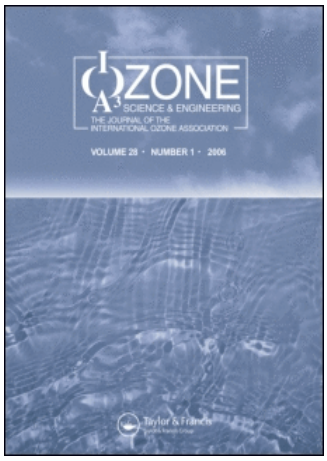

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Presence of Pharmaceuticals and Pesticides in Detroit River Water and the Effect of Ozone on Removal

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Reports by different scientific groups indicate concern about traces of drugs that could make their way into tap water. Studies indicate that activated carbon and ozone are promising treatment methods to remove traces of pharmaceuticals and pesticides. The Windsor Utilities Commission (WUC), Windsor, Ontario, Canada, evaluated the occurrence of pharmaceuticals and endocrine disrupting chemicals in its raw water supply, and the effectiveness of ozone in removing these compounds. The analysis indicated that trace levels of compounds such as carbamazepine, caffeine, cotinine, and atrazine were detected in raw water and that treatment with ozone resulted in a greater removal versus conventional treatment.

Keywords Ozone, Pharmaceuticals, Pesticides, Endocrine Disruptors, Drinking Water, Detroit River Water

INTRODUCTION

The occurrence and fate of pharmaceuticals and personal care products (PPCPs) in surface waters originating from urban sources is one of the leading emerging issues in environmental chemistry. At least 80 PPCPs (e.g., analgesics, antibiotics, antiepileptics, antidepressants, and blood lipid regulators) have been identified in outflows from sewage treatment plants (STPs) and surface waters worldwide (Kolpin et al., 2002; Ternes, 1998). However, many PPCPs remain unidentified. Moreover, little is known regarding the fate, characterization and quantification at drinking water intakes.

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The Detroit River receives a considerable loading of urban and agricultural runoff, as well as STP discharges at the head of the river. The river is the source of drinking water for approximately 4.5 million residents of metropolitan Detroit, Michigan, USA and Windsor, Ontario, Canada. Windsor's main intake for its drinking water treatment plant (WTP) is downstream from Little River Sewerage Treatment Plant, City of Windsor. The contribution of PPCPs from STPs and frequent combined sewer overflows (CSOs) are of concern to Windsor and other surrounding communities. In general, the sources, types, and concentrations of PPCPs in the river water are unknown, but of ecological and human health concern.

Windsor implemented ozone for drinking water treatment for the inactivation of *Cryptosporidium* parvum oocysts, and to improve water quality. WUC thus began to investigate the effectiveness of ozone in removing environmental compounds, such as trace organic compounds, mainly pesticides and pharmaceuticals. Although pharmaceuticals at such low concentrations may seem rather benign, we do not know the effect of a complex mixture of compounds from sewage effluent and overflows. Preliminary analysis indicated that trace levels of some of these compounds were detected in the incoming Detroit River raw water (Jasim et al., 2003a, 2003b). Preliminary studies were conducted utilizing the WUC pilot plant, which is located at the A. H. Weeks Water Treatment Plant in Windsor. The pilot system provides two parallel trains, to evaluate the actual water treatment plant process using ozone, compared to a conventional treatment process (coagulation/flocculation, sand filtration).

Pharmaceuticals are most likely to appear in surface waters from sewage discharges as a product of their human use and consequent excretion (Khan and Ongerth, 2002a, 2002b) and are discharged continuously

into the environment in highly populated areas (Janex et al., 2002). Reports have shown that as much as 50% to 90% of an administered drug can be excreted in original form or a similar biologically active form (Braghetta et al., 2002; McGovern and McDonald, 2003). In sewage treatment plant discharges, PPCPs and endocrine disrupting compounds (EDCs) may be present as a result of incomplete removal during treatment, from combined sewage and storm water overflows, illicit connections, or leaking septic systems. Other point source contamination can result from pharmaceutical manufacturers (7). Agricultural practices can constitute a significant contribution to non-point sources of PPCPs and EDCs. Veterinary antibiotics were detected in surface water supplies in proximity to large-scale hog confinement operation in Iowa (Weyer and Riley, 2001). Some pharmaceuticals have also been shown to leach through subsoil and into groundwater (Heberer, 2002).

HEALTH EFFECTS (HUMAN AND ECOLOGICAL)

Since medical drugs are designed with a specific mode of action, it is expected that they will have a variety of effects on non-target receptors and can possibly cause adverse effects in a target organism (Weyer and Riley, 2001). Antibiotic resistance is the issue receiving the most attention of all the PPCPs, especially since a large portion of antibiotics leave the body and end up in receiving waters (Weyer and Riley, 2001). We do not know what threshold levels are toxic, especially in complex mixtures. It is speculated that EDCs may be responsible for declining sperm counts and decreased sperm motility and function in the human population (Shaw and McCully, 2002; Richthoff et al., 2003). EDCs may cause adverse effects including hormone dependent cancers, reproductive tract disorders, and reduction in reproductive fitness (Snyder et al., 2002).

Effects on wildlife have been documented from PPCPs in surface waters. In Lake St. Clair, upstream from Windsor's intake, male fish have been found to have eggs (Kavanagh et al., 2004). This gonadal intersex is suspected to have occurred from exposure to endocrine disrupting chemicals. Studies in the United Kingdom and United States in the 1990s indicated reproductive abnormalities in fish living below wastewater treatment plants (Yoon et al., 2002).

