**24**	**24**		**24**	**24**	
Ascorbic Acid Dose [mg/L]	**25**	**25**	**0**	**25**	**25**	**0**
Fluoranthene	>94	>94	>94	94.2	>94	82.9
Anthracene	>94	>91	89.7	>94	>91	
acenaphthene	>91	>92	>93	84.3	>92	>93
acenapththylene	>89	>92	>94	>89	>92	>94
Benz[a]anthracene	76.1	>91	84.3	76.8	>91	
Aldrin	>71	>50	>76	60.0	>47	>76
Benzo[a]pyrene	>66	>70	>87	>66	>70	>87
Benzo[k]fluoranthene	62.5	>86	>86	>68	>86	53.9
Pyrene	58.9	53.6	46.0	32.6	45.6	12.3
Benzo[b]fluoranthene	56.4	71.6	31.8	25.6	60.0	0.0
phenanthrene	56.4	67.4	92.6	33.2	45.9	10.4
Galaxolide	55.8	39.6	24.6	38.8	15.1	3.7
naphtalene	50.0	46.3	46.9	41.7	47.5	7.1
Metolachlor	49.6	31.7	35.6	40.7	34.7	21.0
Chrysene	49.0	89.2	87.9	32.4	72.7	15.3
Heptachlor	40.6	39.4	17.7	34.8	25.8	0.0
DDD	40.0	25.0	2.6	30.6	11.5	0.0
Methoxychlor	38.9	43.1	77.0	16.8	17.2	7.3
Musk Ketone	30.5	26.3	31.9	87.6	>94	72.9
DDE	29.2	34.6	17.5	25.0	19.2	0.0
Dieldrin	27.4	28.3	4.2	8.0	2.4	0.0
DDT	27.3	25.0	10.8	21.6	8.1	0.0
γ-Chlordane	25.8	30.2	15.2	15.3	1.9	5.1
α-Chlordane	25.6	28.2	19.8	12.2	2.6	0.0
Endrin	24.3	22.3	20.1	7.3	0.0	8.5
fluorene	20.7	29.9	41.5	13.6	24.3	20.0
Heptachlor Epoxide	20.0	20.6	19.2	3.5	3.9	7.7
β-BHC	17.1	16.7	13.0	8.6	9.9	7.3
γ-BHC	13.5	21.4	8.4	7.4	11.0	0.6
δ-BHC	11.4	20.9	11.2	7.1	9.3	7.6
α-BHC	9.1	26.0	7.6	5.8	14.3	3.4
Mirex	0.0	7.7	43.9	7.7	0.0	36.6

Table 3: Summary of Percent Removal by Ozonation (LC/MS Compounds)

Source Water	PVW	CRW	ORW	ORW	PVW	CRW	ORW
Hydrogen Peroxide Dose [mg/L]					0.075	0.0625	0.0875
H2O2 Reaction Time [min]					1	1	1
Ozone Dose [mg/L]	3	2.5	3.5	7	3	2.5	3.5
Ozone Reaction Time [min]	~5	~5	~5	~5	~5	~5	~5
LC/MS Compounds							
Ethynylestradiol	>99	>99	>99	>99	>99	>99	>99
Estrone	>99	>98	98.9	99.1	>99	>98	>99
Estriol	>99	>99			>99	>99	
Estradiol	>99	>98			>99	>98	
Carbamazepine	>99	>98	>98	>98	>99	>98	>98
Trimethoprim	>98	>98	>98	>98	>98	>98	>98
Hydrocodone	>98	>98			>98	>98	
Gemfibrozil	>98	>98	>98	>98	>98	>98	>98
Triclosan	>97	79.1	>97	>97	>97	81.8	>97
Acetaminophen	96.1	>96	>97	>97	96.4	>96	>97
Oxybenzone	>96	>97	>97	>97	>96	>97	>97
Erythromycin-H_2O	>96	>96	>97	>97	>96	>96	>97
Octylphenol			>93	>93			>93
Naproxen	>91	>94	>95	>95	>91	>94	>95
Diclofenac	>86	>96	>97	>97	>86	>96	>97
Pentoxifylline	85.5	>98	>98	>98	90.0	>98	>98
Caffeine	83.3	>98	>98	>98	87.1	>98	>98
Testosterone	83.0	>98	>97	>97	96.4	>98	>97
Progesterone	82.7	>98	>97	>97	95.7	>98	>97
Fluoxetine	81.8	>98	92.3	>97	80.6	>98	>97
Sulfamethoxazole	>78	>97	>95	>95	>78	>97	>95
Androstenedione	77.7	>99	>98	>98	94.7	>98	>98
Dilantin	71.5	82.5	>97	>97	72.8	88.5	>97
Diazepam	65.7	78.7	96.0	93.7	69.1	85.5	95.8
DEET	63.5	76.4	94.9	93.8	68.0	83.9	96.4
Ibuprofen	55.9	82.5	94.4	93.6	60.5	88.3	96.1
Iopromide	52.5	46.3	75.1	77.4	57.0	60.0	85.5
Meprobamate	39.7	50.2	83.6	80.4	43.3	61.4	84.6
Atrazine	17.3	45.5	71.2	68.4	24.3	51.7	79.9
TCEP	0.0	13.3	4.8	0.0	0.0	15.6	16.0

