The Occurrence and Fate of Pharmaceuticals, Personal Care Products and Endocrine Disrupting Compounds in a Municipal Water Use Cycle:

A Case Study in the City of Ann Arbor

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Abstract

A characterization of the occurrence and fate of a 22 compound target list of pharmaceuticals, personal care products and endocrine disrupting compounds (PPCPs and EDCs) has been performed at various locations within the City of Ann Arbor's (Ann Arbor) water use cycle. Monitoring occurred at four locations within the water use cycle:

- Surface/source water
- Drinking water
- Wastewater influent
- Wastewater effluent

Laboratory analysis indicated the following number amount of target compounds identified in grab samples collected from each monitoring station over the four sampling events:

- 10 of 22 compounds detected in source water (Huron River)
- 4 of 22 compounds detected in finished drinking water
- 17 of 22 compounds detected in wastewater influent
- 15 of 22 compounds detected in treated wastewater effluent

Results of this study indicate a reduction in the concentrations of certain compounds based on samples collected before and after source water and wastewater treatment processes. Collected data indicates variability in the occurrence of PPCPs and EDCs in treated and untreated water and wastewater. Additionally, characterization of this variability and comparison to other source water supplies and treatment processes in Michigan has been identified as an area of additional future study.

INTRODUCTION

Research reviewed over the course of this study indicates that there has been an increase in studies over the past two decades characterizing the occurrence of endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs) in water use cycles in the United States and Europe. PPCPs are often described as a grouping of chemical substances that range from prescription drugs to fragrances and cosmetics. The American Water Works Association (AWWA) defines EDCs as chemicals that interfere with the normal function of the endocrine system. The endocrine system includes endocrine glands and the hormones produced from these glands. Examples of these glands include the pituitary, thyroid, and pancreas. The group of EDCs contains a wide range of compounds such as steroids, pesticides, inorganics, and industrial chemicals.

Compared to established laboratory methods for the analysis of traditional organic compounds, common laboratory protocol for analyzing PPCPs and EDCs are still being developed. As a result, several different analytical methods for characterizing PPCP/EDC compounds in water have been performed in recent studies. In natural waters, solid phase extraction is used along with gas chromatography (GC) paired with mass spectrometry (MS), liquid chromatography (LC) coupled with MS, immunoassays, or a combination of techniques (Snyder, 2003). Choosing between GC and LC analyses is generally based on the physiochemical qualities of the target analyte. Many PPCPs are polar in nature and are not suitable for GC analysis without performing additional preparation and extraction. Therefore, LC analysis, instead of GC analysis, is usually applied when targeting more polar compounds (Boyd, 2003). The ability to analyze samples for pharmaceuticals at low analytical detection limits has improved over time (Daughton, 1999).

Currently, other researchers are evaluating the environmental effects of human and aquatic exposure to PPCPs and EDCs. Additionally, studies completed over the past few decades have recognized that the potential exists for PPCPs to enter the environment from multiple routes, such as, wastewater treatment discharge, industrial discharge, runoff from confined animal feeding operations, and treated sludge applied to agricultural land. (Daughton and Ternes, 1999). PPCPs may enter the treatment process in a reduced form (after passing through body) or by direct discharge of discarded PPCPs.

Points of PPCP and EDC entry into the environment include:

1. Discharge from Wastewater treatment processes such as treatment plant or septic systems,
2. Regulated and unregulated industrial discharges to surface and groundwater,
3. Leaking or overflowing animal waste storage from confined animal feeding operations,
4. Land application of treated animal waste from certain animal feeding operations.

Studies on this topic include the 1999-2000 United States Geological Survey (USGS) National Reconnaissance. The USGS National Reconnaissance was a comprehensive study that characterized the occurrence of PPCPs and EDCs in various surface water resources nationwide. The study reported that water samples collected from 80% of 139 streams monitored in 30 states found one or more of the study's 95 target analytical compounds (including pharmaceuticals, hormones, and other wastewater compounds). The sampling sites

were selected in areas prone to contamination from agricultural, industrial and metropolitan wastewater (Koplin, 2002).

The purpose of the study reported herein was to evaluate the occurrence and fate of certain PPCPs and EDCs at key locations within the City of Ann Arbor's water use cycle. Specifically, data was obtained by performing laboratory analysis of manually collected water samples for a target compound list of pharmaceuticals, personal care products, and endocrine disruptors. The data were used to characterize the occurrence, fate, and transport of the compounds in the water cycle at four locations during four discreet sampling events. This report documents the field and laboratory methods used to complete the analysis of the target compound list. Additionally, this report describes the water use cycle and summarizes the results of the analytical laboratory reports.

The occurrence of PPCPs and EDCs in the Huron River is of interest to the City based on their reliance on the Huron River for the majority of its community water supply. Approximately 80% of the City's community water supply is drawn from the Huron River (Figure 1). Additionally, MDEQ recognizes the need for information regarding certain classes of substances, including PPCPs and EDCs. The collection of basic occurrence data will assist in developing an understanding of the effect(s), if any, PPCPs and EDCs have on the quality of Michigan's water resource (communication, MDEQ).

Figure 1. Huron River Upstream of the City's Water Intake.

The target compound list developed for this study was primarily based on three criteria:

1. Compounds identified in the 1999-2000 USGS National Reconnaissance (Koplin, 2002),
2. Ability to complete analysis using defined laboratory methods, and
3. Frequency of compound occurrence in surface and wastewater in the United States and Europe as reported in reviewed literature.

The target compounds for this study are listed in Table 1.

Table 1. Target Compound List

PPCPS & EDCs	Use/Origin	Analytical Method
Antibiotics		
Sulfadimethoxine	human/veterinary antibiotic	LC/MS/MS
Sulfamethazine	human/veterinary antibiotic	LC/MS/MS
Sulfamethoxazole	human antibiotic	LC/MS/MS
Sulfathiazole	human/veterinary antibiotic	LC/MS/MS
Lincomycin	human/veterinary antibiotic	LC/MS/MS
Tylosin	veterinary antibiotic	LC/MS/MS
Trimethoprim	human antibiotic	LC/MS/MS
Analgesics		
Acetaminophen	pain reliever	LC/MS/MS
Ibuprofen	pain reliever	LC/MS/MS
Antiepileptic		LC/MS/MS
Carbamazepine	antiepileptic/antimanic	LC/MS/MS
Miscellaneous		
Caffeine	stimulant	GC/MS
Cotinine	nicotine metabolite	GC/MS
1,4 Dioxane	solvent stabilizer	GC/MS
Hormones and Sterols		
Testosterone	hormone	GC/MS
Ergosterol	steroidal hormone	GC/MS
Stigmasterol	plant steroid	GC/MS
Sitosterol	plant steroid	GC/MS
Stigmastanol	plant steroid	GC/MS
Progesterone	steroidal hormone	GC/MS
Coprostanol	fecal steroid	GC/MS
Cholesterol	plant/animal steroid	GC/MS
Dihydrocholesterol	plant/animal steroid	GC/MS