EVALUATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN DES MOINES SOURCE AND FINISHED WATERS

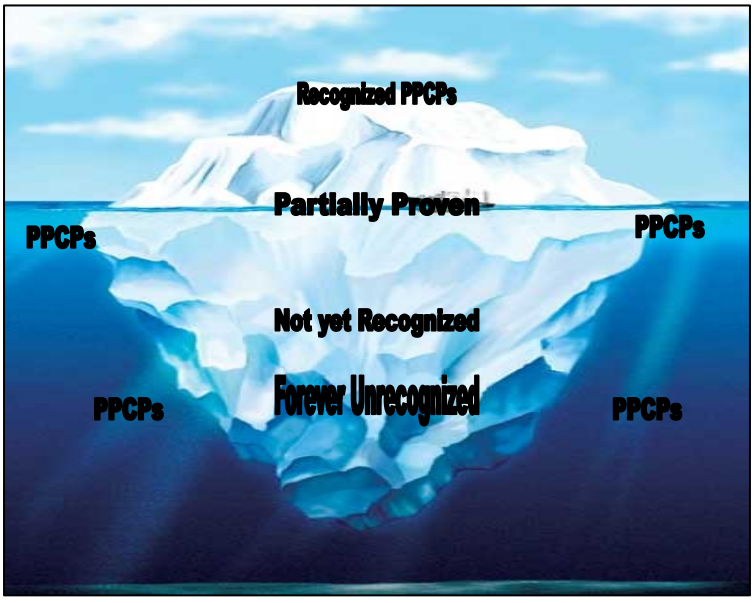
Barb Duff 2006

I. Introduction

Pharmaceuticals and personal care products (PPCP) and endocrine disrupting compounds (EDC) are a topic of investigation at Des Moines Water Works (DMWW). Potentially there are many PPCPs and EDCs that could be in the source water. The water industry defines PPCPs as a group of chemical substances that include prescription drugs (animal or human), fragrances and cosmetics. The American Water Works Association (AWWA) defines EDCs as chemicals that interfere with the normal function of the endocrine system, including the pituitary and thyroid glands and the pancreas. EDCs include such things as steroids, pesticides, and certain industrial chemicals. Water customers are increasingly concerned about the possible presence of these compounds in their drinking water.

Currently most water suppliers are unaware if these contaminants are present in their source or finished waters. Water suppliers need the resources and testing procedures to evaluate the presence/absence of these compounds and the tools to protect their finished product. Research to identify these potentially toxic contaminants needs to be pursued. Researchers and water suppliers are presently on the tip of the PPCP iceberg shown in the diagram below.

The PPCP ICEBERG



The United States Geological Survey (USGS) has discovered that most of the recognized "neglected contaminants" are found in the ng/L (part per trillion) range. Some of these contaminants, when used therapeutically, have been shown to cause unintended environmental consequences. Feminization of fish and bacteria resistance in humans are examples of this.

According to Dana Koplin of USGS, most PPCP investigative work has evaluated wastewater. Wastewater treatment plant effluent can potentially reach drinking water intakes. PPCPs and EDCs are used in the livestock industry also. Could the waste from animal confinements and feedlots be affecting the source waters for drinking water facilities as well?

The DMWW mission is: *Provide quality water, anticipate and meet the needs and expectations of an expanding base of Iowa customers and be committed to exceeding customer expectations and anticipate future needs.* To fulfill this mission, DMWW must be diligent and proactive in evaluating the presence or absence of these types of contaminants in its water sources, and in evaluating the effectiveness of water treatment to remove them.

II. Assessment Of PPCP Present In DMWW Source And Finished Water

The Raccoon and Des Moines Rivers, source waters for DMWW, have not been examined for many of these compounds. Since water consumers are dependent on water treatment facilities for removal of health-threatening contaminants from their drinking water, water utilities need to be aware of any PPCPs and EDCs that may exist in their source waters, and anticipate removal strategies if and when these contaminants are detected at a level of concern.

Research conducted by the DMWW laboratory in 2005 and 2006 indicated that estrogen, estrogen mimickers and pharmaceuticals were present in both DMWW source waters at varying times of the year. As a follow-up to this monitoring, samples were sent to the University of Iowa Hygienic Labs (UHL) to determine what other PPCPs might be present in DMWW samples. An overview of results of the DMWW and UHL studies are shown on the next page. Comprehensive results may be found in Appendix A and B.