Table 4: Summary of Percent Removal by Ozonation (GC/MS Compounds)

Source Water	PVW	CRW	ORW	ORW	PVW	CRW	ORW
Hydrogen Peroxide Dose [mg/L]					**0.075**	**0.0625**	**0.0875**
H2O2 Reaction Time [min]					**1**	**1**	**1**
Ozone Dose [mg/L]	**3**	**2.5**	**3.5**	**7**	**3**	**2.5**	**3.5**
Ozone Reaction Time [min]	**~5**	**~5**	**~5**	**~5**	**~5**	**~5**	**~5**
phenanthrene	>96	>95	>94	>94	>96	>95	>94
Pyrene	>94	>94	>94	>94	>94	>94	>94
Fluoranthene	>94	>94	>94	>94	>94	>94	>94
Anthracene	>94	>91	>93	>93	>94	>91	>93
acenaphthylene	>89	>92	>91	>91	>89	>92	>91
Benzo[b]fluoranthene	>74	>89	>90	>90	>74	>89	>90
Aldrin	>71	>50	>74	>74	>71	>50	>74
Benzo[k]fluoranthene	>68	>86	>87	>87	>68	>86	>87
Benzo[a]pyrene	>66	>70	>91	>91	>66	>70	>91
acenaphthene	90.8	89.7	>91	>91	91.7	90.1	>91
naphtalene	90.7	>87	>68	>68	>92	>87	56.8
Methoxychlor	85.4	89.8	>94	>94	>92	90.8	86.5
fluorene	82.5	>93	>93	>93	83.0	>94	>93
Benz[a]anthracene	77.5	87.1	>93	85.8	76.0	88.0	>93
Galaxolide	76.1	87.1	90.8	90.1	76.8	89.1	90.8
Chrysene	76.0	90.7	>92	>92	>80	>92	>92
Metolachlor	73.4	80.4	91.7	88.2	81.6	86.2	93.7
DDD	64.1	66.5	>90	>90	64.1	75.8	>90
Endrin	53.8	10.0	22.5	25.5	0.0	>93	38.7
DDE	53.5	>57	>70	>70	51.2	>61	>70
Heptachlor	38.3	53.7	66.7	68.2	33.7	55.2	66.7
DDT	34.7	56.6	58.2	64.5	27.5	61.2	70.9
Musk Ketone	20.1	29.7	49.6	41.3	2.8	33.9	68.4
β-BHC	10.4	0.0	22.3	15.8	19.5	0.0	30.4
γ-Chlordane	8.2	0.0	0.0	0.0	2.2	0.0	0.0
Dieldrin	5.4	0.0	6.5	13.0	0.0	0.0	3.3
α-Chlordane	2.3	0.0	0.0	0.0	0.0	0.0	0.0
γ-BHC	1.4	4.5	23.8	18.6	2.8	13.8	26.5
δ-BHC	0.6	1.0	17.9	11.9	6.9	8.6	25.8
α-BHC	0.5	9.2	26.7	17.6	5.4	16.4	28.1
Heptachlor Epoxide	0.0	0.0	5.5	0.0	0.0	7.2	10.4
Mirex	0.0	>23	0.0	0.0	0.0	>23	>70

