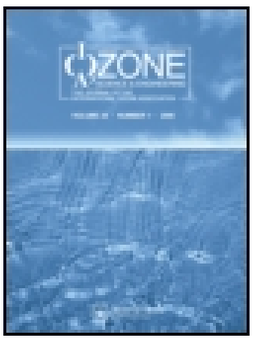

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Occurrence, Treatment, and Toxicological Relevance of EDCs and Pharmaceuticals in Water

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Over the past decade a great amount of interest has arisen regarding the occurrence and fate of trace organic contaminants in the aquatic environment. Of particular concern are human hormones and pharmaceuticals, many of which are ubiquitous contaminants in conventional municipal wastewater treatment plant effluents when measured with ng/L detection limits. As analytical procedures and bioassay techniques become more readily available and increasingly sensitive, new contaminants will be discovered. The presence or absence of any chemical in a wastewater effluent is essentially a function of analytical detection capability. This poses a unique challenge for drinking water treatment plants intent on the removal of organic contaminants, as complete removal is merely a reflection of reporting limits. The investigation described here sought to determine the occurrence, treatment, and human health relevance of a chemically diverse group of emerging contaminants.

Keywords Ozone, Advanced Oxidation Process, Pharmaceuticals, Endocrine Disruptors, EDCs

INTRODUCTION

In 1965 Stumm-Zollinger and Fair of Harvard University published the first known report indicating that steroid hormones are not completely eliminated by wastewater treatment (Stumm-Zollinger and Fair, 1965). In an article published in 1970, Tabak and Bunch investigated the fate of human hormones during wastewater treatment and stated "since they (hormones) are physiologically active in very small amounts, it is important to determine to what extent the steroids are biodegraded" (Tabak and Bunch, 1970). As early as the 1940s, scientists were aware that certain chemicals had the ability to mimic endogenous estrogens and androgens (Schueler, 1946; Sluczewski and Roth, 1948). In 1977, researchers from the University of Kansas published the first known report specifically addressing the discharge of pharmaceuticals from a wastewater treatment plant (Hignite and Azarnoff, 1977). Despite these early findings, the issue of steroids and pharmaceuticals in wastewater outfalls did not gain significant attention until the 1990s, when the occurrence of natural and synthetic steroid hormones in wastewater was linked to reproductive impacts in fish living downstream of outfalls (Purdom et al., 1994; Desbrow et al., 1998; Routledge et al., 1998).

Since the initial link between trace contaminants (sub-μg/L) in wastewater effluents and ecological impacts in receiving waters, many studies have focused on the occurrence of these contaminants (Halling-Sorensen et al., 1998; Ternes et al., 1998; Daughton and Ternes, 1999; Snyder et al., 1999; Metcalfe et al., 2000; Ternes and Hirsch, 2000; Snyder et al., 2001; Kolpin et al., 2002; Vanderford et al., 2003). As a result, pharmaceuticals and steroid hormones have been detected in many water bodies around the world (Kolpin et al., 2002; Cargouet et al., 2004; Petrovic et al., 2004). One major contributor of such widespread contamination is municipal wastewater discharge, which impacts surface water quality by contaminating receiving water bodies with chemicals not completely removed by current wastewater treatment processes.

Indirect potable water reuse, either planned or unplanned, can occur when wastewater treatment plant discharge comprises a significant portion of the receiving stream's total flow. In some cases, effluent dominated surface waters are used as source waters for drinking water treatment facilities. Global water sustainability depends in part upon effective reuse of water. In particular, the reuse of municipal wastewater is critical for irrigation and augmentation of potable water supplies. However, public perception and concern regarding trace

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hormones and pharmaceuticals has generated resistance to reuse projects. It is necessary to obtain accurate information on the elimination of these contaminants from wastewater, the impact of wastewater discharge on surface water or groundwater drinking water supplies, and the removal efficiency of the remaining contaminants by conventional and advanced drinking water treatment processes.

