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**ASSESSMENT OF ADVANCED TREATMENT TECHNOLOGIES AND PROCESSES FOR REMOVAL OF  
CHEMICAL POLLUTANTS FOR WATER REUSE**

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**ABSTRACT:** This study seeks to observe and evaluate the elimination endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) from reclaimed water in both field and laboratory scale experiments through use of advanced oxidative treatment (AOT) technologies for treatment of reclaimed water for water reuse. In field experiments, reclaimed water treatment pilot plants that employ different AOT mechanisms will be compared. The AOTs of interest for water reuse in pilot plants include a combination of ozonation, microfiltration and peroxide for oxidative treatment of chemical contaminants and inactivation of microbial contaminants.

This research project evaluates the effectiveness of advanced treatment pilot plants at reducing the concentrations of these compounds. Native concentrations of compounds of interest and estrogenicity were determined by GC/MS and the yeast estrogen screening (YES) assay. In bench-scale research, experiments were expanded to determine how well each technology removes individual compounds of interest. In these bench-scale tests, contaminants were spiked into the reclaimed waters which were then subject to an expanded suite of advanced treatment technologies, such as O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub> photocatalysis, peracetic acid (PAA), PAA/UV and microfiltration to develop a comparative understanding of the usefulness of each technology and observe the elimination kinetics and possible daughter compounds of the contaminants.

Preliminary results indicate a decrease in the concentrations of contaminants in field-scale pilot plants during treatment with microfiltration followed by ozonation at varying doses of O<sub>3</sub>. In this field test, effluent concentration of estradiol (E2) is near 200 ng/L, which is reflected in the estradiol equivalent concentration (EEQ) determined by the YES assay. Following microfiltration, the concentration of E2 decreases below 2 ng/L as determined by GC/MS. However, the YES assay allows for greater sensitivity and allows for measurable detection of estrogenic activity throughout the treatment process. The results demonstrate how the estrogenic activity decreases throughout the treatment train to result in 98% removal in EEQ after ozonation at 5 mg/L of O<sub>3</sub>.

The concentrations of more recalcitrant pollutants (*i.e.* N,N-diethyl-3-methylbenzamide (DEET) or bisphenol-A) are also reduced by 50% or greater during the treatment process, but they are still detectable after O<sub>3</sub> and may be a cause for concern.

**KEY TERMS:** advanced oxidation technologies/processes, endocrine disrupting compounds, water reuse, yeast estrogen screen, pharmaceuticals and personal care products.

## INTRODUCTION

Many regions of the United States are experiencing rapid population growth and are facing the challenge of meeting the demands placed on their water supply for potable, irrigation, and industrial uses. To meet these hurdles, utilities are turning to reuse water as an alternative water supply source (Ammerman, 1998). However, endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), n-nitrosodimethylamine (NDMA), and other pollutants at low concentrations (e.g., halogenated solvents, disinfection by-products (DBPs), and pesticides) that have been detected in lakes and streams nationwide (Kolpin et al., 2002) have raised concern over water reuse and its impact on public health. These chemicals enter natural waters through wastewater treatment plant effluents. These findings not only suggest that conventional wastewater treatment processes do not effectively remove these compounds from the wastewater stream but also place stricter treatment guidelines on water reuse projects. Advanced oxidation processes (AOPs), such as UV/H<sub>2</sub>O<sub>2</sub> and

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O<sub>3</sub> generate highly reactive, nonselective radical species that degrade many of these pollutants, forming potentially less harmful oxidation products (Oppenländer, 2003).