Table 5: Average Removals by Ozone and Chlorine (LC/MS Compounds)

	Ozone	O3+H2O2	Cl 5.5	Cl Ambient
Ethynylestradiol	>99	>99	>99	>99
Estrone	>98	>98	>99	>99
Estriol	>99	>99	>99	>99
Estradiol	>98	>98	>99	>99
Carbamazepine	>98	>98	>98	>98
Trimethoprim	>98	>98	>98	>98
Hydrocodone	>98	>98	>98	75.0
Gemfibrozil	>98	>98	97.3	>96
Triclosan	>91	>91	>97	>97
Acetaminophen	>96	>96	>96	>96
Oxybenzone	>97	>97	81.7	>96
Erythromycin-H_2O	>96	>96	92.1	25.0
Octylphenol	>93	>93	>93	>93
Naproxen	>93	>93	>93	>93
Diclofenac	>93	>93	>90	>90
Pentoxifylline	>93	>95	>94	>94
Caffeine	>93	>94	80.9	21.7
Testosterone	>92	>97	53.3	39.7
Progesterone	>92	>96	80.1	26.0
Fluoxetine	>90	>92	72.6	44.9
Sulfamethoxazole	>90	>90	67.8	22.1
Androstenedione	>91	>96	68.4	37.1
Dilantin	>83	>85	64.0	18.6
Diazepam	80.2	83.5	61.2	30.8
DEET	78.3	82.7	36.0	17.8
Ibuprofen	77.6	81.6	26.1	20.5
Iopromide	58.0	67.5	17.0	14.9
Meprobamate	57.9	63.1	12.9	25.2
Atrazine	44.7	52.0	13.2	4.3
TCEP	1.7	9.3	8.8	4.1

Table 6: Average Removals by Ozone and Chlorine (GC/MS Compounds)

	Ozone	O3+H2O2	Cl 5.5	Cl Ambient
phenanthrene	>95	>95	>94	>90
Pyrene	>94	>94	>91	>92
Fluoranthene	>94	>94	>92	>89
Anthracene	>92	>92	>92	>91
acenapththylene	>91	>91	>83	>61
Benzo[b]fluoranthene	>84	>84	>65	>61
Aldrin	>65	>65	>74	>74
Benzo[k]fluoranthene	>80	>80	>78	>69
Benzo[a]pyrene	>75	>75	52.8	30.2
acenaphthene	>90	>91	53.3	28.5
naphtalene	>81	>78	72.1	29.8
Methoxychlor	>89	>89	40.0	19.2
fluorene	>89	>90	47.7	32.1
Benz[a]anthracene	>85	>85	39.0	32.2
Galaxolide	84.7	85.6	75.4	40.1
Chrysene	>86	>88	32.6	20.2
Metolachlor	81.8	87.1	22.5	14.0
DDD	>73	>76	53.0	13.8
Endrin	28.8	>65	29.5	80.2
DDE	>60	>60	27.1	14.7
Heptachlor	52.9	51.9	20.0	3.4
DDT	49.8	53.2	21.0	9.9
Musk Ketone	33.1	35.0	23.7	7.4
β-BHC	10.9	16.6	24.5	4.9
γ-Chlordane	2.7	0.7	22.2	5.3
Dieldrin	4.0	1.1	30.7	19.3
α-Chlordane	0.8	0.0	19.9	5.0
γ-BHC	9.9	14.3	15.6	8.6
δ-BHC	6.5	13.8	14.4	6.3
α-BHC	12.2	16.6	14.5	8.0
Heptachlor Epoxide	1.8	5.9	14.2	7.9
Mirex	0.0	0.0	17.2	14.8

Pilot Plant Testing of Ozonation with Biological Filtration

Pilot plant testing was performed using the on-site 6-gpm pilot plant facility. Two tests were conducted to evaluate removal by ozonation and biological filtration. Under normal operation, the pilot plant effluent is returned to the head of the full-scale water treatment plant. During this testing sequence, the pilot plant effluent was pumped to the full-scale drying beds and not returned to the head of the plant.