Antidepressant drugs of selective serotonin reuptake inhibitors (SSRIs) are known to be potent spawning inducers in aquatic invertebrates at environmentally relevant concentrations such as low ppb levels (Fong, 1998). Ecological consequences (e.g., population, community, ecosystem-wide effects) of this are not yet known.

Routine screening being done on EDCs may not be fully adequate in predicting ecosystem and human health effects because the effects may not be manifested until after long, chronic exposures. For example, the metamorphosis of fertilized frog eggs was inhibited by low levels of perchlorate after a 70-day exposure, but not after the 14-day exposure recommended by the Endocrine Disrupter Screening and Testing Advisory Committee's (EDSTAC) method for testing EDCs (McDonald and McDonald, 2003). Furthermore, in a realistic scenario, aquatic organisms would be exposed to EDCs during entire life cycles.

REMOVAL OF PPCPs AND EDCs IN WATER TREATMENT PROCESSES

Drinking water should be safe from contaminants including EDCs and PPCPs. The problem is that most of these compounds are not regulated, so it is not known what is "safe." Therefore, until the regulations catch up with the research, we aim to remove or reduce the levels of contaminants in our waters. According to Carlson (2000), molecular weight and relative hydrophobicity of a compound will influence its removal by treatment processes (Weyer and Riley, 2001). Many EDCs and PPCPs are low molecular weight compounds that are relatively hydrophilic, and are thus not suited for removal by traditional treatments. It has been reported by many studies that conventional water and sewage treatment plants would be expected to remove less than 20% of most EDCs and PPCPs (Fong, 1998). Some drugs, such as clofibric acid, a blood lipid regulator, have such low removal efficiencies from STPs that the concentrations in surface waters are more a function of dilution than degradation (19). Carbamazepine, an anti-epileptic drug that is frequently detected in STP effluent, was reported to have only 7% removal efficiency from sewage treatment (Ternes, 1998). In order to improve removal of EDCs and PPCPs, more than one treatment process should be employed at a particular water treatment plant. For example, pesticide research has shown that they can be removed by a variety of treatment setups: 44–55% of atrazine was degraded using ozone/hydrogen peroxide treatment (Nelieu et al., 2000); 70–80% of pirimiphos methyl, an organophosphate insecticide, was degraded using an ozone process (Chiron et al., 1998); powdered activated carbon (PAC) adsorption followed by Pulsator floc-sedimentation and ozonation effectively removed metolachlor and terbutylazine from incoming drinking water (Griffini et al., 1999).

Current research has shown that ozone treatment and ozone treatment coupled with other treatments remove (at varying degrees) a range of contaminants from water. Of the oxidation processes, ozone reacts more readily with organic compounds than do chlorine dioxide or chlorine (Fong, 1998). The use of O_3/H_2O_2 is considered more cost effective for micropollutant removal in river water than UV/ H_2O_2 (Fong, 1998). Another process, using UV/ozone treatment, removed greater than 90% of chlorinated phenols and polyaromatic hydrocarbons

(PAHs) (Vollmuth and Niessner, 1995). Ozone improves biodegradation and has been shown to be effective for removing some pharmaceutical compounds, particularly those that contain functional groups such as phenols, amines or double bonds (Weyer and Riley, 2001; Janex et al., 2002). It has been shown that ozone can cleave the aromatic ring of a phenol, attack double bonds (e.g., forming carbonyls), and form hydroxylamines and amine oxides from secondary and tertiary amines, respectively (Huber et al., 2003). For some compounds that do not react directly with ozone, degradation can occur by reactions with OH radicals. Therefore, advanced oxidation, such as ozone combined with hydrogen peroxide, shows promise in removing or reducing pharmaceuticals in water.

Zweiner and Frimmel (2000) found that the lipid regulator, clofibric acid, and analgesic, ibuprofen, were not efficiently removed with ozone alone, but were 90% reduced when hydrogen peroxide (1.4 mg/L) was coupled with a higher dose of ozonation (3.7 mg/L).

Water quality parameters also need to be taken into account as factors that can affect removal efficiencies of pharmaceuticals and endocrine disrupting compounds. The oxidation of some PPCPs is pH-dependent. For example, the deprotonated phenol group of 17a-ethinylestradiol reacted faster than when protonated, likewise, the amine group of the antibiotic roxithromycin reacts faster when non-protonated (Andreozzi et al., 2003a, 2003b; Huber et al., 2003). Natural organic matter (NOM) can absorb contaminants decreasing their ability to be oxidized from advanced treatment processes, as in the case of carbamazepine and diclofenac. However, NOM can act as a sensitizer increasing photolysis of pharmaceuticals in surface waters such as the case of sulphamethoxazole, clofibric acid, oflaxocin and propranolol (Andreozzi et al., 2003c).

Rate constants for reactions of ozone and O_3/H_2O_2 with certain pharmaceuticals, including bezafibrate, carbamazepine, diclofenac, 17a-ethinylestradiol, iopromide, sulfamethoxazole and roxithromycin have been determined in bench-scale experiments (Andreozzi et al., 2003a, 2003b; Huber, 2003). Some drugs can be expected to be completely transformed during ozone treatment. Complete oxidation of an organic chemical to carbon dioxide and water is called mineralization. Andreozzi et al. (2003a) believe clofibric acid may be completely mineralized (CO_2 + H_2O + chlorine ions) by O_3/H_2O_2. Some compounds may be partly mineralized, for example, Andreozzi et al. (2003b) reported 30–40% mineralization of paracetamol, and several byproducts of carbamazepine were detected after ozonation. Partial mineralization plus transformation of the parent compounds should attenuate their toxicity; it is expected that most ozone byproducts would be less potent than their therapeutically designed parent compounds and metabolic byproducts. For example, 17a-ethinylestradiol ozonation by-products were shown to be significantly reduced in their estrogenicity than 17a-ethinylestradiol in a yeast estrogen test (von Gunten et al., 2003). However, this hypothesis needs to be tested for more compounds. Also, in assessing the overall value of ozone treatment to water quality, one has to consider ozonation byproducts created by reactions with natural organic matter, such as carboxylic acids, ketones, and aldehydes, and subsequent reactions from chlorination or chloramination. These by-products are be a focus of this study, but if found as non-target compounds, will be reported qualitatively.

