



## Endocrine Disruptors, Pharmaceuticals, and Personal Care Products in Drinking Water: An Overview of AwwaRF Research to Date

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Endocrine disrupting chemicals (EDCs), pharmaceutically active compounds (PhACs), and personal care products (PPCPs) are important classes of emerging contaminants that occur ubiquitously in municipal wastewater effluents and subsequently occur in source waters for drinking water treatment plants. While EDCs, PhACs, and PPCPs have been known to occur in U.S. waters for over 30 years, it is only in the past decade that information linking these chemicals to impacts on aquatic species has brought the issue to the forefront. These compounds are receiving growing attention from the scientific community, regulatory agencies, and the public at large because a number of them have been reported to interfere with human and animal hormone systems, and thus have the potential to produce adverse developmental and reproductive outcomes at sub-nanogram levels of exposure.

In light of the concern regarding the potential risk associated with these

compounds, the Awwa Research Foundation has established a comprehensive research program to address the issue and provide necessary information to drinking water utilities. In addition, recognizing the global nature of the issue, the Foundation has partnered on several research initiatives with domestic and international agencies such as the Water Environment Research Foundation (WERF), the WaterReuse Foundation, and the Global Water Research Coalition (GWRC).

This article highlights major results from a number of AwwaRF's completed studies and some preliminary results from ongoing studies.

### **Occurrence**

A large number of occurrence studies have been published in the literature but only a few studies, including several funded by AwwaRF, have focused on drinking water supplies. For each of the AwwaRF occurrence studies discussed below,

### **AwwaRF Reports on EDCs, PhACs, and PPCPs**

- ***Assessment of Waters for Estrogenic Activity*** (2003, order #90940F)
- ***Endocrine Disruptors and Pharmaceuticals in Drinking Water*** (2001, order #90849)
- ***Occurrence Survey of Pharmaceutically Active Compounds*** (2005, order #91051)
- ***Removal of Iodinated X-Ray Contrast Media During Drinking Water Treatment*** (2004, order #2788)
- ***Triclosan Reactivity in Chlorinated and Monochloraminated Waters*** (2006, order #91134)
- ***Water Quality Improvements During Aquifer Storage and Recovery*** (2005, order #91056F)

sensitive chemical and/or biological methods were developed and tested prior to conducting the studies.

***Assessment of Waters for Estrogenic Activity*** (2003, report order #90940F) consisted of a survey of U.S. source and finished waters to determine the presence of estrogenic compounds in water using *in vivo* tests in combination with *in vitro* tests. Ninety finished water samples from 72 facilities were tested using the E-screen bioassay. The vast majority of the finished water samples (76 samples, or 84 percent of those tested) did not contain estrogenic activity above the level of detection for this assay (0.029 nanogram(s) per liter [ng/L] estradiol equivalents). Thirteen of the remaining 14 samples were below 0.27 ng/L estradiol equivalents. In contrast to the finished waters, 61 percent of source water samples exhibited some estrogenic activity. When *in vivo* bioassays were performed, no significant responses were found in fish exposed to drinking water sources.

***Occurrence Survey of Pharmaceutically Active Compounds*** (2005, order #91051) used chemical analysis to determine the presence of PhACs in water. Eighteen drinking water sources were monitored. The list of compounds selected for monitoring was based on an evaluation of the use patterns of prescription drugs and their metabolism. The study showed that although a large number of PhACs are used in the U.S., a relatively limited number of the compounds can be detected with traditional analytical methods.