The entire pilot plant process scheme includes ozonation, coagulation, flocculation, and two dual media filters. Raw water, from Lake Mead, was supplied to the 22.7 L/min (6-gpm) pilot plant prior to any chemical addition. A flowmeter maintained the desired flow rate throughout the testing period. A syringe pump was used to introduce the target list of compounds into the process stream. Two static mixers followed the injection to assure adequate mixing.

The ozone contactor is made-up of 12 cells to provide approximately 24 minutes of contact at the design flow rate of 22.7 L/min (6-gpm). Each 15 cm (6-inch) diameter polyvinyl chloride (PVC) contactor cell provides 2 minutes of contact time at the design flow rate for a total 24 minutes of contact time. Ambient air supplied the ozone generator (model SGC21, Pacific Ozone Technology, Benicia, CA) to produce the ozone feed gas. The ozone feed gas concentration was measured (model HI-X, IN USA Inc., Needham, MA), controlled by a gas rotameter, and injected counter currently through a porous stone diffuser mounted horizontally near the bottom of cell 1. Contactor cells 3, 5, and 9 were equipped with dissolved ozone monitors (model 26506 indicating instrument, model 31331.15 sensor, Hach Ultra Analytics-Orbisphere, Grants Pass, OR) used to calculate disinfection levels and other ozone parameters such as half-life, CT, demand, and decay rate. The dissolved ozone monitors were calibrated using the indigo method (Standard methods 4500-O3). The off gas from each contactor cell was collected into a central manifold. A sample line from the manifold supplied a sample conditioning system (model SC010-R, IN USA Inc., Needham, MA) and an off gas concentration monitor (model HI-LR, IN USA Inc., Needham, MA). The feed gas concentration, off gas concentration, and dissolved ozone measurements are all interfaced into computer software, which calculates critical operating parameters such as ozone decay rate, transferred ozone dose, ozone demand, CT, ozone half-life, and *Cryptosporidium* log inactivation. CT was determined from an AwwaRF investigation of Cryptosporidium inactivation using Lake Mead water.

A small rapid mix chamber followed ozonation. Ferric chloride as added at a dosage of 0.6 mg/L from a dilution of the full scale plant ferric chloride. The full scale plant ferric chloride contains 40% ferric chloride and has a specific gravity of around 1.44. Dilution were made and fed at 2.3 mL/min using a peristaltic pump. Four stages of flocculation followed the rapid mix allowing about 20 minutes of flocculation time again simulating the full scale plant. Mixing was provided by manual speed heavy duty continuous mixers with G-value modeling the full scale plant.

A flow splitter followed the flocculation process, where the process stream was spilt into two 3-gpm streams which fed two shallow bed, dual media filters. One 10-inch stainless steel filter contained 20 inches of anthracite and 11 inches of sand, which models the full-scale filter media. The other filter contained 20 inches of exhausted GAC (F100, Calgon Carbon Corp., Pittsburgh, PA) and 10 inches of sand. Individual filter effluent sample ports are available to monitor filter effluent water quality. During previous studies, biological activity had developed to remove ozonation disinfection byproducts and residual ammonia from bromate mitigation. These filters should provide an indication of removal by a fixed-film biological filter.

An ozone disinfection goal of 1.0-log Cryptosporidium inactivation was desired for testing according to the draft Long Term 2 Enhanced Surface Treatment Rule (LT2ESWTR). The pilot plant was operated to achieve this disinfection goal using raw Lake Mead water. Once achieved, a solvent spike was added to the raw water to observe any changes to ozone demand resulting from the methanol addition. A syringe pump delivered the solvent spike at a feed rate of 100 uL/min. A summary of the solvent quantities used is provided in Table 7. Methylene chloride was substituted for benzene in the solvent blank, since the laboratory does not maintain a supply of benzene. After reaching steady state ozone conditions with the solvent mixture, injection of the target list was initiated to achieve a 200 ng/L spike. A syringe pump delivered the EDC spike at a feed rate of 100 uL/min. After 40 minutes, adequate time had allowed ozone contactor to reach steady state and samples were

collected. Any ozone residual remaining in the samples collected from the ozone contactor was quenched with 50 mg/L of ascorbic acid. Since bench scale experiments found ozone was capable of removing a majority of the target compounds, the second test evaluated biological filtration without ozonation. After 50 minutes, ozone was turned off allowing the full dose of spiked compounds to travel directly onto the biological filters. After 90 minutes, the chemical spike was turned off and sampling was designed to follow the chemical plug through the pilot plant. Samples were preserved to pH less than 2 with concentrated sulfuric acid.