DMWW Estradiol Scan Results

ESTRADIOL SPRING SNAPSHOT
DES MOINES WATER WORKS
3 MONTH AVERAGE - MARCH - MAY

SAMPLE LOCATION	SITE ID	AVE. ESTRADIOL ppt
Raccoon River	RR	2.24
RR Duplicate	RR DUP	2.50
Des Moines River	DMR	3.55
Infiltration Gallery	LL	1.98
Finished Water Fleur	HL	1.91
Maffitt Raw	MR	4.16
Maffitt Finished	MF	2.17

ESTRADIOL RAIN EVENT SNAPSHOT
DES MOINES WATER WORKS
June-06

SAMPLE LOCATION	SITE ID	ESTRADIOL ppt
Raccoon River	RR	2.91
Des Moines River	DMR	4.56
Infiltration Gallery	LL	2.08
Finished Water Fleur	HL	2.63
Crystal Lake	CL	2.16
Maffitt Raw	MR	2.24
Maffitt Finished	MF	<1.5

ESTRADIOL SUMMER (DRY) SNAPSHOT
DES MOINES WATER WORKS
AVERAGE OF JUNE, JULY AND AUGUST

SAMPLE LOCATION	SITE ID	ESTRADIOL ppt
Raccoon River	RR	<1.5
Des Moines River	DMR	<1.5
Infiltration Gallery	LL	<1.5
Finished Water Fleur	HL	<1.5
Crystal Lake	CL	<1.5
Maffitt Raw	MR	<1.5
Maffitt Finished	MF	<1.5

ESTRADIOL FALL SNAPSHOT (DRY)
DES MOINES WATER WORKS

SAMPLE LOCATION	SITE ID	ESTRADIOL ppt
Raccoon River	RR	<1.5
Duplicate	RR DUP	<1.5
Des Moines River	DMR	<1.5
Infiltration Gallery	LL	<1.5
Finished Water Fleur	HL	<1.5
Crystal Lake	CL	<1.5
Maffitt Raw	MR	<1.5
Maffitt Finished	MF	<1.5

UHL PPCP Scan Results:

**** Pink indicates substance was present***

USAGE	DRUG	MRL ng/L	PPCP DETECTED IN DMWW SOURCE AND FINISHED WATERS								
			6-Mar	6-Jul	6-Oct	6-Mar	6-Jul	6-Oct	6-Mar	6-Jul	6-Oct
			RIVERS			ALLUVIAL			FINISHED		
Anit-inflammatory	Acetaminophen	5									
	Ibuprofen	2									
Stimulant	Caffeine	26									
	1,7-Dimethylxanthine	10									
	Cotinine	3									
Insect Repellant	DEET	5									
Anti-seizure drug	Carbamazepine	1									
Veterinary antibiotic	Lincomycin	2									
	Tylosin	1									
Anti- bacterial	Sulfadimethoxine	1									
	Sulfamethazine	1									
	Sulfamethoxazole	1									
	Sulfathiazole	1									
Synthetic antibiotic	Trimethoprim	2									
Anit-microbrial	Triclosan	39									

III. Assessment Of Compounds Of Most Concern To The Utility And Customer

Some EDCs are suspected carcinogens. EDCs have caused feminization of fish at ng/L levels. Estrogens and estrogen mimickers can disrupt fish reproduction and growth in fish and can cause mutations in amphibians.

DMWW's watersheds are extensively impacted by both human and animal waste, both sources of EDCs. Some examples of agricultural and urban estrogens and estrogen mimickers are:

Agricultural:

1. pesticides (insecticides such as o,p-DDT, endosulfan, dieldrin, methoxychlor, kepone, dicofol, toxaphene, chlordane;
2. herbicides such as alachlor, atrazine and nitrofen;
3. fungicides such as benomyl, mancozeb and tributyl tin;
4. nematocides such as aldicarb and dibromochloropropane);
5. pharmaceuticals (including estrogens);
6. natural estrogens

Urban:

1. plasticizers (bisphenol A, phthalates);
2. pharmaceuticals (drug estrogens - birth control pills, DES, cimetidine);
3. ordinary household products (breakdown products of detergents and associated surfactants, including nonylphenol and octylphenol);
4. industrial chemicals (polychlorinated biphenyls (PCBs), dioxin and benzo(a)pyrene);
5. heavy metals (lead, mercury, and cadmium);
6. natural estrogens