BACKGROUND

The Windsor Water Treatment Centre serves three municipalities whose total population is approximately 230,000. Raw water is drawn from the Detroit River, which connects Lake St. Clair and Lake Erie. The Windsor Water Treatment Centre was upgraded in 1994 by the construction of a second drinking water treatment plant (A. H. Weeks Plant) at the site of the original plant, with a capacity of 268 million liters per day. Raw Detroit River water has a small range in variation of key water quality parameters, low values of turbidity (except for occasional spikes), color, and total organic carbon (1.5–1.8 mg/L), and a moderate hardness (100–150 mg/L as $CaCO_3$).

MATERIALS AND METHODS

Pilot Plant

The pilot plant used in this study had two identical process trains constructed of organically inert materials (stainless steel, glass, or fluorocarbons; Jasim et al., 2003b). Each side of the pilot plant shared identical physical characteristics, which allowed for direct comparison between the two sides of the plant with a common raw water quality (Figure 1).

The A. H. Weeks Water Treatment Plant

The ozone system at the A.H. Weeks WTP was designed to provide 2-logs *Cryptosporidium* oocysts inactivation. The operation of the ozone system to achieve the design goal of 2-log inactivation of *Cryptosporidium* oocysts provides a substantial additional log inactivation credit for *Giardia* and viruses far in excess of maximum values shown in regulatory disinfection tables (Jasim et al., 2002).

The plant consists of two identical process trains, each include; ozone contactor, rapid mix, four flocculation tanks, and a plate settler. The plant has eight filters, provided with air scour. The ozone system consists of two ozone generators with a total capacity of 1000 kg per day of Ozone at 12% wt., two power supply units and two destruct units, supplied by Ozonia North America (NJ, US). Ozone is produced using liquid oxygen (LOX), which is supplied by Air Liquide- Canada.

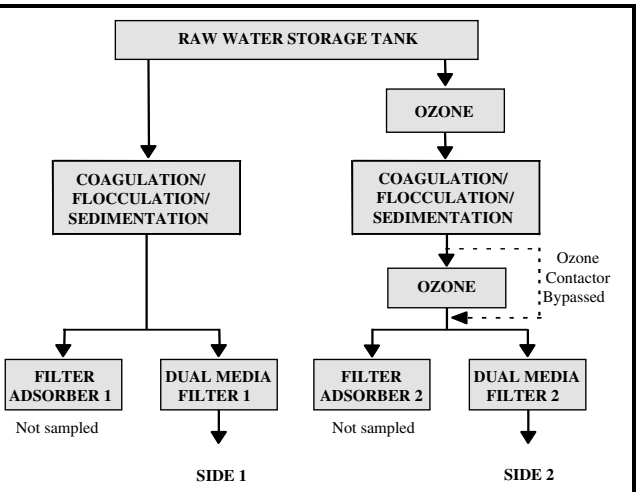

FIGURE 1. Pilot plant configuration.

SAMPLING AND ANALYSIS

Solid-Phase Extraction and Analysis by GC/MS

The analysis for the first set of experiments was conducted in 2002 to investigate the presence of trace pharmaceuticals and personal care products in the Windsor raw water supply, and the effect of different treatment processes in removing these compounds. The analysis was conducted by Tulane University, New Orleans, LA (Jasim et al., 2003a) by gas chromatography/mass spectrometry (GC/MS) in 2002–2003 and by Oakland University, Rochester, MI in 2004. Samples were acidified and shipped in amber glass bottles in coolers. The target list for the first set of experiments included 11 compounds, listed in Table 1.

In 2004, grab samples were collected weekly from June 23–August 11. For this sampling period, a different method was used for the analysis of select target compounds (ibuprofen, atrazine, caffeine, triclosan, 17a-ethinylestradiol): one 2L samples were extracted with Strata-X (Phenomenex, Torrence, CA) solid phase cartridges, washed with 5% aqueous methanol, and eluded with 2 ml methanol followed by 0.2 ml dichloromethane, and concentrated under a stream of nitrogen to 0.1–1.0 ml. Samples were analyzed without derivatization by GC/MS using selected ion monitoring by the method of Soliman et al. (2004).

TABLE 1. Target Compounds—First Set of Experiments

Target Compound	Type
Clofibric Acid	Lipid Regulator
Estrone	Steroid
17B-Estradiol	Steroid
Ibuprofen	Analgesic
Naproxen	Analgesic
Acetaminophen	Analgesic
Bisphenol-A	Fungicide & Disinfectant
Chlorophene	Fungicide & Disinfectant
Triclosan	Fungicide & Disinfectant
Fluoxetine	Antidepressant
Caffeine	Human activity marker

Extraction and Analysis by LC/MS-MS—Initiated 2005

Sample analysis by a liquid chromatography-tandem mass spectrometry (LC/MS-MS) method in the 2002–2003 period were conducted by Great Lakes Institute of Environmental Research (GLIER) of the University of Windsor in order to achieve lower detection limits (Hua et al., 2003; Jasim et al., 2003b).