Table 7. – Summary of Solvents Used During Testing

	Solvent Mix Volume (mL)	EDC Mix Volume (mL)
Methanol	3.25	3.25
Methylene Chloride	1.0	0.875
Hexane	0.625	0.625
Toluene	0.125	0.125
Acetone	5	5
Benzene	0	0.125

Results

Water quality characteristics are shown in Table 8. During the testing period, the water temperature slowly increased from 17.3°C to 19.0°C as the ambient air warmed the water in the pilot plant. The ozone CT was calculated using the post ozone temperature value.

Table 8. – Summary of Water Quality Parameters During Testing

	Average Value
Raw Water pH	8.14
Raw Water Temperature (°C)	17.3
Post Ozone Temperature (°C)	17.9
Filter Effluent Temperature (°C)	19.0
Post Ozone Dissolved Oxygen (mg/L)	19.0

The transition from raw water to the solvent control run showed that the decay rate was increased on the raw water. Therefore, the ozone dose was increased from 1.93 mg/L to 2.29 mg/L to maintain the disinfection goal of 1.0-log Cryptosporidium inactivation (Table 9). The increased decay rate indicates that advanced oxidation is likely occurring due to solvent addition. When the solvent mixture ended, raw water again flowed through the pilot plant while the EDC mixture was prepared. At the same ozone dose of 2.29 mg/L, the CT increased from 4.77 mg-min/L to 7.29 mg-min/L with raw water once the solvents had passed and steady state conditions were achieved. The ozone decay rate appeared to be 40% faster when using the solvent blank. The solvent demand was apparent in the online dissolved ozone residual measurements from cell 3 of the ozone contactor (Figure 1). Then, the EDC mixture was introduced to the system. A larger ozone demand prompted an increase in the ozone dose from 2.29 mg/L to 2.39 mg/L. After steady state conditions were achieved, a 1.17-log Cryptosporidium inactivation was achieved and sampling was performed. Samples were collected after steady state conditions were achieved (Figure 2).

Table 9. – Summary of Ozone Operating Parameters

	Raw Water	Raw w/Solvent	Raw Water	Raw w/EDC Spike
Transferred Ozone Dose (mg/L)	1.93	2.29	2.29	2.39
Ozone Demand (mg/L)	0.87	0.91	0.91	1.33
Half Life (min)	5.99	3.74	6.07	4.30
Ozone Decay Rate (1/min)	-0.1157	-0.1855	-0.1141	-0.1611
Cell #3 Ozone Residual (mg/L)	0.65	0.63	0.85	0.54
Cell #9 Ozone Residual (mg/L)	0.15	0.06	0.2	0.07
CT (mg-min/L)	5.55	4.77	7.29	4.2
Cryptosporidium Inactivation (log)	1.55	1.33	2.03	1.17