Another focus for DMWW is long-term monitoring of pharmaceuticals from both human and livestock sources. Most streams harbor antibiotic-resistant bacteria. These enter source waters via wastewater treatment plant effluents by means of human waste and disposal of unused antibiotics through the sanitary sewer system. Incidence of pharmaceuticals in the environment may be increasing due to veterinarial use. Livestock pharmaceuticals are sometimes over-used because they are cheap and have shown to promote health and market weight. Seasonal monitoring of pharmaceutical concentrations in watershed samples will provide valuable information to customers and assist in developing water treatment strategies designed for removal of these compounds.

IV. Roadmap of PPCP Evaluation

A. 2006

1. Work with Des Moines University (DMU) to assess estrogens and estrogen mimickers in the Raccoon River (RR) watershed to identify hotspots in the watershed.
2. With DMU, begin remediation studies of these estrogens and estrogen mimickers.
3. Submit seasonal source and finished water samples to UHL.
4. Submit source and finished water samples to USGS for a comprehensive PPCP study.

5. Split samples with USGS to compare ELISA method with GC-MS method.

B. 2007 - 2008
   1. Assess sulfonamides and identify hot spots in the RR watershed by use of ELISA test kits.
   2. Assess sulfonamide remediation.
   3. Continue work with DMU to assess estrogens and estrogen mimickers in the RR Watershed. Continue remediation of estrogens and estrogen mimickers in conjunction with DMU.
   4. Acquire the GC-MS method to assess estrogens and assess feasibility of incorporating this method in the DMWW laboratory.
   5. If DNR/USGS/DMWW grant proposal is successful work with DNR and USGS as a team to conduct a comprehensive study of the RR watershed utilizing polar organic chemical integrative samplers (POCIS). This would include both PPCP and Deck's. POCIS samplers sample over an extended period of time, producing an accurate assessment of the various types and concentrations of PPCPs and EDCs present in the watershed.
   6. If the DNR/USGS/DMWW grant proposal is not successful, conduct a comprehensive seasonal overview of PPCPs in the RR watershed by submitting samples to USGS and/or UHL for analysis.
   7. Conduct remediation studies on compounds found in DMWW finished waters.
   8. Assess carbamazepine health issues, hot spots and possible remediation.

C. 2009 – 2011
   1. Explore the feasibility of acquisition of a LC-MS-MS for PPCP detection
   2. Continue working with DMU on estrogens and estrogen mimickers in the RR. If RR study is complete, begin studying the Des Moines River (DMR) watershed with DMU
   3. Conduct a seasonal PPCP scan of the DMR coordinating analysis through UHL and USGS
   4. Investigate nitrate and *E.coli* hotspots in the DMR watershed, and follow up with ELISA assays of the hotspots for common PPCPs.
   5. Seek funding for additional POCIS studies with USGS and IDNR.

V. Conclusion:

DMWW has begun to chip away at the PPCP and EDC iceberg. In 2006, carbamazepine, sulfamethoxazole, and estradiol were detected in the finished drinking water. These compounds were in the ng/L range and currently not considered a human health concern. However, DMWW still needs to investigate possible removal strategies for these compounds, not only to secure consumer confidence but also to be prepared for future drinking water regulations.

Appendix A:

DES MOINES WATER WORKS
TREATMENT PLANT
ESTRADIOL STUDY
2006
MRL FOR ESTRADIOL = 1.5PPT

Raccoon River	=	**RR**
		RR
Duplicate	=	**DUP**
Des Moines River	=	**DMR**
Infiltration Gallery	=	**LL**
Finished Water Fleur	=	**HL**
Crystal Lake	=	**CL**
Maffitt Raw	=	**MR**
Maffitt Filter Effluent	=	**MF**

