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

Saad Y. Jasim, Ph.D., P. Eng. Walkerton Clean Water Centre

Co-Authors

- Antonette Irabelli, WUC, ON
- Linda Schweitzer, OU, MI
- Shamima Ahmed. OU, MI
- Paul Yang, MOE, ON

Endocrine Disrupting Chemicals

Research has shown that some environmental pollutants can affect reproductive hormone levels and reproductive tissues in fish. **Chemicals that can alter hormone levels** that control growth, reproduction and development are considered Endocrine **Disrupting Chemicals.**

Endocrine Disrupting Chemicals

"Environmental chemicals that interact adversely with glands and hormones that control or regulate many biological processes" (USEPA, 1998)

Pharmaceuticals and Personal Care Products

Pharmaceuticals;

- Generally used to treat symptoms
- Improved and expanded human life
- Used for veterinary & Agricultural purposes

Personal Care Products;

- Shampoos,
 Fragrances
- Herbal Remedies, etc.

Neutral Drugs and Atrazine Identified in STP Effluent



Note 1: Site 1, STP effluent; Site 2, Little River/Detroit River confluence; Site 3, Downstream of combined sewage overflow (CSO); Site 4, Reaume Park; Site 5, Raw water intake of WUC. Note 2: the concentrations are averages of 3 samples (Hua et. al 2003).

Background

- Total population served 230,000 (would increase to 250,000 by September 2005)
- Raw water source is the Detroit River
- Ozone was implemented in June 2001
- The application of ozone provided a major improvement in water quality

OBJECTIVES

Investigate the presence of Pharmaceuticals, Personal Care Products, and Pesticides in source water (Detroit River)

Compare the removal of these compounds by conventional water treatment processes vs. ozone treatment (Pilot Scale and Full Scale)

Detroit River Raw Water Quality

Low turbidity (occasional spikes)
Colour and sometimes odour
DOC usually in the range of 1.5-1.8 mg/L. High levels of DOC can reach 5.0-6.0 mg/L

Hardness (100-150 mg/L as CaCO3).



Location of Windsor's water intake and STP outflows in the Detroit River



Windsor Pilot Plant



Pilot Plant Configuration

Existing Knowledge

- In 2002, samples were collected from the pilot plant and analysis was conducted by Tulane University
- Trace levels of colfibric acid, Bisphenol A, and naproxen were detected in raw water samples only
- The findings of that study confirm the presence of pharmaceuticals in Detroit River raw water
- Drinking water appeared to be free of these compounds

March 2002 Result

			Blank	RAW	F 1	F 2	A.H.
							Weeks
	RT	Q 1	ng/L	ng/L	ng/L	ng/L	ng/L
Clofibric Acid	17.58	128	ND	103	ND	ND	ND
lbuprofen	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	90.62	66.68	80.19	91.48	93.57
Bisphenol A	32.13	357	26	NQ	NQ	NQ	NQ
Est-d4*	36.18	346	84.33	77.21	82.14	74.62	90.7
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							
**Not Quantitative							

Average for Compounds in Raw Water and Filters Effluent, September 2002



Average for Compounds in Raw Water and Filters Effluent, April 2002



Average for Compounds in Pilot Plant Raw Water and Filters Effluent, June 2003



Comparison of the Monthly Average Degradation of Carbamazepine, Atrazine, Cotinine and Caffeine, using Ozone vs. Conventional Treatment Process (without ozone)



New Study Partners

- Windsor Utilities Commission
- AWWARF
- International Joint Commission
- City of Detroit, Michigan
- Ontario Ministry of the Environment
- University of Windsor
- Oakland University, Rochester, MI
- Health Canada
- Earth Tech Canada
- Centre of Environmental Health of Ontario

New Study Objectives

- Objective 1: Identification and determination of the seasonal river loading and dynamics of major acidic and neutral PPCPs and pesticides in the intakes of the water treatment plants in Windsor and Detroit.
- Objective 2: Determination of the effect of ozone, pH control, versus conventional drinking water treatment (WUC, City of Windsor, Ontario, Canada; and Detroit Water and Sewerage Department, Detroit, MI, USA)

Objectives cont.

- Objective 3: Identification of byproducts of ozone treatment of EDCs, PPCPs, and herbicides.
- Objective 4: Fate and Transport. The fate and transport of the EDCs and PPCPs from their point of discharge to the Detroit River to the raw water intake will be evaluated in this phase of the study.

Preliminary Results

Initial preliminary results of the new two years project detected nine of 19 (Extended later to **39) target compounds including:** sulfamethoxazole, acetaminophen, cephalexin, caffeine, triclosan, naproxen, estradiol, carbamazepine, atrazine and others. 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.

Preliminary Results

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, but not in fullscale 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 indicates 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.
- The effect of the ozonation process was noticeable at the post filtration. The level of these compounds was reduced, which is related to the effect of ozone on the removal and degradation of these compounds.

WALKERTON CLEAN WATER CENTRE

 Established by the Ontario Government as one of the steps it has taken to ensure clean drinking water

Opened in Walkerton on January 4, 2005

OUR VISION & OUR GOAL

 To create a world-class institute dedicated to safe and secure drinking water for the people of Ontario.

 To become renowned for our knowledgebased, innovative approach to training.

WCWC Research Program

The Centre has established a Research Advisory Committee. The Centre activities in research will include:

 Advice to the Minister of Environment on research and development priorities.

Sponsor research;

Provide <u>Scholarships</u> to Universities, and

-Develop Partnership with research groups

WCWC Scholarships

 The Walkerton Clean Water Centre announced on February 2, 2006 its scholarship program.
 Three Scholarships for graduate studies on water quality
 All universities in Ontario are eligible

Participation in Research

The Walkerton Clean Water Centre has joined recently a research team to study the effect of membrane filtration on the removal of pharmaceuticals and endocrine disruptors.

Research Team

 University of Ottawa; Drs. T. Matsuura (Chemical Engineering, Professor Emeritus), R. Narbaitz (Civil Engineering, Professor and Chairman), A. Tremblay (Chemical Engineering, Professor, Chairman and Director of Industrial Membrane Research Center)

 National University of Singapore; Dr. S. Ramakrishna (Mechanical Engineering, Professor and Dean of the Faculty of Engineering)

Hyflux Inc.; Dr. Venki (Vice President)

Ontario Ministry of the Environment; Dr. P. Yang (Laboratory Services)

 Ontario Ministry of the Environment, Dr. Shahram Tabe (Standards Development Branch)

Walkerton Clean Water Centre: Dr. Saad Jasim (Chief Executive Officer)