

Report as of FY2007 for 2007AL65B: "Assessing the Effectiveness of Various Treatment Methods for Removing Endocrine Disrupting Compounds from Domestic Wastewater"

Publications

- Conference Proceedings:
 - ◆ Poladia, N., R. W. Peters, and R. A. Angus, November 2007, Investigation of the Effectiveness of Various Treatment Methods to Remove Endocrine Disrupting Compounds from Wastewater, in 2007 Annual AIChE Meeting, Salt Lake City, UT.

Report Follows

Synopsis: Assessing The Effectiveness Of Various Treatment Methods For Removing Endocrine Disrupting Compounds From Domestic Wastewater

Robert Angus and Robert W. Peters

Problem and Research Objectives

In recent years, it has been determined that various synthetic and natural compounds can mimic, or interfere with the action of natural hormones and disrupt the endocrine systems of humans and wildlife. These substances, collectively referred to as endocrine-disrupting compounds (EDCs), have been linked to a variety of adverse effects in both humans and wildlife. Numerous EDCs, most of which act as estrogens, have been detected in various surface waters and ground waters.

A major source of estrogens in rivers appears to be treated wastewater effluent. Investigations worldwide have detected bioactive estrogens in waters receiving treated wastewater. Municipal wastewater is a complex mixture of natural and synthetic organic chemicals. The most powerful EDCs that are common in treated wastewater include the natural hormones 17 β -estradiol (E2), its breakdown product, estrone (E1), and 17 α -ethinylestradiol (EE2), the synthetic estrogen used in birth control pills. Other non-steroidal organic chemicals have been shown to possess estrogenic activity, but are much weaker than the steroid hormones. These include the degradation products of nonionic surfactants, such as alkylphenol-polyethoxylates, and plasticizers, such as bisphenol A.

Current technologies for treating municipal wastewater are only partially successful at removing EDCs. Steroid hormones are especially difficult to remove completely. They contain steroid rings that are resistant to degradation by the microorganisms used in wastewater treatment plants. Not only are steroids not efficiently removed from the waste during treatment but, those not removed are actually activated by the treatment. Steroids are excreted in human waste as biologically inactive glucuronide or sulfate conjugates, but are hydrolyzed back to the active native molecule by microbial activity in the treatment plant. As a result, both natural and synthetic estrogens and their degradation products tend to pass through wastewater treatment systems in bioactive forms and can reach concentrations in receiving waters sufficient to produce deleterious biological effects on organisms living in the waters.

Reports of EDCs in water have raised substantial concern among regulatory agencies as well as operators of wastewater treatment facilities and water purification plants. It is clear that current methods often fail to remove steroids efficiently. It would be of great benefit to the health and well being of aquatic organisms, as well as humans living downstream from wastewater treatment plants (WWTPs), if practical methods could be developed to increase the efficiency of removal of EDCs during the treatment of municipal wastewater. Treatment technologies, such as activated carbon and reverse osmosis appear to be capable of removal of many trace contaminants. However, they are costly to install and maintain. Research is needed to better understand the fate of these compounds during wastewater treatment, removal kinetics, and to develop less expensive treatment alternatives.

The research had two major objectives: (1) to investigate the effectiveness of various advanced oxidation process (AOP) techniques (used singly or in combination) in degrading the potent steroid EE2 in aqueous solution, and (2) analyzing water and sediments in rivers in the Birmingham area receiving treated wastewater to determine whether the estrogens are present in concentrations sufficient to disrupt endocrine systems of aquatic organisms in the receiving waters.

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Methods

Advanced Oxidation Processes – Experiments were conducted using 1 L volumes of deionized water spiked with 1 μM 17 α -ethinylestradiol (EE2, Steraloids, Inc., Newport, RI, USA). After treatment, 100 mL of the water was passed through a Varian Speck C18 10 mL column (35 mg sorbent). The columns were eluted with 5 mL HPLC grade methanol, dried under nitrogen gas, and reconstituted to a volume of 100 μL with HPLC grade methanol and subjected to HPLC analysis as described below.

Treatments are done for 5, 10, 15, and 20 minutes and consist of:

Sonication (1.4 kHz), H_2O_2 (1,000 ppm), UV (16 lamps, 5 W each), O_3 (100 ppm) and the following combinations: Sonication + H_2O_2 , Sonication + O_3 , Sonication + UV, UV + O_3 , UV + H_2O_2 , UV + O_3 + H_2O_2 , and Sonication + UV + O_3 + H_2O_2 .

