Emerging Contaminants of Concern in the Delaware River Basin

Vulnerability Assessment Preliminary Report



Delaware River Basin Commission West Trenton, New Jersey

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1.0 Introduction

There are more than 85,000 chemicals commercially available in the United States with new chemicals and technologies introduced each year. The number of substances released to the environment, improved analytical methods and a growing body of information on adverse effects has increased interest by scientists, the public and regulators in substances and toxic effects not historically monitored or assessed. These emerging contaminants of concern (ECOC) are substances that have been detected in humans or other living organisms, have been found to be toxic in some way, or are persistent in the environment. Therefore, the substance may have the potential to cause adverse effects on human health or the environment. Examples of ECOC include phthalates, perfluorooctanoic acids, brominated flame retardants, nanoparticles, pharmaceuticals and personal care products. A number of efforts are underway within the Delaware River Basin to identify, understand and prioritize ECOC. Studies sponsored by the United States Environmental Protection Agency (USEPA), United States Geological Survey (USGS), basin states and private industry have generated and continue to generate data on ECOC from locations within the Delaware River Basin. In 2006, the Delaware River Basin Commission (DRBC) included a select number of ECOCs in ongoing fish tissue monitoring. This DRBC staff report summarizes efforts to monitor emerging contaminants in the Delaware River Basin by the USEPA, USGS, DRBC, basin states, academics and stakeholders.

2.0 Delaware River Basin Commission

The DRBC monitoring schedule in 2004, 2005, 2006 includes fish tissue analysis of polybrominated diphenyl ethers (PBDE) and perfluorooctanoic acids (PFOA) along with the priority pollutants dioxins, PCB, chlorinated pesticides and metals.

A proposed list of target ECOC for ambient water monitoring in the mainstem of the Delaware River by the DRBC is presented below. The compounds listed have published analytical methods for detection in surface water therefore eliminating the need for time consuming and expensive method development. Most of the compounds are USGS surface water target compounds and have been detected in the Delaware River Basin. The list also includes the pharmaceutical carbamazepine because it has been detected in sewerage treatment plant discharges and has been identified through risk assessment to be a high risk in aquatic environments. PBDE and PFOA compounds are included in the DRBC list because they have been detected in Delaware River Basin fish tissue.

Proposed DRBC Target List For Emerging Contaminants of Concern

- sulfamethoxazole
- trimethoprim
- carbamazepine
- diltiazem

- dehydronifedipine
- acetaminophen
- codeine
- diazinon
- N,N-diethyltoluamide (DEET)
- ethanol-2-butoxy-phosphate
- bis(2-ethylhexyl)phthalate
- nonylphenol
- tri(2-chloroethyl)phosphate
- tri(dichlorisopropyl)phosphate
- bisphenol A
- Triclosan
- ethynylestradiol
- Perfluorooctanoic acids (PFOA)
 - Perfluoropentanoate
 - Perfluorohexanoate
 - Perfluoroheptanoate
 - Perfluorooctanoate
 - Perfluorononanoate
 - Perfluorodecanoate
 - Perfluoroundecanoate
 - Perfluorododecanoate
 - Perfluorobutanesulfonate
 - Perfluorohexanesulfonate
 - Perfluorooctanesulfonate
- Polybrominated Diphenyl Ethers (PBDE)
 - 2,2',4-TriBDE (BDE-17)
 - 2,4,4'-TriBDE (BDE-28)
 - 2,2',4,4'-TetraBDE (BDE-47)
 - 2,3',4,4'-TetraBDE (BDE-66)
 - 2,3',4',6-TetraBDE (BDE-71)
 - 2,2',3,4,4'-PentaBDE (BDE-85)
 - 2,2',4,4',5-PentaBDE (BDE-99)
 - 2,2',4,4',6-PentaBDE (BDE-100)
 - 2,2',3,4,4',5'-HexaBDE (BDE-138)
 - 2,2',4,4',5,5'-HexaBDE (BDE-153)
 - 2,2',4,4',5,6'-HexaBDE (BDE-154)
 - 2,2',3,4,4',5',6-HeptaBDE (BDE-183)
 - 2,3,3',4,4',5,6-HeptaBDE (BDE-190)
 - DecaBDE (BDE-209)

3.0 United States Geological Survey

The USGS has conducted a number of monitoring projects for ECOC (Focazio, 2004; <u>http://www.clw.csiro.au/video_html/danakolpinSep04.html</u>). The USGS criteria for selecting compounds to measure is based on the quantities in use, anticipated environmental behavior, pathways for release, health significance (known and potential), ability to measure the compound, potential as chemical indicators/tracers and stakeholder priorities. The USGS target compound list for streams is shown in Table 1. (<u>http://toxics.usgs.gov/regional/contaminants.html</u>)