This project sought to determine the treatment efficacy of various processes at bench, pilot, and full scale for the removal of emerging contaminants by monitoring the concentration decrease of the parent compounds. Reaction by-products and the corresponding structural changes were beyond the scope of this study; however, oxidative processes generally do not result in appreciable mineralization and reaction byproducts are expected. This study shows that the majority of emerging contaminants can be readily oxidized using ozone or UV-advanced oxidation. Free chlorination effectively removed more target compounds than chloramination. Magnetic ion-exchange provided minimal contaminant removal; however, contaminants that were negatively charged at ambient pH were well removed. Activated carbon, both in powdered and granular forms, was effective for contaminant adsorption. Carbon type, contact time, and dose or regeneration are influential parameters in removal efficacy by activated carbon. Although not discussed here, tight membrane filtration (reverse osmosis and nanofiltration) was more effective than loose membrane filtration (ultrafiltration and microfiltration). No single treatment process was capable of removing all contaminants consistently to below the analytical method reporting limit. Moreover, each treatment process provided advantages and disadvantages that are discussed later. A multi-barrier approach would provide the most comprehensive removal strategy for the treatment of organic contaminants.

OCCURRENCE IN DRINKING WATER

Target compounds were selected based on an iterative process that considered likelihood of occurrence, literature review, toxicity potential, and chemical structure. The ultimate goal was to have target chemicals that were representative of compound classes. The diversity of chemical structure was critical in order to build QSAR models which permit rapid screening of future contaminants. Analytical methods employed in this study have been published previously (Snyder et al., 2003; Vanderford et al., 2003; Trenholm et al., 2006; Vanderford and Snyder, 2006).

Samples of raw and finished drinking water were collected from 20 drinking water treatment plants from geographically diverse locations across the United States. Treatment plants were selected based upon known wastewater influence in the source water. Therefore, these utilities have the highest potential to contain EDC/PPCP compounds, making them good candidates for evaluating efficiencies of full-scale treatment process. Summary results from drinking water EDC/PPCP monitoring are presented in Tables 1 and 2. These two tables show the number of detections above the method reporting limit (detects), percent frequency of detection (% freq), minimum (min), maximum (max), median, and average (ave).

TABLE 1. Concentrations in US Raw Drinking Waters (ng/L, n=20)

	Max	Med	Freq(%)
Dilantin	40	13	91
Meprobamate	73	10	91
Sulfamethoxazole	173	20	91
Atrazine	1011	44	87
Carbamazepine	69	19	83
Gemfibrozil	38	9.8	78
Atenolol	48	10	74
Trimethoprim	19	2.7	74
Estrone	2.0	0.4	74
Naproxen	44	16	70
TCEP	534	115	65
TCPP	721	175	57
DEET	105	85	48
Metolachlor	119	20	48
Nonylphenol	141	89	48
Triclosan	8.8	3.0	43
Galaxolide	65	36	43
EEq(ng/L)	6.18	0.091	75

It is important to note that the min, max, median, and average values are calculated only from detectable values, thus values less than the MRL are not factored into the average reported. Diazapem, diclofenac, estradiol, ethynyl estradiol, fluoxetine, pentoxifylline, and testosterone were not detected in any of the raw or finished water samples evaluated.

Ozone was found to be highly effective for the removal of the majority of target compounds, while chlorine and UV were significantly less effective (Tables 3, 4, and 5). Tight membranes and activated carbon were found to be highly effective; however, removal efficiency using activated carbon is largely dependent on water quality (Snyder et al., 2006).

TOXICOLOGICAL RELEVANCE

Despite relatively widespread occurrence, the target contaminants do not appear to be relevant to human health at the concentrations occurring in drinking water. The preliminary hazard assessment for a subset of target pharmaceuticals is shown in Table 6. It is interesting to note that for many of the pharmaceuticals evaluated, the most toxic endpoint is not the therapeutic endpoint, but rather it is a side effect such as carcinogenicity.

TABLE 2. Concentrations in US Finished Drinking Waters (ng/L, n=20)

	Max	Med	Freq (%)
Atrazine	990	26	91
Meprobamate	43	9.2	83
Dilantin	32	9.4	74
Carbamazepine	18	5.4	61
Atenolol	26	2.8	57
TCEP	470	121	48
TCPP	508	177	48
DEET	99	79	43
Gemfibrozil	2.0	1.0	35
Metolachlor	36	17	35
Dioctyl phthalate	117	82	35
Nonylphenol	104	84	17
Galaxolide	34	31	17
Linuron	8.1	6.2	17
Sulfamethoxazole	3.0	0.39	13
Triclosan	1.2	1.1	9
Genistein	2.9	2.1	9
EEq (ng/L)	0.077	0.077	5