In this study, we investigated the elimination of commonly occurring EDCs, PPCPs, and other emerging pollutants of concern from reclaimed water in field and laboratory scale experiments designed to comparatively evaluate different advanced treatment technologies. The goal is to assess the effectiveness of contaminant removal and suitability for water reuse applications of different oxidative advanced treatment technologies. The field experiments were based at pilot wastewater reuse treatment plants and focused on the effects of ozonation, UV, UV/H<sub>2</sub>O<sub>2</sub>, and/or microfiltration as treatment technologies on the native concentrations of contaminants. In laboratory experiments, the treatments evaluated are being expanded to include the effects of O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub> photocatalysis, peracetic acid (PAA), and PAA/UV on contaminants spiked into reuse water. Many of these technologies have been individually demonstrated to reduce the concentration of certain contaminants in laboratory experiments (Snyder et al., 2006, Rosenfeldt and Linden, 2004; Huber et al. 2003; Oppenländer, 2003). However, direct comparison of these technologies side-by-side under conditions as they may be employed to treat reclaimed waters is limited.

## EXPERIMENTAL

The chemicals evaluated in this study are listed in Table 1 and represent a selection of compounds that have come under scrutiny due to their estrogenic activity or their persistence in conventional treatment processes (Westerhoff et al. 2005). Analytes were extracted from aqueous samples with C-18 SPE disks or Envi-Carb SPE cartridges and determined by GC/MS after derivatization. Additionally, total estrogenic activity was also determined by yeast estrogen screen (YES) assays. This bioassay detects compounds that bind with the human estrogen receptor (hER) that is integrated into yeast cells (*Saccharomyces cerevisiae*). The YES assay allows for greater sensitivity to quantitatively detect a variety of known and unidentified compounds that exhibit estrogenic activity via a receptor mechanism (Routledge and Sumpter, 1996) as compared to conventional chemical analyses. The YES assay will also detect estrogenic decay products that may not be quantitatively assessed in conventional chemical analyses allowing for more accurate assessment of the effectiveness of each technology to remove overall estrogenic compounds to trace levels.

In field-scale experiments at pilot water reuse facilities, native or indigenous levels of contaminants and estrogenic activities in the reuse water were determined (Table 1). In some experiments, NDMA was spiked at higher concentrations to evaluate elimination targets. In ongoing bench-scale research, the list of analytes of interest is being expanded to determine the effectiveness of the expanded list of technologies at removal of individual compounds (Table 1). In these bench-scale tests, contaminants are being spiked into the reclaimed waters at higher (1-100 µM) concentrations in order to avoid errors originating from extraction procedures and to produce better resolution of degradation kinetics and breakdown compounds. The spiked waters are being treated with an expanded suite of oxidation processes: O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub> photocatalysis, peracetic acid (PAA) and PAA/UV. UV light will be provided from both medium- and low pressure (MP and LP) Hg lamps. Waters from different wastewater treatment plants across the U.S. will be employed such that a variety of conditions (e.g., radical scavenging, TOC, turbidity or UV absorbance) can be taken into account when comparing treatment choices.

Table 1. Chemicals evaluated in field and bench-scale experiments.

Compound name (abbreviation)	Environments evaluated	
	Field Scale <sup>1</sup>	Bench Scale <sup>2</sup>
n-nitrosodimethylamine (NDMA)	X	X
n-octylphenol (OP)	X	X
n-nonylphenol (NP)	X	X
N,N-diethyl-3-methylbenzamide (DEET)	X	X
Triclosan (TCS)	X	X
Bisphenol-A (BPA)	X	X
Estrone (E1)	X	X
Estradiol (E2)	X	X
Ethinyl estradiol (EE2)	X	X
Estriol (E3)	X	X
Progesterone (PS)		X
Atrazine (ATZ)		X
tri(2-chloroethyl) phosphate (TCEP)		X
Carbamazepine		X
Metolachlor (MET)		X