In April 2005, a broader range of compounds was investigated during weekly sampling, which was carried on through 2006. All analysis is being done at the Laboratory Services Branch of the Ministry of Environment (MOE), using three accredited methods. The target list, shown in Table 2, contains thirty-seven (37) acid and neutral drugs, antibiotics, ten (10) endocrine disruptors and three (3) perfluoro surfactants i.e., Perfluorooctane sulfonate, Perfluorobutane sulfonate and Perfluorooctanic acid, methoprene, malathion (mosquito larvacide and adulticide), Bacillus Thruingiensis (Bti, mosquito larvacide) and a group of nineteen pesticides. These pesticides include atrazine and its environmental decomposition by-products, alkylated atrazine and mosquito larvacides/adulticides and their environmental decomposition by-products.

The endocrine disruptors are being analyzed using an MDS Sciex API4000 QTrap LC/MS/MS system (Applied Biosystems, Foster City, CA). D_{10}-carbamazepine, $^{13}C_6$-sulfamethazine phenyl, D_3-ibuprofen, D_6-gemfibrozil, D_4-diclofenac Sodium and D_{16}-bisphenol used as method surrogates to ensure the quality of analysis. The pesticides and their metabolites are being done by using a LECO Pegasus III GC/Time-of-flight mass spectrometry system (Rio de Janeiro, Brazil). Extraction and analysis of emerging organic compounds is being conducted using solid phase extraction followed by LC/MS-MS analysis (Laboratory Service Branch method E3454), "The Determination Of Pharmaceuticals & Personal Care Products (PPCPs), Hormones And Steroids In Aqueous Environmental Matrices By LC-MS-MS Analysis." Extraction and analysis of triazine herbicides is done by the Ministry by using liquid-liquid extraction followed by GC/TOF-MS analysis (Laboratory Service Branch method E3435, "The Determination Of Triazine Herbicides In Water, Vegetation, And Soil By GC/TOF-MS." These methods were accredited by the Canadian Association of Environmental Analytical Laboratories, with performance that equals or exceeds that of comparable Environmental Protection Agency (EPA) methods.

TABLE 2. Target Compounds List by Ontario Ministry of the Environment, Canada

Compound Name	Minimum Detection Limit (μg/L)	Compound Name	Minimum Detection Limit (μg/L)
PPCPs		Endocrine Disruptors	
Monensin	0.10	Bisphenol A	0.11
Meclocycline	0.20	Diethylsilbestrol	0.85
Tetracycline	0.23	17-a-Estradiol	0.40
Lincomycin	0.04	Esterone	0.41
Erythromycin	0.17	Equiline	0.30
Roxithromycin	0.11	19-Norethersterone	0.37
Trimethoprim	0.02	17-a-Ethinylestradiol	0.40
Chlorotetracycline	0.81	Progesterone	15.3
Sulfadimethoxine	0.05	Estriol	0.27
Sulfamerazine	0.05	17-b-Estradiol	0.20
Sulfamethazine	0.05	**Pesticides**	
Oxytetracline	0.30	De ethyl Simazine	44
Sulfachloropyridzine	0.18	De ethyl Atrazine	225
Carbamazepine	0.01	Atraton	78
Sulfamethoxazole	0.09	Simazine	88
Penicillin G	2.15	Prometone	41
Doxycycline	0.13	Atrazine	91
Ciprofloxacin	0.12	Propazine	117
Tyrosine Tartrate	0.31	Metribuzin	193
Naproxen	0.03	Alachlor	181
Kentoprofen	0.02	Ametryne	105
Chloramphenicol	0.02	Prometryne	95
Gemfibrozil	0.04	Terbutryne	189
Ibuprofen	0.14	Metolachlor	163
Bezafibrate	0.01	Cyanazine/Bladex	183
Diclofenac	0.04	Butachlor	270
Indomethacin	0.66	Methoprene	30
Virginiamycin M1	0.75	Malathion	25
Sulfadiazine	0.26	Methoprene acid	15
Carbadox	0.20	Methoxycitronellal	45
Clofibric acid	0.06	Piperonyl butoxide	10
4-acetamidophenol	0.09		
Warfarin	0.03		
Amoxicillin	0.47		
Lasaloid A	0.28		

RESULTS AND DISCUSSION

Samples Analyzed by GC/MS

The March 2002 samples analyzed by GC/MS are presented in Table 3. Table 3 also identifies the retention time (RT) and quantification ion (Q1) for each compound (3). These compounds have been previously detected in Canadian wastewater treatment plant effluents by other researchers (Metcalfe et al., 2000).

In 2004, ibuprofen was detected in three raw water samples, at concentrations of 66 ng/L on June 23, 134 ng/L on July 14, and 113 ng/L on August 11 (data not shown). Ibuprofen was not detected in the treated water samples. Atrazine was consistently reported in raw and conventionally treated samples, and was reduced in ozonated samples. Table 4 shows the data for atrazine in raw and treated waters. During the week of 7/27/04, there was a significant rain event of 1.11 inches of rain. Thus, it was expected that there would have been significant runoff contributing to non-point source pollution from agricultural runoff, which may explain the presence of atrazine and other chemicals in the raw water.