Project #2758, "**Evaluation of Conventional and Advanced Treatment Processes to Remove Endocrine Disruptors and Pharmaceutically Active Compounds,**" investigated the occurrence of EDCs and PhACs in 20 full-scale drinking water facilities. The insect repellent DEET was the most common contaminant of both raw and finished drinking waters, occurring in 100 percent of raw water

samples and 90 percent of finished water samples. Carbamazepine, dilantin, sulfamethoxazole, and meprobamate were the pharmaceuticals which occurred most frequently in raw water (>80 percent of samples) while meprobamate, dilantin, ibuprofen, and iopromide occurred most frequently in finished drinking water (>65 percent of samples). In general, pharmaceuticals rarely occurred in concentrations greater than 10 ng/L in raw water and finished drinking waters. Atrazine, a widely used herbicide which is a known EDC, occurred at the highest concentrations of any contaminant tested in both raw and finished water, but far below the maximum contaminant level of 3 micrograms per liter ( $\mu\text{g/L}$ ). Hormones occurred infrequently or not at all, with no detections of 17  $\beta$ -estradiol or ethinyl estradiol at a reporting limit of 1.0 ng/L. The final report for this project is expected to be published in mid-2007.

### **Treatment**

Project #2758, referred to above, also involved testing of physical, chemical, and biological treatment processes to determine removal potential at environmentally relevant concentrations. Process testing was completed at bench scale, pilot scale, and full scale. The list of chemicals investigated included 36 EDCs and PPCPs representative of the types of chemicals known or likely to occur in source waters, with a broad range of physical-chemical structure behavior. Several key results came from evaluating various treatment processes:

- Coagulation and flocculation—During spiking studies using natural water, hydrophobic compounds were able to bind to particles and were subsequently removed during settling, while more water soluble contaminants were not removed. Coagulation at bench scale was conducted using both alum and ferric chloride. Few EDCs and PPCPs could be removed

by coagulation or softening alone. In summary, coagulation was found to be largely ineffective for EDCs/PPCP removal at bench, pilot, and full scale.

- **Activated carbon**—Hydrophobic compounds exhibited higher removal using activated carbon as compared to compounds that are more hydrophilic. Powdered activated carbon (PAC) was found to be highly effective for removing target compounds; however, PAC dose and contact time were critical in order to achieve efficient contaminant removal. All target compounds could be removed by granulated active carbon (GAC), but water soluble contaminants could break through the GAC relatively quickly. The x-ray contrast media iopromide and the pharmaceuticals ibuprofen, meprobamate, sulfamethoxazole, and diclofenac were some of the compounds found to be most recalcitrant for activated carbon removal. Steroid hormones and other hydrophobic contaminants were effectively removed by activated carbon.

- **Free chlorine and chloramines**—Both chlorine and chloramines have the potential to react with various EDCs and PPCPs. Free chlorine is a stronger and faster oxidant than chloramine. Chlorine reacted with phenol and amine functional groups, but was nearly non-reactive with most ketone and alcohol groups. It is also important to note that oxidation with chlorine is pH-dependent, with increased oxidation at lower pH. Free chlorine was found to oxidize approximately half of the EDCs and PPCPs investigated. Hormones with a phenol functional group were rapidly oxidized by free chlorine, while hormones with a ketone group were only partially oxidized by free chlorine. Chloramine was much less efficient at removing EDCs/PPCPs when compared to free chlorine. The antibiotics sulfamethoxazole, trimethoprim, and erythromycin are among the compounds that showed high removal by free chlorine but low removal by chloramine.

## Ongoing Projects

- **“Cooperative Research on Endocrine Disruptors”** (with GWRC) (project #2914)
- **“Comprehensive Utility Guide for Endocrine Disruptors and Pharmaceuticals In Drinking Water”** (project #3033)
- **“Effects of Microbes on the Leaching of Vinyl Chloride and Organotin From PVC Piping Used in Drinking Water Delivery”** (project #2991)
- **“Evaluation of Conventional and Advanced Treatment Processes to Remove Endocrine Disruptors and Pharmaceutically Active Compounds”** (project #2758)
- **“Impact of UV and UV-Advanced Oxidation Processes on Toxicity of Endocrine-Disrupting Compounds in Water”** (project #2897)
- **“Removal and Fate of EDCs and Pharmaceuticals in Bank Filtration Systems”** (project #3136)
- **“Research Strategy Workshop on Pharmaceuticals and Personal-Care Products in the Water Cycle”** (with GWRC) (project #2972)
- **“Toxicological Relevance of Endocrine Disruptors and Pharmaceuticals in Drinking Water”** (project #3085)
- **“Water Quality Changes Associated With Aquifer Storage and Recovery”** (project #2974)