Date	RR	RR DUP	DMR	LL	HL	CL	MR	MF
3/30/2006	2.71	3.10	6.34	3.54	2.68	-----	3.84	3.15
4/4/2006	2.46	2.85	1.92	1.05	0.68	-----	1.64	1.25
4/25/2006	1.56	1.56	2.38	1.34	2.38	-----	7.00	2.10
5/8/2006	3.14	-----	3.92	2.75	<1.50	2.43	4.76	3.07
5/22/2006	3.16	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50
5/30/2006	<1.50	<1.50	<1.50	<1.50	<1.50	-----	<1.50	<1.50
6/5/2006	3.12	-----	1.49	<1.50	<1.50	<1.50	1.41	na
6/19/2006	2.91	-----	4.56	2.08	2.63	2.16	2.24	1.17
6/29/2006	1.13	-----	1.05	1.17	0.61	1.35	0.00	0.50
7/17/2006	2.67	-----	<1.50	<1.50	2.09	1.77	2.00	0.30
7/31/2006	1.34	-----	2.54	<1.50	<1.50	-----	0.37	<1.50
8/28/2006	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50
9/5/2006	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50	<1.50

Appendix B:

DMWW SEASONAL PPCP SCAN CONDUCTED BY UHL 2006 MAFFITT PLANT

Units: ng/L

DRUG	SAMPLE ID					
	Mar-06	Jul-06	Oct-06	Mar-06	Jul-06	Oct-06
	MR			MF		
Acetaminophen	<5.0	<1	<1	<5.0	<1	<1
Caffeine	<20	<26	<62	24	26	<62
Carbamazepine	7.3	4.2	3.3	5.8	5.1	3
Cotinine	2.1	3.4	<1	2.3	4.4	<1
1,7-Dimethylxanthine	<10.0	5.4	<3.6	15	<1	<3.6
DEET	9.5	12	6.4	6.4	16	<5.0
Ibuprofen	<2.0	<1	<1	<2.0	<1	<1
Lincomycin	<2.0	<1	<1	<2.0	<1	<1
Sulfadimethoxine	<1.0	1.1	4.6	4.9	<1	<1
Sulfamethazine	<1.0	1.1	1.1	1.8	<1	<1
Sulfamethoxazole	<1.0	4.9	13	17	<1	1.7
Trimethoprim	<2.0	<1	<1	<2.0	<1	<1
Sulfathiazole	NA	<1	<1	NA	<1	<1
Triclosan	NA	<39	<3.7	NA	55	<3.7
Tylosin	NA	<1	<1	NA	<1	<1

Appendix B continued:

DMWW SEASONAL PPCP SCAN CONDUCTED BY UHL
2006

Units: ng/L

DRUG	SAMPLE ID											
	Mar-06	Jul-06	Oct-06	Mar-06	Jul-06	Oct-06	Mar-06	Jul-06	Oct-06	Mar-06	Jul-06	Oct-06
	DMR			RR			LL			HL		
Acetaminophen	<5.0	<1	<1	55	<1.0	<1.0	<5.0	<1	<1	<5.0	<1	<1
Caffeine	48	49	64	46	54	110	20	27	<62	23	<26	<62
Carbamazepine	3.4	3.6	3.9	4.2	5.1	5.5	3.2	4	2.7	<1.0	1.7	1.5
Cotinine	5.1	8.5	1.8	4.1	11	4.4	<1.0	<3.2	<1	1.7	3.5	<1
1,7-Dimethylxanthine	12	5.8	4.7	14	9.1	9	<10.0	5.8	6.8	<10.0	<4.6	<3.6
DEET	5.9	29	16	11	35	27	<5.0	<8.4	<5	<5.0	14	<5
Ibuprofen	3.8	<1	<1	<2.0	18	<1.0	<2.0	<1	<1	5.7	<1.0	<1
Lincomycin	4.9	<1	<1	4.9	<1.0	1.3	<2.0	<1	<1	<2.0	<1.0	<1
Sulfadimethoxine	2	<1	<1	6.7	<1.0	<1.0	4	1.8	1.7	<1.0	<1.0	<1
Sulfamethazine	1.6	<1	<1	5.1	1.2	<1.0	2.8	2.3	1.9	<1.0	<1.0	<1
Sulfamethoxazole	13	5.9	13	9.3	6.2	14	21	4.7	4.5	<1.0	<1.0	<1
Trimethoprim	2.6	<1	1.4	<2.0	1.6	<1.0	<2.0	<1	<1	<2.0	<1.0	<1
Sulfathiazole	NA	<1	<1	NA	<1.0	<1.0	NA	<1	<1	NA	<1.0	<1
Triclosan	NA	<39	<3.7	NA	<39	<3.7	NA	<39	<3.7	NA	<39	<3.7
Tylosin	NA	<1	<1	NA	<1.0	<1.0	NA	<1	<1	NA	<1.0	<1