Figure1. – Ozone Residual Decrease Resulting from Solvent Ozone Demand

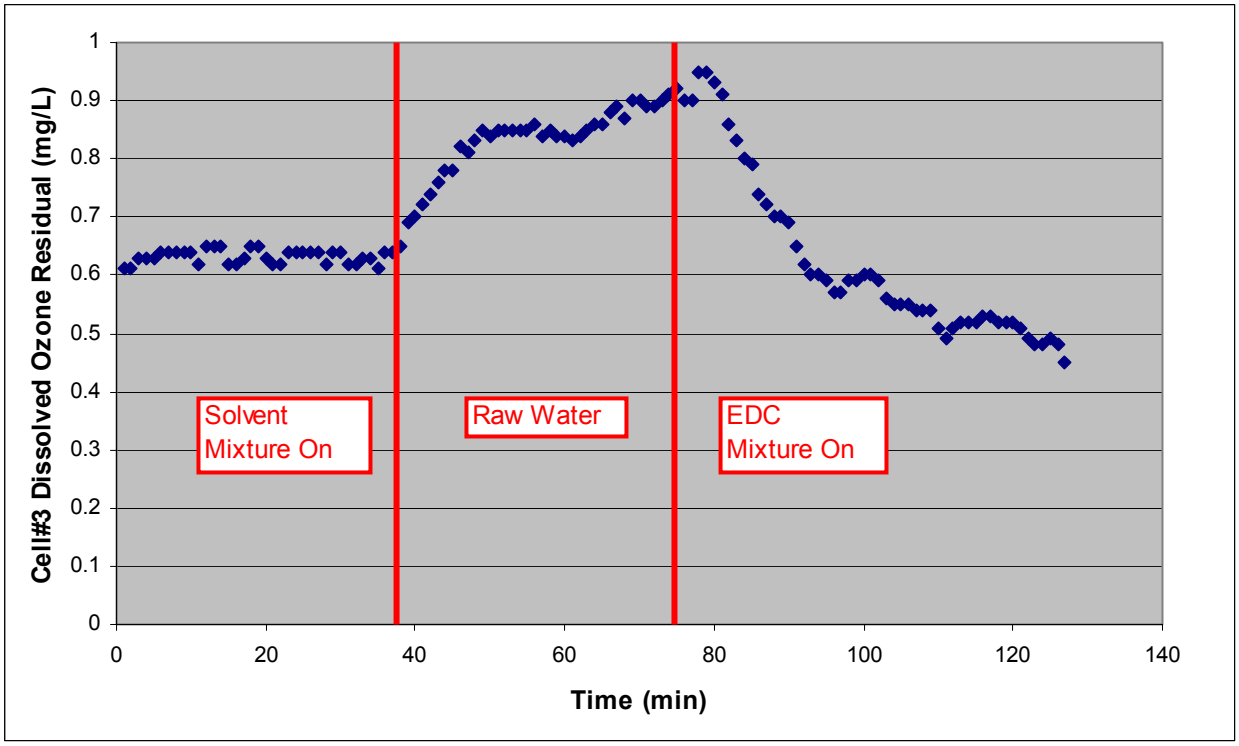
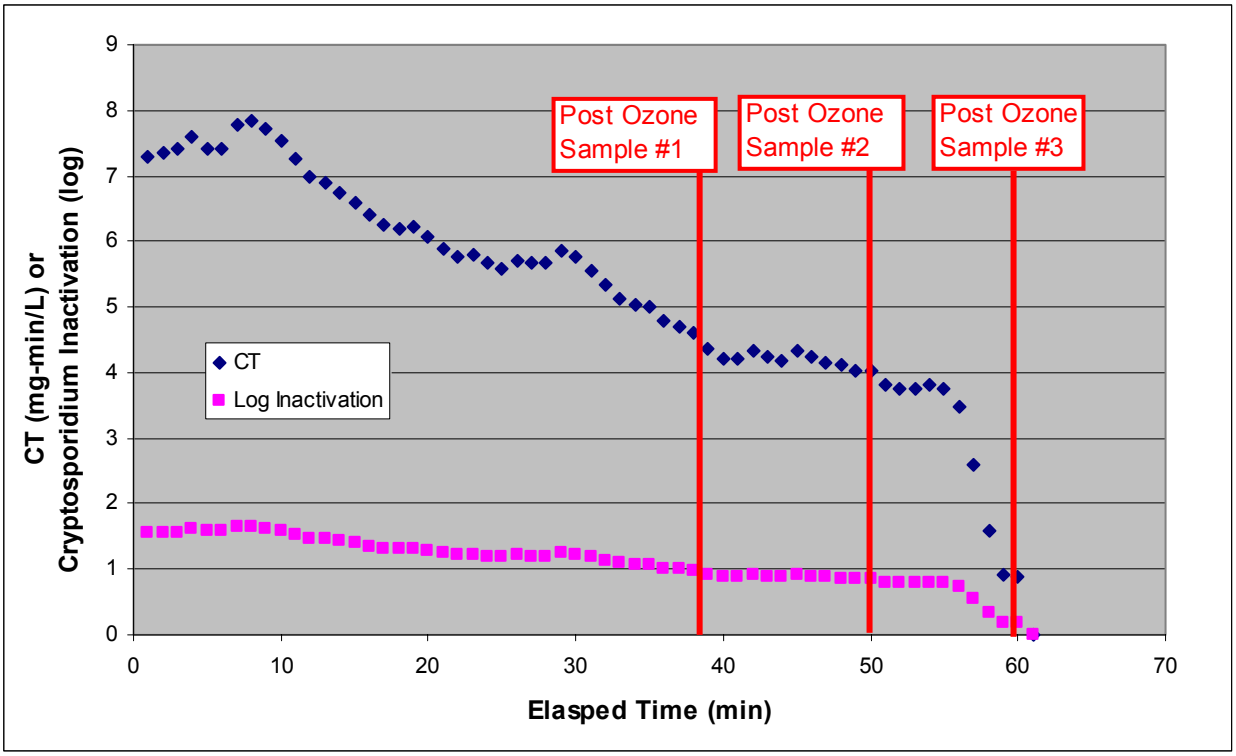