<sup>1</sup> native concentrations of contaminants measured

<sup>2</sup> contaminants spiked into reclaimed water

## RESULTS AND DISCUSSION

During the first phase of the project, pilot-scale experiments were conducted in the field at treatment plants that employ ozonation, microfiltration and peroxide treatment. Microfiltration of wastewater effluent revealed reduction of endocrine disruptors and estrogenic activity by 40-90% (Figure 1a), suggesting that many of the contaminants are particle bound. This conclusion is justified by the overall low water solubility or high hydrophobicity of the analytes. Ozonation reduced contaminants further to achieve 90% or greater removal of estrogenic activity or measured estrogenic compounds (Figure 1b). Concentrations of EDCs and other contaminants in pre-microfiltration waters were in the ng/L range. Similarly, ozonation and addition of  $\text{H}_2\text{O}_2$  at 5 mg/L also achieved elimination of estrogenic activity and associated estrogenic compounds by 90% or greater (results not shown). The total sum of estrogenic compounds, as measured by GC/MS appears higher compared to the total estrogenicity as measured with YES due to varying potency of many of the estrogenic compounds that are present, many of which are unknown or not identified by direct analysis (GC/MS) in this study (e.g., alkylphenol ethoxylates).

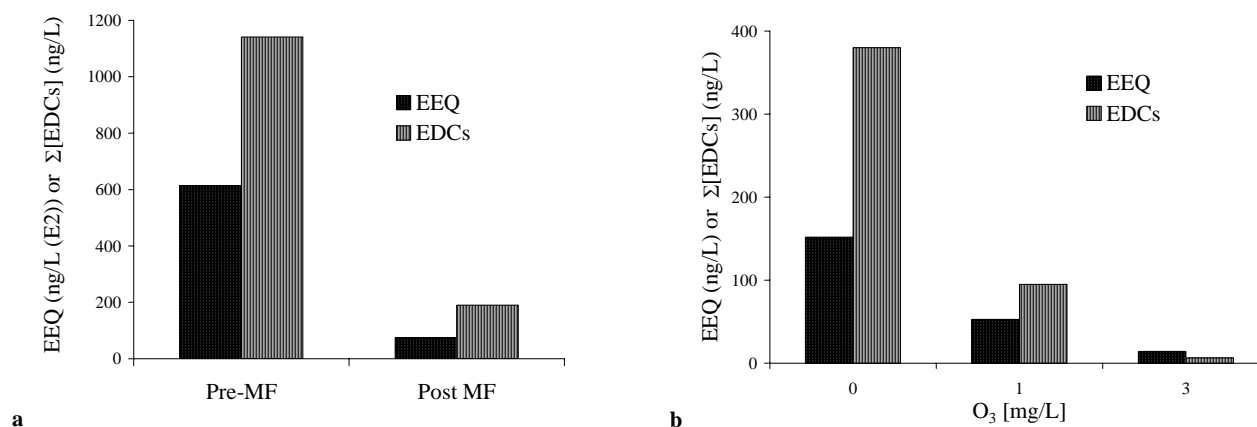


Figure 1. a: Reduction of the sum of concentrations of measured estrogens (NP, OP, BPA, E1, E2, EE2 and E3) as determined by GC-MS analysis and estrogenic activity as measured with YES (EEQ represents estradiol equivalent concentrations measured by YES). b: Reduction of the sum of concentrations of measured estrogens and estrogenic activity during treatment with  $\text{O}_3$ .

In this same study, *N,N*-diethyl-meta-toluamide (DEET) did not appear to be degraded or eliminated from water either by microfiltration, ozonation or combination of  $\text{O}_3/\text{H}_2\text{O}_2$  (Figure 2). This compound is more recalcitrant to these treatment processes and its breakdown is currently being investigated in bench tests, along with other compounds (e.g., carbamazepine, metolachlor). In similar research, however, Snyder et al. (2006) observed elimination of DEET by 76% at 2.5 mg/L of  $\text{O}_3$ , which suggests that the native water matrix may play a role in removal efficiencies.

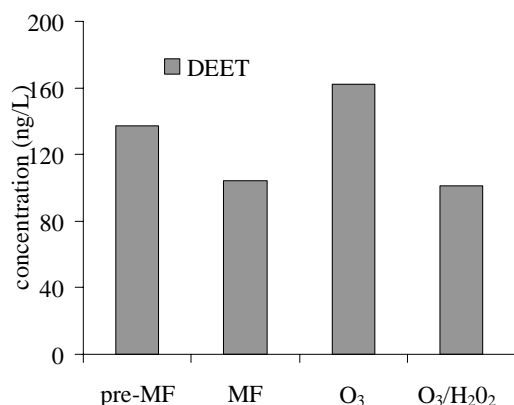


Figure 2. Concentrations of DEET in a water reuse pilot facility prior to treatment with microfiltration (pre-MF), following microfiltration (MF) and after ozonation and combination of ozonation and microfiltration. The concentrations of both  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  were 5 mg/L when employed.