Samples Analyzed by LC/MS—2002–2003

The results indicated the presence of certain compounds in Detroit River water, such as carbamazepine, cotinine, atrazine and caffeine during the sampling period

TABLE 3. Results for March 2002 Samples

Compound	RT	Q1	Blank (ng/L)	Raw (ng/L)	Conventional PP (ng/L)	O_3 PP (ng/L)	A. H. Weeks WTP (ng/L)
Clofibric Acid	17.58	128	ND	103	ND	ND	ND
Ibuprofen	19.49	263	ND	ND	ND	ND	ND
Acet-d4*	19.68	284	ND	ND	ND	ND	0.17
Acetaminophen	19.74	280	ND	ND	ND	ND	ND
Caffeine	27.32	194	ND	ND	ND	ND	ND
Fluoxetine**	27.83	104	ND	ND	ND	ND	ND
Clorophene**	29.9	275	ND	ND	ND	ND	ND
Naproxen	30.74	243	ND	63	ND	ND	ND
Triclosan	31.29	200	ND	ND	ND	ND	ND
Bis-d14*	32.04	368	91	67	80	91	94
Bisphenol A	32.13	357	26	NQ	NQ	NQ	NQ
Est-d4*	36.18	346	84	77	82	75	91
Estrone	36.21	342	ND	ND	ND	ND	ND
17B-Est	36.39	285	ND	ND	ND	ND	ND
Cholesterol	40.33	329	6.3	6.3	6.3	11.3	1.8

*% Recovery of Surrogate Standard. PP = Pilot Plant; O_3 = ozonated. **Not Quantitative.

from September 2002 until the end of June 2003 (Jasim et al., 2003b).

Side 1 of the pilot plant was operated in a conventional mode, which included rapid mixing, flocculation, sedimentation and filtration. Side 2 implemented a pre-coagulation ozonation process with ozone applied at a range of 1.5–2.00 mg/L. Alum and Magnafloc LT 22 were added to both sides of the pilot plant at dosages of 30–50 mg/L and 0.05–0.1 mg/L respectively. Figures 2 to 5 indicate the average of the concentration of these compounds in raw water on a monthly basis (Jasim et al., 2003b).

Atrazine was identified in raw water samples at a wide range of concentrations from 5.6 to 78.6 ng/L. The highest concentration was detected in June 2003. Higher reduction of atrazine was achieved when pre-coagulation ozonation was implemented. Reduction of atrazine was 67 to 96 % on average on Side 2 of the pilot plant where ozone was used, compared to 0–13% on average, when conventional treatment processes were used (Figure 5).

The effect of the ozonation process was noticeable at the post sedimentation stage. The level of these compounds was reduced (Figures 2–5), which is related to the effect of ozone on the removal of these compounds prior to the filtration process.

Future studies would include investigation for the presence of such compounds in the water intakes for different communities. An arrangement has been made to develop a study to evaluate the removal of these chemical compounds by conventional and ozone treatment plants located in the City of Windsor and the City of Detroit. These plants have different intake locations in the Detroit River. The experiments will provide useful information about the presence of these compounds in Detroit River

TABLE 4. Results for Removal of Atrazine Sampling Period June–August, 2004

	Treatment Train							
Date	Raw A (ng/L)	Raw B (ng/L)	Con. A (ng/L)	Con. B (ng/L)	FS O_3 A (ng/L)	FS O_3 B (ng/L)	PP O_3 A (ng/L)	PP O_3 B (ng/L)
06/30/04	< LOQ	< LOQ	57	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
07/14/04	148	149	130	147	86	133	< LOQ	< LOQ
07/21/04	< LOQ	116	75	104	101	106	< LOQ	< LOQ
07/28/04	73	75	95	127	95	59	57	65

Con. = Conventional; FS = Full Scale; PP = Pilot Plant; O_3 = Ozonated.No quantifiable compound detected on 08/11/04 and 08/18/04. LOQ (Limit of Quantitation) = 50 ng/L.

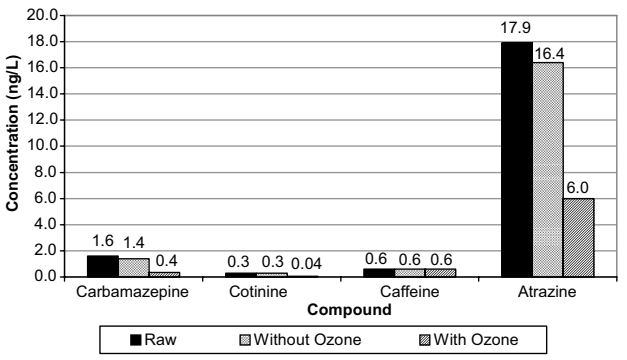

FIGURE 2. Average for compounds in raw water and filters effluent, September 2002.

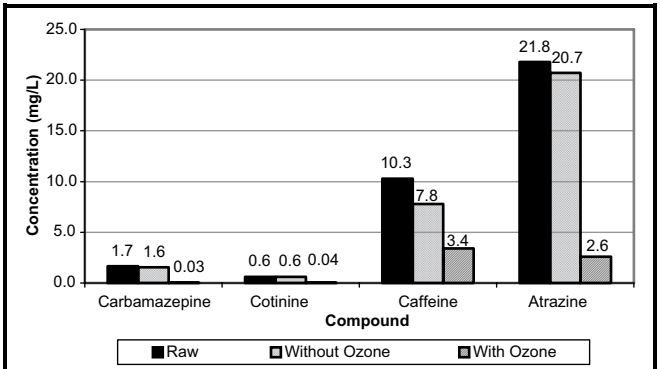

FIGURE 3. Average for compounds in raw water and filters effluent, April 2003.