Figure 2. – Ozone Contactor Effluent Sampling at Steady State Conditions



Compound Removal by Ozonation

During pilot plant testing, 22 of the 30 LC/MS compounds analyzed were greater than 97% removed (Table 10). These removals were consistent with the bench scale results from Colorado River water with the exception of triclosan. The pilot testing also provided some kinetic data from samples collected at 2, 6, and 24 minutes. Removal of the remaining 8 compounds gradually increased with longer contact times. At least 50% of the experienced removal occurred within the first cell of the ozone contactor (~2 minutes of contact time). TCEP was poorly removed by ozone during both bench-scale and pilot-scale experiments.

Table 10. – Comparison of Percent Removal of LC/MS Compounds by Ozonation During Bench-Scale and Pilot-Scale Testing of Colorado River Water

Test Scale	Pilot	Pilot	Pilot	Pilot	Bench	Bench
Ozone Dose [mg/L]		2.39	2.39	2.39		2.5
Ozone Reaction Time [min]		2	6	24		~10
LC/MS Compounds	Raw Spiked Concentration (ng/L) (n=9)	Percent Removal			Raw Spiked Concentration (ng/L) (n=1)	Percent Removal
Ethynylestradiol	169 ± 13	>99	>99	>99	100	>99
Estrone	182 ± 14	>99	>99	>99	95	>98
Estriol	164 ± 11	>99	99.0	>99	104	>99
Estradiol	173 ± 10	>99	>99	>99	95	>98
Carbamazepine	122 ± 14	>99	>99	>99	65	>98
Trimethoprim	110 ± 12	>99	>99	>99	88	>98
Hydrocodone	81 ± 6	>98	>98	>98	63	>98
Gemfibrozil	139 ± 12	>99	>99	>99	67	>98
Triclosan	102 ± 8	>99	>99	>99	44	79.1
Acetaminophen	39 ± 3	92.1	>97	>97	28	>96
Oxybenzone	77 ± 5	>98	>98	>98	38	>97
Erythromycin-H_2O	111 ± 23	>99	>99	>99	25	>96
Naproxen	58 ± 5	>98	>98	>98	17	>94
Diclofenac	111 ± 8	>99	>99	>99	28	>96
Pentoxifylline	101 ± 9	96.8	>99	>99	64	>98
Caffeine	104 ± 7	94.2	>99	>99	78	>98
Testosterone	164 ± 10	91.5	99.3	>99	90	>98
Progesterone - APCI	163 ± 11	90.8	99.3	>99	70	>98
Fluoxetine	82± 12	>98	>98	>98	50	>98
Sulfamethoxazole	57 ± 4	>98	>98	>98	38	>97
Androstenedione	175 ± 12	87.5	98.9	>99	94	>99
Progesterone - ESI	106 ± 9	89.6	>99	>99	48	>97
Dilantin	89 ± 9	41.7	72.0	82.8	46	82.5
Diazepam	107 ± 11	45.9	70.1	82.0	67	78.7
DEET	135 ± 12	41.4	62.2	75.8	85	76.4
Ibuprofen	117 ± 7	40.1	69.2	83.2	47	82.5
Iopromide	112 ± 11	30.4	43.8	63.7	58	46.3
Meprobamate	127 ± 8	22.7	40.8	54.3	71	50.2
Atrazine	130 ± 12	15.5	43.2	54.2	59	45.5
TCEP	88 ± 9	0.0	4.9	0.0	45	13.3