Preliminary bench-scale experiment results indicate effective removal of estrogens and androgens under UV/H<sub>2</sub>O<sub>2</sub> (Figure 3), with either LP or MP lamps. However, only small removal of ATZ, MET and TCS is observed, even though many of these compounds are easily degraded in buffered DI water, which suggests that the reclaimed water matrix interferes with the UV/H<sub>2</sub>O<sub>2</sub> process. Further results of the bench-scale studies are expected to reflect those obtained in field measurements and reveal limitations or advantages of certain treatment processes. Through an expanded array of oxidative processes, as outlined above, the susceptibility of different compounds to each treatment process will be evaluated. This knowledge may aid in development of optimal treatment technologies that can surpass the limits observed in the field tests (Figures 1 and 2), where a measurable contaminant residual remained after treatment or the compounds were not degraded appreciably. Therefore, bench scale testing also aims to identify those oxidative processes that are most effective at treatment of less labile compounds that resist conventional wastewater treatment or more commonly employed AOPs such as UV/H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub>.

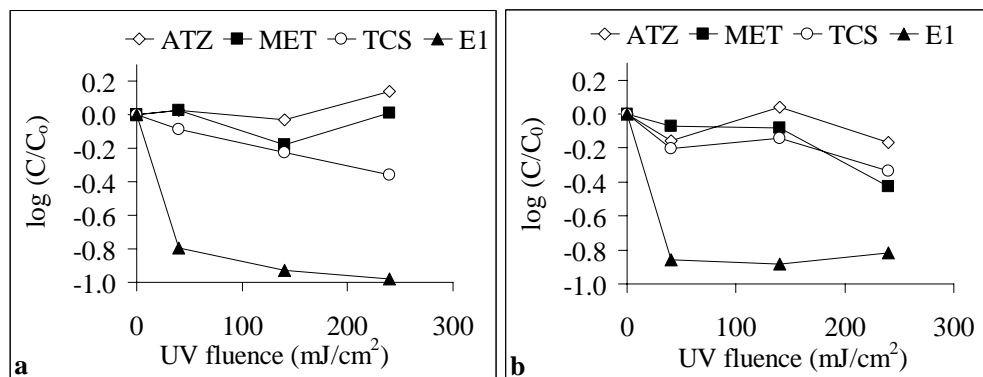


Figure 3. Elimination of spiked atrazine (ATZ), metolachlor (MET), triclosan (TCS) and estrone (E1) in reclaimed water with UV/H<sub>2</sub>O<sub>2</sub> in a bench-scale experiment. **a:** Medium pressure UV; **b:** low pressure UV (254 nm). Concentration of H<sub>2</sub>O<sub>2</sub> was 5 mg/L

The differences in bench-scale removal efficiencies for each contaminant are anticipated to be similar to field experiments. More persistent compounds, such as DEET or TCEP, which have been reported to be difficult to eliminate from water through some oxidative processes (e.g., chlorination, ozonation) will exhibit different removal efficiencies during different treatment processes (Snyder et al., 2006; Westerhoff et al., 2005). We seek to expand the bench scale experiments to include more recalcitrant compounds (such as TCEP) to evaluate optimal removal mechanisms. Additionally, we expect the variations in the water matrices of the tested reuse waters (e.g., turbidity, UVT, TOC, etc.) will have a significant impact on the efficiency of the various treatment processes. For instance, photosensitizing constituents such as natural organic matter and nitrate may contribute to the formation of radical species that aid in the removal of contaminants. Or, conversely, OH radical scavengers such as natural organic matter, carbonates may react preferentially with radical species and interfere with the AOP process.

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