- **Ozone**—Ozone is a powerful oxidant and was found to be highly effective for reducing the concentration of the majority of EDCs and PPCPs tested. Of particular interest, it was observed that ozone could remove the ketone steroids (testosterone, progesterone, and androstenedione), which were not appreciably removed by chlorine. Ozone was found to be highly effective for the removal of most target compounds with the exception of the flame retardant tris-chloroethylphosphate (TCEP). The herbicide atrazine, the x-ray contrast media iopromide, and the anti-anxiety pharmaceutical meprobamate were also challenging to oxidize, with less than 50 percent removal at typical drinking water ozone doses. Ozone in combination with hydrogen peroxide forms an advanced oxidation process (AOP), which produces elevated concentration of hydroxyl radicals. Hydroxyl radicals are extremely powerful oxidizers and are essentially non-selective. However, the addition of hydrogen peroxide for advanced oxidation provided only a minor increase for removal of EDCs and PPCPs tested.
- **Ultraviolet (UV)**—Most drinking water applications of UV disinfection use relatively low-energy UV. At a typical disinfection dose of 40 millijoules per square centimeter ( $\text{mJ}/\text{cm}^2$ ), UV was ineffective for the removal of most target compounds. The antibiotic sulfamethoxazole, the antimicrobial triclosan, and the pharmaceutical diclofenac were removed by greater than 50 percent while the remaining 33 target compounds exhibited only poor removal. High-energy UV is more oxidative and thus able to degrade many organic contaminants. UV at higher doses ( $>400\text{mJ}/\text{cm}^2$ ) was able to remove several target compounds by direct photolysis. The combination of higher dose UV ( $400\text{ mJ}/\text{cm}^2$  and higher) with hydrogen peroxide (3 milligrams per liter [ $\text{mg}/\text{L}$ ] and above) provided excellent removal of most target compounds.
- **Membrane treatment**—Ultrafiltration (UF) and microfiltration (MF) were of little value for target compound removal in general. Some data suggest that UF/MF membranes can absorb target compounds either directly to the membrane surface or to organic particles on the membrane. Nanofiltration (NF) provided good removal of many target compounds. Reverse osmosis (RO) was highly effective for removing all target compounds. Trace quantities of some target compounds were able to breach RO membranes; however, in a double-pass RO system, all target compounds were removed to less than detection.
- **Magnetic ion-exchange media (MIEX®)** was found to be ineffective for the removal of most EDCs and PPCPs. Diclofenac and triclosan were well removed ( $>80$  percent) while naproxen had moderate removal ( $>50$  percent) using MIEX®. All other compounds were removed by less than 50 percent, with most less than 20 percent. MIEX® did not appear to be a viable process for removal of the majority of EDCs and PPCPs tested, but is effective for contaminants that are negatively charged at ambient pH (i.e., triclosan and diclofenac).
- **Biodegradation**—Batch biologically active sand tests showed that acetaminophen, caffeine, gemfibrozil, ibuprofen, and estrogen hormones were rapidly biodegraded, while atrazine, carbamezepine, iopromide, and others were slowly degraded. A simulated aquifer storage and recovery (ASR) experiment using soil columns revealed similar trends, although most compound removal was superior in the soil column as compared to batch tests. Removal of target compounds during soil permeation of reuse water used for irrigation was evaluated. Few of the compounds were detected in the source water, but those detectable were rapidly attenuated except

for the antibiotic sulfamethoxazole. Biologically-active carbon was quite effective for the removal of most target compounds, presumably by binding to the activated carbon as opposed to biodegradation. Riverbank filtration (RBF) was found to be effective for the majority of target compounds except for atrazine, carbamazepine, dilantin, and TCEP. A computer model for biodegradation was also applied and agreed reasonably well with removal trends observed.