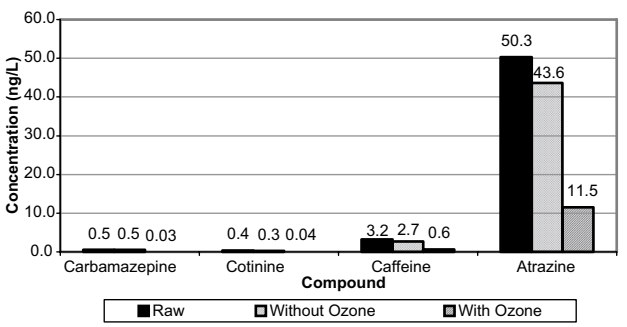

FIGURE 4. Average for compounds in pilot plant raw water and filter effluent, June 2003.

raw water, and the seasonal variation effect on their concentrations.

Analysis by LC/MS-MS during 2005

Raw water, conventionally treated, and the pilot plant and full-scale ozonated grab samples were evaluated for the chemicals listed in Table 2. All chemicals were below the method detection limits. The method detection limits are high, but ensure accuracy and reproducibility. The method detection limits for the endocrine disrupting chemicals are above what may be expected in surface waters, therefore, it was not a surprise that they were not detected. Further work will be done to try to reduce the detection limits. A few chemicals were detected and concentrations estimated, although they were technically below the reported method detection limits that were determined with 95% confidence in 10 samples during method validation. Thus, the following chemicals may be present, but their concentrations could only be estimated: sulfamethoxazole was found once in a raw water sample at 1.4–2.1 ng/L and naproxen was found in one raw water sample at approximately 0.2 ng/L. Bisphenol A was detected in two raw water samples and two pilot plant effluents at approximately 35–40 ng/L (estimated), but not in full-scale treatment effluent. Diethylstilbestrol was detected in two raw water samples and estimated to have a concentration of 74 ng/L and 78 ng/L.

CONCLUSIONS

The results of this study indicate the presence of certain compounds in Detroit River raw water. Carbamazepine, cotinine, atrazine and caffeine were detected during the sampling period from September 2002 until the end of June 2003. Ibuprofen was detected in June 23 and July 7, 2004.

Filters effluents indicated clearly that removal of the compounds was higher when pre-coagulation ozonation was implemented, compared to conventional treatment processes when ozone was not used.

The study provides a unique and advanced level of information for water supply and treatment for the Great Lakes Region. The findings of this study, agrees with current research applied in different locations in North America and Europe, which has shown that ozone treatment and ozone treatment coupled with other treatments remove a wide range of contaminants from water. The experiments provided useful information about the presence of these compounds in Detroit River raw water, and the seasonal variation effect on their concentrations. The findings of this study provides information to other communities that use Detroit River water as a source for drinking water, about the presence of these compounds in the river, and the treatment processes that are capable of removing them.

Since other treatment processes show little ability to remove pharmaceuticals, ozonation shows great promise and should be considered the focus of treatment studies for the removal of these compounds in the Great Lakes Region.

Present ongoing studies involve the evaluation of full-scale water treatment plant performance in the removal of these compounds. Partners in the new research effort include the Detroit Water and Sewerage Department, the International Joint Commission (IJC), Ontario Ministry

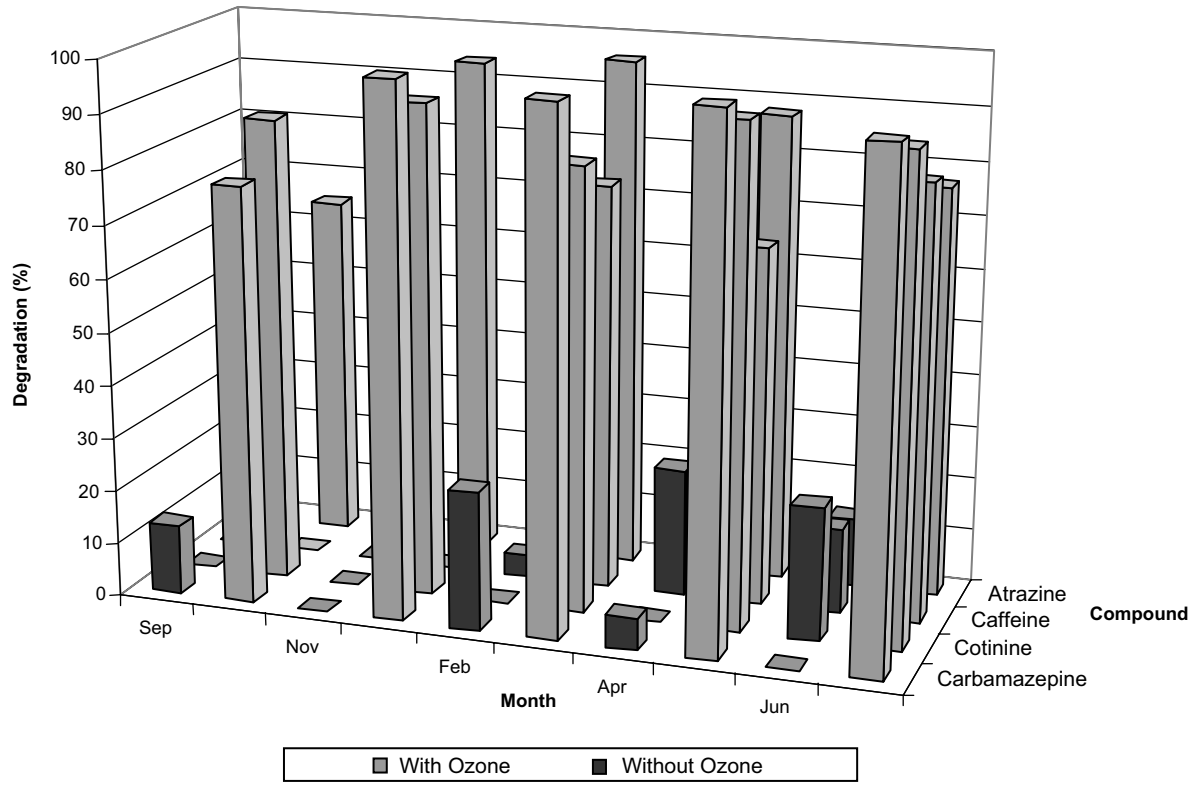

FIGURE 5. Comparison of the monthly average removal—Ozone vs. conventional treatment process (without ozone).