There was greater variability in percent removal by ozonation of the GC/MS compounds. Only 13 of the 32 compounds showed greater than 80% removal during pilot plant testing. Select compounds which were not removed at all during bench scale testing showed some removal during pilot-scale testing. Once again, the kinetic data generated showed removal increased with longer contact times. A majority of the removal again occurred within the first contactor cell (~2 minutes). Overall, the bench-scale results coincided well with the pilot plant results for the GC/MS compounds.

Table 11. – Comparison of Percent Removal of GC/MS Compounds by Ozonation During Bench-Scale and Pilot-Scale Testing of Colorado River Water

Test Scale	Pilot	Pilot	Pilot	Pilot	Bench	Bench
Ozone Dose [mg/L]		2.39	2.39	2.39		2.5
Ozone Reaction Time [min]		2	6	24		~10
GC/MS Compounds	Raw Spiked Concentration (ng/L) (n=9)	Percent Removal			Raw Spiked Concentration (ng/L) (n=1)	Percent Removal
Anthracene	195 ± 18	>94	94.4	>94	114	>91
acenaphthene	138 ± 10	>92	>92	>92	128	89.7
acenapththylene	135 ± 13	88.9	>92	>91	131	>92
naphtalene	86 ± 6	>88	>88	>88	80	>87
Aldrin	64 ± 5	>84	>84	>84	20	>50
Fluoranthene	244 ± 24	85.6	89.3	94.1	188	>94
phenanthrene	243 ± 17	89.3	89.7	92.9	230	>95
fluorene	175 ± 13	65.2	82.3	88.6	187	>93
Benz[a]anthracene	107 ± 13	76.0	78.1	86.8	123	87.1
Benzo[a]pyrene	187 ± 16	73.0	83.2	86.6	34	>70
Pyrene	256 ± 25	76.6	77.4	86.1	194	>94
Metolachlor	143 ± 23	55.9	73.4	83.0	183	80.4
Galaxolide	57 ± 8	68.5	77.3	81.4	106	87.1
Chrysene	160 ± 13	54.3	56.2	74.1	130	90.7
Benzo[k]fluoranthene	145 ± 17	44.9	53.9	71.8	75	>86
Methoxychlor	146 ± 17	39.1	51.4	62.8	160	89.8
Benzo[b]fluoranthene	143 ± 15	39.0	43.2	61.4	95	>89
Heptachlor	80 ± 9	18.6	28.7	49.5	33	53.7
Dieldrin	145 ± 26	28.3	7.7	48.3	106	0.0
DDD	127 ± 11	30.0	26.9	43.7	96	66.5
α-Chlordane	98 ± 8	18.5	8.3	37.5	78	0.0
DDT	77 ± 8	24.9	11.9	35.3	68	56.6
γ-Chlordane	89 ± 8	21.0	5.1	34.9	53	0.0
DDE	71 ± 10	13.7	15.1	34.0	26	>57
Musk Ketone	161 ± 31	19.4	23.8	33.7	198	29.7
Mirex	36 ± 5	27.8	27.8	33.3	13	>23
Endrin	153 ± 25	8.1	21.1	33.3	157	10.0
Heptachlor Epoxide	138 ± 14	18.1	14.5	30.9	141	0.0
δ-BHC	144 ± 13	9.6	0.0	19.8	172	1.0
α-BHC	131 ± 12	9.8	9.1	19.8	154	9.2
γ-BHC	135 ± 14	5.3	8.2	19.1	159	4.5
β-BHC	144 ± 13	7.0	2.9	19.0	156	0.0

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