Additional results for attenuation of selected EDCs through ASR are reported in ***Water Quality Improvements During Aquifer Storage and Recovery*** (2005, order #91056F). The results show better removal under aerobic ASR conditions. The effects of co-metabolism on removal of the same EDCs is currently being investigated in project #2974, ***Water Quality Changes Associated With Aquifer Storage and Recovery***, a partnership project with the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO). EDC removal through RBF is being further investigated in ongoing project #3136, ***Removal and Fate of EDCs and Pharmaceuticals in Bank Filtration Systems***, a collaboration project with Water Technology Center (TZW Germany).

## Health Effects

One of the most highly anticipated projects conducted by the Foundation on the topic of EDCs, PhACs, and PPCPs is project #3085, ***Toxicological Relevance of Endocrine Disruptors and Pharmaceuticals in Drinking Water***. The study, which is expected to be completed in 2008, is assessing the potential human health impacts from trace concentrations of EDCs and pharmaceuticals in drinking waters. A screening-level review of mammalian toxicity data was conducted to identify those compounds for which sufficient data exist in order to characterize their potential to produce human health effects after prolonged, low-level exposures. A comprehensive literature review and human health risk assessments were conducted for the selected compounds. Risk assessments will result in recommendations for levels in drinking water that are protective of human health. Health effects data were compiled and acceptable daily intakes were developed for 14 EDCs and 16 pharmaceuticals.

The study will also compare drinking water risks from these contaminants with risks from similar chemicals found in bottled water and other dietary items.

## Future Directions

AwwaRF recognizes that issues related to EDCs, PhACs, and PPCPs will continue to challenge water utilities and the drinking water community. In January 2007, AwwaRF's Board of Trustees authorized the development of a strategic research initiative aimed at identifying and resolving these issues. EDCs, PhACs, and PPCPs were selected as one of the first two topics that will be addressed by AwwaRF's new strategic research initiative program. The initiative represents a commitment by AwwaRF to sustain a multi-year, multi-project research program that will significantly advance knowledge and identify solutions for key problems associated with these compounds. The initiative will begin in 2007 with the development of overarching objectives and a detailed research agenda.

An additional literature review was conducted to assess human exposure and toxic responses to natural products that may act as EDCs, primarily naturally occurring phytoestrogens found in plants. A comparative risk assessment will be conducted to compare the risk of trace estrogenic EDCs in drinking waters to that from intake of natural estrogens in the human diet.

### Summary

Results to date from AwwaRF research on EDCs, PhACs, and PPCPs show that although these compounds can sometimes be found in drinking water supplies, the concentrations at which they are found are extremely small and are believed highly unlikely to pose any threat to human health via drink water exposure. The presence of these compounds in drinking water supplies often correlates directly to upstream discharge of treated wastewater. Utilities that wish to reduce the concentrations of the majority of these compounds should consider advanced processes such as ozonation, AOPs, GAC, RO, or tight nanofiltration membranes, or a combination of processes. However, conventional drinking water plants using free chlorine disinfection will be able to destroy most natural and synthetic estrogenic steroid hormones, which are the compounds of greatest concern due to their potency.

While research has established the occurrence and treatability of many representative EDCs, PhACs, and PPCPs in drinking water, additional research is needed to enable water utilities and

regulators to determine the toxicological significance of these emerging contaminants and the appropriate level of treatment to reduce the associated risk. If water utilities choose to (or are compelled to) implement additional treatment measures for these compounds based solely on occurrence data, without regard to toxicological significance, there is a risk of spending tremendous amounts of public funds for very little public health benefit. 💧

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