of the Environment (MOE), Health Canada, Oakland University, University of Windsor, Wayne State University, The Centre for Environmental Health of Ontario, and Earth Tech Canada. The focus of this two-year study will be to examine the concentrations of target compounds before and after various treatment processes and as a function of pertinent parameters including ozone dose, hydrogen peroxide dose, pH, alkalinity, total organic carbon (TOC), turbidity, and temperature.

Initial preliminary results of the new two year project detected nine of 19 target compounds including: sulfamethoxazole, acetaminophen, cephalexin, caffeine, triclosan, naproxen, estradiol, carbamazepine, and atrazine. Carbamazepine was found at concentrations less than 10 ng/L in raw and treated samples. Atrazine was consistently detected in Detroit raw water at 26–233 ng/L. Future studies will be conducted on sewage treatment effluent that may be a source of these chemicals. The different methods used in this study are being evaluated and future studies will strive for the lowest method detection limits possible with high accuracy and precision.

NOMENCLATURE

CSO	combined sewer overflow
EDC	endocrine disrupting compound
EPA	Environmental Protection Agency
EPSTAC	Endocrine Disrupter Screening and Testing Advisory Committee
GC/MS	gas chromatography – mass spectrometry
IJC	International Joint Commission
LC/MS-MS	liquid chromatography – tandem mass spectrometry
LOX	liquid oxygen
MOE	Ministry of Environment (Ontario)
NOM	natural organic matter
PAC	powdered activated carbon
PAH	polyaromatic hydrocarbon
PPCP	pharmaceutical and personal care products
SSRI	selective serotonin reuptake inhibitors
STP	sewage treatment plant
TOC	total organic carbon
WTP	water treatment plant
WUC	Windsor Utilities Commission

REFERENCES

1. Andreozzi, R., V. Caprio, R. Marotta, and A.J. Radovnikovic, "Ozonation and H_2O_2/UV Treatment of Clofibric Acid in Water: A Kinetic Investigation", *Hazard Mater.*, 103:233–246 (2003a).
2. Andreozzi, R., V. Caprio, R. Marotta, and D. Vogna, "Paracetamol Oxidation from Aqueous Solutions by Means of Ozonation and H_2O_2/UV System", *Water Res.*, 37:993–1004 (2003b).