Analysis of River Water Samples – Samples were taken from local rivers (Five Mile Creek, Cahaba River, Buck Creek) up- and downstream from wastewater treatment plants. Samples were collected in 2 L acid-washed glass jars with 15 mL of methanol added. They were immediately placed on ice and transported to the lab. In the lab, 1.0 L of each sample was passed through a series of filters (Whatman 52 [7 μm], followed by Whatman GF/A [1.6 μm], followed by Millipore RW0304700 [0.45 μm]) to remove particulates. The filtered water samples were then each passed through a Varian Bond Elut C18 solid phase extraction column (500 mg sorbent). The columns were eluted with 5 mL HPLC grade methanol, dried under nitrogen gas, and reconstituted to a volume of 100 μL with HPLC grade methanol and subjected to HPLC analysis as described below.

HPLC Analysis - For HPLC analysis, 10 μL of the reconstituted sample was injected into a Perkin-Elmer HPLC system. The column used was a Varian CP30705 Microsorb 100 C18, particle size 3 μm , 100 \times 46 mm. Organic constituents of the sample were separated using a water:acetonitrile solvent gradient. The gradient started with a 1:1 water:acetonitrile mixture. The proportion of acetonitrile increased up to 100% in a linear fashion for a period of 20 min and then was held at 100% acetonitrile for a further 10 min. With this gradient, EE2 elutes from the column at about 6.2 min. Organic compounds eluting from the column were detected by UV absorbance at 225 nm.

Quantification of the amount of EE2 eluting from the HPLC column was done by comparison of the peak volume with that of a known sample containing 10 nmoles in 10 μL (1 mM solution). By passing a 1mM EE2 standard solution through a C18 column, extracting and reconstituting, as was done with all samples, it was determined that the process has a 78.5% extraction efficiency.

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Findings

Advanced Oxidation Processes –

Preliminary results (Table 1) indicate that the AOPs, performed individually, are not very effective in breaking down EE2 within 20 minutes of treatment. However, combinations of treatments appear to be much more effective. As further data become available, we will model the degradation kinetics of the various treatments and compare them statistically.

Table 1. Preliminary treatment performance results.

Treatment	Mean \pm std. error*
Control	6.92 \pm 0.08
O ₃	6.75 \pm 0.23
Sonication	7.57 \pm 0.02
O ₃ + Sonication	6.16 \pm 0.00

*nmoles per 10 μ L sample after 20 min treatment.

Analysis of River Water Samples – Currently, samples have been collected from the Cahaba River and Buck Creek. Some of them appear, based on retention times, to have steroids in concentrations sufficient to affect aquatic organisms living in the rivers. Further analysis with mass spectrometry will be necessary to confirm the identities of the suspected steroids.

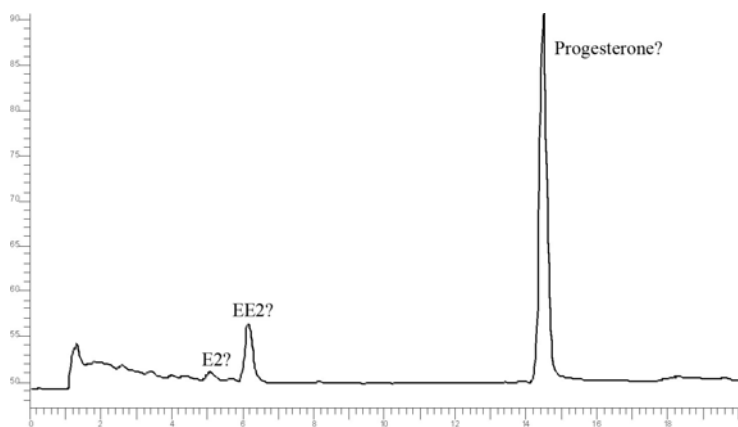


Figure 1. HPLC chromatogram of a sample of Cahaba River water collected downstream of the Riverchase WWTP in July, 2007. Peak identifications, based on retention times, are tentative. E2 = 17 β -estradiol, EE2 = 17 α -ethinylestradiol.

Although the project period is over, the project is not complete by any means. Numerous different AOP treatment combinations have been performed and await HPLC analysis. These will be done this summer by a graduate student in biology. Further river water samples will be collected and analyzed this summer as well. An updated report will be filed as these data are analyzed.