TABLE 3. Contaminant Removal using UV at 40 mJ/cm^2

<30% Removal	30–70% Removal	>70% Removal
Testosterone	Sulfamethoxazole	
Progesterone	Triclosan	
Androstenedione	Diclofenac	
Estriol	Acetaminophen	
Ethynylestradiol		
Estrone		
Estradiol		
Erythromycin		
Trimethoprim		
Naproxen		
Hydrocodone		
Ibuprofen		
Caffeine		
Fluoxetine		
Meprobamate		
Diazepam		
Dilantin		
Carbamazepine		
DEET		
Atrazine		
Galaxolide		
TCEP		
Iopromide		
Pentoxifylline		
Metolachlor		
Gemfibrozil		
Musk Ketone		

TABLE 4. Contaminant Removal using Free Chlorine (3.5 mg/L dose)

<30% Removal	30–70% Removal	>70% Removal
Testosterone	Ibuprofen	Estriol
Progesterone	Metolachlor	Ethynylestradiol
Androstenedione	Gemfibrozil	Estrone
Caffeine		Estradiol
Fluoxetine		Erythromycin-H_2O
Meprobamate		Sulfamethoxazole
Diazepam		Triclosan
Dilantin		Trimethoprim
Carbamazepine		Naproxen
DEET		Diclofenac
Atrazine		Hydrocodone
Galaxolide		Acetaminophen
TCEP		Musk Ketone
Iopromide		
Pentoxifylline		

TABLE 5. Contaminant Removal using Ozone (2.5 mg/L dose)

<30% Removal	30–70% Removal	>70% Removal
Musk Ketone	Meprobamate	Testosterone
TCEP	Atrazine	Progesterone
	Iopromide	Androstenedione
		Estriol
		Ethynylestradiol
		Estrone
		Estradiol
		Erythromycin-H2O
		Sulfamethoxazole
		Triclosan
		Trimethoprim
		Naproxen
		Diclofenac
		Ibuprofen
		Hydrocodone
		Acetaminophen
		Carbamazepine
		Dilantin
		Diazepam
		Caffeine
		Fluoxetine
		DEET
		Metolachlor
		Galaxolide
		Pentoxifylline
		Gemfibrozil

TABLE 6. Risk Assessment for Selected Pharmaceuticals

Drug	Toxic effect	ADI (mg/kg-d)	DWEL (μg/L)	Max Finished Water Conc. (μg/L)	Margin of Exposure (Finished Water)
Atenolol	Developmental, human	0.0027	81	0.020	0.00025
Atorvastatin	Cancer, rat	0.00054	16	< 0.00025	0.000015
o-hydroxy atorvastatin				< 0.00050	0.000031
o-hydroxy atorvastatin				< 0.00050	0.000031
Carbamazepine	Cancer, rat	0.00034	10	0.018	0.0018
Diazepam	Developmental, rat	0.00016	4.8	< 0.00025	0.000052
Diclofenac	Developmental, mouse	0.0016	48	< 0.00025	0.0000052
Enalapril	Developmental, human	0.00023	6.9	< 0.00025	0.000036
Fluoxetine	Developmental, human	0.0010	30	< 0.00050	0.000017
Gemfibrozil	Cancer, rat	0.00056	39	0.0021	0.000054
Meprobamate	Systemic, mouse	0.0061	180	0.043	0.00024
Naproxen	Reproductive/ Developmental, mouse	0.046	1,400	< 0.00050	0.00000036
Phenytoin	Cancer, mouse	0.000083	5.8	0.015	0.0026
Risperidone	Cancer, mouse & rat	0.000014	0.41	0.00034	0.00084
Simvastatin	Cancer, rat	0.00054	16	< 0.00025	0.000015
Simvastatin hydroxy acid				< 0.00025	0.000015
Sulfamethoxazole	Developmental, rat	0.28	8,400	0.0030	0.00000036
Triclosan	Systemic, hamster	0.012	360	0.0012	0.0000033
Trimethoprim	Developmental, rat	0.10	3,000	< 0.00025	0.000000083

CONCLUSIONS

Trace EDCs and PPCPs do occur at detectable levels in drinking water when analytical methods capable of ng/L reporting limits are used. Ozonation will greatly reduce the number of trace contaminants in drinking water; however, some highly resilient chemicals will not be appreciably removed. In the case of several pharmaceuticals evaluated, the predicted drinking water equivalent levels (DWELs) occur at orders of magnitude higher concentration than those detected in drinking water. It is unlikely that pharmaceuticals pose significant threats to human health at the concentrations that may occur in drinking water.

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