3. Andreozzi, R., R. Marotta, and N. Paxeus, "Pharmaceuticals in STP Effluents and Their Solar Photodegradation in Aquatic Environment," *Chemosphere* 50:1319–1330 (2003c).
4. Braghetta, A.H., T. Gillogly, B. Brownawell, and M. Benotti. "Removal of Pharmaceuticals and Endocrine Disrupting Compounds Through Advanced Wastewater Treatment Technologies", Water Quality and Technology Conference. Seattle, Washington, DC (November 2002).
5. Carlson. M, "Current and Emerging Drinking Water Treatment Technologies", Presentation at the Endocrine Disruptors and Pharmaceutically Active Chemicals in Drinking Water Workshop, Chicago, Illinois (April 2000).
6. Chiron S., A. Rodriguez, and A. Fernandez-Alba, "Application of Gas and Liquid Chromatography Mass Spectrometry to the Evaluation of Primiphos Methyl Degradation Products in Industrial Water under Ozone Treatment", *J Chrom. A*., 823(1–2):97–107 (1998).
7. Daughton, C.G. and T.A. Ternes, "Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change?", *Environ. Health Perspect*., 107(supp 6):907–938 (1999).
8. Fong, P.P. "Zebra Mussel Spawning is Induced in Low Concentrations of Putative Serotonin Reuptake Inhibitors". *Biol. Bull*., 194:143–149 (1998).
9. Griffini, O., M.L. Bao, D. Burrini, D. Santianni, C. Barbieri, and F. Pantani, "Removal of Pesticides During the Drinking Water Treatment Process at Florence Water Supply, Italy", *J. Water Services Res. Technol-Aqua*, 48(5):177–185 (1999).
10. Heberer, T. "Occurrence, Fate and Removal of Pharmaceutical Residues in the Aquatic Environment: A Review of Recent Research Data", *Toxicol. Lett*., 131:5–17 (2002).
11. Hua, W., E.R. Bennett, X.-S. Miao, C.D. Metcalfe, and R.J. Letcher, "Major Neutral and Acidic Pharmaceuticals and Chloro-S-Triazine Herbicides in Wastewater Effluent and Surface Water from the Upper Detroit River", Proceedings of Society of Environmental Toxicology and Chemistry (SETAC), Austin, TX (November 2003).
12. Huber, M.M., S. Canonica, G.-Y. Park, and von U. Gunten, "Oxidation of Pharmaceuticals During Ozonation and Advanced Oxidation Processes", *Environ. Sci. Technol*., 37:1016–1024 (2003).
13. Janex, M.L., A. Buchet, Y. Levi, and T. Ternes. "Pharmaceutical Compounds: Occurrence in the Environment and Fate in Drinking Water Treatment", Proceedings Water Quality and Technology Conference. Seattle, Washington (November 2002).
14. Jasim, S.Y., S. Mazloum, D. Grimm, and G. Boyd, "Evaluation of the Presence of Endocrine Disruptors Chemicals (EDCs) in Detroit River and the Effect of Water Treatment Processes on Their Removal," Proceedings 16th World Congress, International Ozone Association, Las Vegas, Nevada (2003a).
15. Jasim, S.Y., S. Mazloum, K. Rakness, Glenn Hunter, and N. Biswas. "Optimization of the Ozone System at the A.H. Weeks Water Treatment Plant, Windsor, Ontario", IOA-PAG Conference Raleigh, NC, (May 2002).
16. Jasim, S.Y., W. Hua, R. Letcher, F. Lemieux, S. Mazloum, G. Krantzberg, and M. Burrows, "Endocrine Disrupters Chemicals (EDCs) Presence in Water Supplies and Effect of Treatment Process on Removal-A Great Lakes Region Concern", Proceedings Water Quality Technology Conference, Philadelphia, PA, (November 2003b).
17. Kavanagh, R.J., G.C. Balch, Y. Kiparissis, A.J. Niimi, J. Sherry, C. Tinson, and C.D. Metcalfe, "Endocrine Disruption and Altered Gonadal Development in White Perch (Morone Americana) From the Lower Great Lakes Region", *Environ. Health Perspect*., 112:898–902. (2004).
18. Khan, S. and J.E. Ongerth, Pharmaceutical Residuals in Water — Compounds, Sources, and Controlling Characteristics. Proceedings Water Quality and Technology Conference. Seattle, Washington, November 10–14 (2002a).
19. Khan, S.J. and J.E. Ongerth, "Estimation of Pharmaceutical Residues in Primary and Secondary Sewage Sludge Based on Quantities of Use and Fugacity Modeling", *Water Sci. Technol*. 46, 105–113, (2002b).
20. Kolpin, D. W., E. T. Furlong, M. T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, and H. T. Buxton, "Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance", *Env. Sci. Technol*., 36:1202–1211 (2002).
21. McGovern, P. and H.S. McDonald, "Endocrine Disruptors: The Next Generation of Regulatory Concern?", *Water Env. Technol*., 15(1):35–39 (2003).
22. Metcalfe, C., B. Koenig, T. Ternes, and R. Hirsch, Environmental and Resource Studies, Trent University, Peterborough, ON, Canand 2000 ACS National Meeting, Division of Environmental Chemistry, 2000.
23. Nelieu, S., L. Kerhoas, and J. Einhorn, "Degradation of Atrazine into Ammeline by Combined Ozone/Hydrogen Peroxide Treatment in Water", *Environ. Sci. Technol*., 34(3):430–437 (2000).
24. Richthoff, J., L. Rylander, B.A.G. Jonsson, H. Akesson, L. Hagmar, E.P. Nilsson, M. Stridsberg, and A. Giwercman, "Serum levels of 2,2′,4,4′,5,5′-hexachlorobiphenyl (CB-153) in Relation to Markers of Reproductive Function in Young Males From the General Swedish Population", *Environ. Health-Persp*., 111 (4): 409–413 (2003).
25. Shaw, I. and S. McCully, "A Review of the Potential Impact of Dietary Endocrine Disrupters on the Consumer", *Inter. J. Food Sci. Technol*., 37(5):471–476 (2002).
26. Snyder, S., B. Vanderford, R. Pearson, and D. Rexing. "Analytical Methods for Measuring Endocrine Disruptors in Water", Proceedings Water Quality and Technology Conference. Seattle, Washington (November 2002).
27. Soliman, M.A., J.A., Pedersen, and I.H. Suffet, "Rapid Gas Chromatography-Mass Spectrometry Screening Method for Human Pharmaceuticals, Hormones, Antioxidants and Plasticizers in Water", *J. Chromatogr*., 1029:223–227 (2004)
28. Ternes, T.A. "Occurrence of Drugs in German Sewage Treatment Plants and Rivers", *Water Res*., 32 (11): 3245–3260 (1998).
29. Vollmuth, S. and R. Niessner, "Degradation of PCDD, PCDF, PAH, PCB and Chlorinated Phenols During the Destruction Treatment of Landfill Seepage Water in Laboratory Model Reactor (UV, Ozone and UV/Ozone)", *Chemosphere*, 30(12):2317–2331 (1995).
30. von Gunten, U., J. Huber, D. McDowell, and T. Ternes, "Oxidation of Pharmaceuticals During Ozonation: Kinetics and Product Formation", Abstract; Water Quality Technology Conference, American Water Works Association, Nov. 1–6, 2003, Philadelphia, PA, USA, 2003.
31. Weyer, P. and D. Riley. "Endocrine Disruptors and Pharmaceuticals in Drinking Water", American Water Works Association Research Foundation, Denver, Colorado (2001).
32. Yoon, Y., P. Westerhoff, S. Snyder, R. Song, and B. Levine, "A Review of Endocrine Disrupting Compounds and Pharmaceuticals by Drinking Water Treatment Processes", Proceedings Water Quality and Technology Conference. Seattle, Washington (November 2002).
33. Zwiener, C. and F.H. Frimmel, "Oxidative Treatment of Pharmaceuticals in Water", *Water Res*., 34:1881–1885 (2000).