Removal of Endocrine Disruptors, Pharmaceuticals, and Personal Care Products During Water Treatment

Paul Westerhoff, Ph.D., P.E. *– Associate Professor, Department of Civil and Environmental Engineering, Arizona State University*

The drinking water industry faces a number of questions as the regulatory and public communities become aware of the presence of compounds in water that were previously not detectable. With analytical advances over the past decade, several new classes of organic compounds in the part-per-trillion (ppt) range have been identified. Collectively termed endocrine disrupting compounds (EDCs) or pharmaceuticals and personal care products (PPCPs), these compounds raise a central question: If EDCs and PPCPs are present in raw drinking water supplies, will conventional water treatment processes remove the compounds, or are advanced treatment processes necessary?

With funding from AWWA Research Foundation, researchers at Arizona State University and the Southern Nevada Water Authority conducted bench-scale studies that simulate water treatment plant processes on model and natural waters spiked with 30 to 80 different EDC and PPCP compounds at environmentally relevant concentrations. General conclusions from these treatability studies are as follows:

Coagulation (alum or ferric) removed less than 20 percent of the compound concentration. Slightly higher removal rates were observed in the presence of a hydrophobic dissolved organic carbon (DOC) material, indicating some partitioning of hydrophobic EDC and PPCP compounds with the DOC and concurrent removal. EDCs or PPCPs associated with particulate matter (i.e., that were adsorbed) were effectively removed during coagulation, sedimentation, and nonbiological filtration.

Lime softening at pH 9 or pH 11 removed less than 20 percent of the compound concentration.

Powder-activated carbon (PAC) added with a 4 hour contact time in a 5 milligram per liter (mg/L) dose achieved more than 90 percent removal of many of the EDC and PPCP compounds studied; some compounds were removed to below detection levels. Other compounds had lower removals (40 to 60 percent); these included ibuprofen, sulfamethoxazole, meprobamate, and iopromide. A trend in removal capability was observed, with hydrophobic compounds (octanol-water partition coefficient ($\log K_{ow}$)>5) having better removal than more polar compounds (deprotonated acids). Removal was dependent upon the PAC brand, PAC dose, and the presence of DOC in the water.

Biofiltration was simulated using biological acclimated sand. Some compounds appeared to biodegrade; these included acetaminophen, caffeine, DEET, estrone, estradiol, naproxen, ibuprofen, and gemfibrozil. Almost all showed some partitioning into the biofilm, but lab-scale tests left unclear whether the sorption mechanism is sustainable. Other compounds were persistent, such as iopromide and meprobamate, and were not biodegraded.

Chlorination (1 to 6 mgCl_2/L dose to achieve 1 mgCl_2/L residual after 24 hours) either removed compounds by more than 90 percent or led to less than 20 percent removal. More reactive compounds contained aromatic structures with hydroxide functional groups, while less reactive compounds had carboxyl groups or lacked aromatic structures. The use of some chlorine residual-quenching agents such as thiosulfate appeared to react with EDCs and PPCPs, and should be avoided in monitoring studies.

Ozonation (1 to 8 mgO_3/L for 3 to 5 minutes) oxidized similar compounds as chlorination but achieved slightly higher percentage removals. Compounds that were less reactive, including progesterone, testosterone, iopromide, musk ketone, meprobamate, and TCEP, lacked aromatic carbon with attached hydroxyl functional groups. Addition of hydrogen peroxide during ozone addition is an advanced oxidation process (AOP) which forms hydroxyl radicals that slightly increased the removal of most EDCs and PPCPs compared to ozone addition only.

Membrane treatment (ultrafiltration and nanofiltration) demonstrated a range of removal capability in bench-scale tests using dead-end cells. Ultrafiltration (1000 dalton charged membrane) adsorbed many hydrophobic compounds ($\log K_{ow}$>4) and led to less than 30 percent of the initial compound concentration in the permeate. Nanofiltration also exhibited a high adsorption capacity for hydrophobic EDCs and PPCPs. In the bench-scale tests, hydrophobicity leading to adsorption, and polarity leading to charge repulsions appeared more important than molecular weight in overall EDC or PPCP removal. Although not directly tested during the study, the literature strongly suggests most EDCs and PPCPs would have high removal by reverse osmosis (RO). However, most drinking water facilities are not likely to install RO because of pretreatment requirements, their cost relative to other technologies, and the corrosive nature of the finished water.

In general, removal of an EDC or PPCP was dependent upon its intrinsic chemical properties, including molecular weight, octanol-water partition coefficient, aromatic carbon content, and functional group composition. Therefore, as additional compounds are identified in water, a fundamental approach can be utilized to evaluate their potential for removal.

Initial validation of findings from the bench-scale studies has begun. Pilot-scale and full-scale evaluations are underway. Preliminary pilot-scale findings confirm the trends and general percentage removal capabilities observed at bench-scale. Therefore, some important conclusions can be drawn.

• Conventional treatments such as coagulation, sedimentation, and filtration will remove less than 25 percent of most EDCs and PPCPs.

• If chlorine is used during conventional treatment, then approximately one-third of the EDCs and PPCPs examined will have greater than 90 percent removal for compounds with aromatic carbon and amine or hydroxyl functional groups; less than 20 percent removal of other compounds can be expected. The byproducts of EDCs and PPCPs reactive with chlorine have not been identified and may be of concern. Preliminary work using bioassays suggests that chlorination byproducts of 17ß-estradiol may exhibit estrogenic activity.

• The addition of PAC to conventional water treatment plants, similarly to what is currently used seasonally to control odor and taste, may be effective in removing more than 75 percent of EDCs and PPCPs.

• Ultraviolet (UV) irradiation is capable of oxidizing aromatic EDCs and PPCPs, but requires approximately 100 times higher UV dosages (greater than 5000 mJ/cm^2) than those required for microbial disinfection (5 to 50 mJ/cm^2). UV irradiation is unlikely to be used for EDC or PPCP removal in surface water treatment plants, but may be appropriate for smaller well head treatment systems.

• Advanced treatment processes such as membranes and AOPs can be very effective at removing EDCs and PPCPs.

Byproducts of oxidation and metabolites of biodegradation of EDCs and PPCPs are important future research topics, to identify the daughter products and determine whether they pose any health risks. Upgrading conventional treatment plants to include ozone and biofiltration on granular-activated carbon media together should be very effective at removing EDCs and PPCPs. Many EDCs and PPCPs that are not oxidized well by ozone were reduced during biofiltration and/or adsorption. Biofiltration should aid in reducing oxidation byproducts of EDCs and PPCPs. This combined treatment should be the focus of future research.

A thought to ponder: a glass of distilled water sitting on a counter overnight in a well-ventilated office building will accumulate detectable levels of several PPCP compounds such as stimulants, antidepressants, and fragrances, so is it appropriate to remove these compounds to below detection limits in water treatment plants? What level of removal or level of analytical detection is appropriate? Public perception rather than health effects might drive water treatment plants to remove many PPCP compounds. The water industry already uses ozone and/or activated carbon processes for aesthetic reasons to remove organic trace and odor compounds (methylisoborneol, Geosmin) that occur at ppt levels. The drinking water industry must determine what levels of removal are necessary, and what concentrations of EDC and PPCP compounds will be acceptable to the public and to regulatory communities.

Contact Paul Westerhoff at p.westerhoff@asu.edu

Southern Nevada Water Authority's new 900 million gallon per day ozone treatment facility. Photo courtesy of Carollo Black & Veatch, who designed the facility.