Table 1. Target Compounds for USGS National Reconnaissance of Emerging Contaminants in US Streams

Veterinary and Human Antibiotics			
Tetracyclines	Sulfonamides		
Chlortetracycline	Sulfachlorpyridazine		
Doxycycline	Sulfamerazine		
Oxytetracycline	Sulfamethazine		
Tetracycline	Sulfathiazole		
Fluoroquinolones	Sulfadimethoxine		
Ciprofloxacin	Sulfamethiazole		
Enrofloxacin	Sulfamethoxazole		
Norfloxacin	Others		
Sarafloxacin	Lincomycin		
Macrolides	Trimethoprim		
Erythromycin-H2O (metabolite)	Carbadox		
Tylosin	Virginiamycin		
Roxithromycin			

Human Drugs				
Prescription Metformin (antidiabetic agent) Cimetidine (antacid) Ranitidine (antacid) Enalaprilat (antihypertensive) Digoxin Diltiazem (antihypertensive) Fluoxetine (antidepressant) Paroxetine (antidepressant, antianxiety) Warfarin (anticoagulant) Salbutamol (antiasthmatic) Gemfibrozil (antihyperlipidemic) Dehydronifedipine (antianginal metabolite) Digoxigenin (digoxin metabolite)	Non-Prescription Acetaminophen (analgesic) Ibuprofen (anti-inflammatory, analgesic) Codeine (analgesic) Caffeine (stimulant) 1,7-Dimethylxanthine (caffeine metabolite) Cotinine (nicotine metabolite)			

Industrial and Household Wastewater	Products		
Insecticides	Polycyclic aromatic hydrocarbons		
Diazinon	(fossil fuel and fuel combusion		
Carbaryl	indicators)		
Chlorpyrifos	Naphthalene		
cis-Chlordane	Phenanthrene		
N,N-diethyltoluamide (DEET)	Anthracene		
Lindane	Fluoranthene		
Methyl parathion	Pyrene		
Dieldrin	Benzo(a)pyrene		
Plasticizers	Antioxidants		
bis(2-Ethylhexyl)adipate	2,6-di-tert-Butylphenol		
Ethanol-2-butoxy-phosphate	5-Methyl-1H-benzotriazole		
bis(2-Ethylhexyl)phthalate	Butylatedhydroxyanisole (BHA)		
Diethylphthalate	Butylatedhydroxytoluene (BHT)		
Triphenyl phosphate	2,6-di-tert-Butyl-p-benzoquinone		
Detergent metabolites	Others		
<i>p</i> -Nonylphenol	Tetrachloroethylene (solvent)		
Nonylphenol monoethoxylate	Phenol (disinfectant)		
(NPEO1)	1,4-Dichlorobenzene (fumigant)		
Nonylphenol diethoxylate (NPEO2)	Acetophenone (fragrance)		
Octylphenol monoethoxylate	p-Cresol (wood preservative)		
(OPEO1)	Phthalic anhydride (used in		
Octylphenol diethoxylate (OPEO2)	plastics)		
Fire retardants	Bisphenol A (used in polymers)		
Tri(2-chloroethyl)phosphate	Triclosan (antimicrobial		
Tri(dichlorisopropyl)phosphate	disinfectant)		

Sex and Steroidal Hormone	s
Biogenics 17 <i>b</i> -Estradiol 17 <i>a</i> -Estradiol Estrone Estriol Testosterone Progesterone <i>cis</i> -Androsterone	Pharmaceuticals17a-Ethynylestradiol (ovulation inhibitor)Mestranol (ovulation inhibitor)19-Norethisterone (ovulation inhibitor)Equilenin (hormone replacement therapy)Equilin (hormone replacement therapy)SterolsCholesterol (fecal indicator)3b-Coprostanol (carnivore fecal indicator)
	Stigmastanol (plant sterol)

In a USGS study, surface waters were monitored in 1999 through 2000 for 95 organic wastewater contaminants (OWC) in 139 streams including Assinpink Creek in New Jersey. The sampling sites are shown in the map below (Figure 1). The most commonly detected compounds were coprostranol, cholesterol, N-N-diethyltoluamide, caffeine, tri(2-chloroethyl)phosphate, triclosan, 4-nonylphenol, nonylphenol monoethoxylate

(NPEO1), tris (2-butoxy-ethyl)phosphate, and octylphenol ethoxylate (OPEO1) at low $\mu g/L$ (ppb) concentrations. The frequency and concentration of the contaminants measured are shown below (Figure 2). The detection of multiple contaminants in surface water was observed.



Figure 1. Pharmaceuticals, hormones, and other organic wastewater contaminants were measured in 139 streams during 1999 and 2000. (Kolpin et al., ES&T, 2002)



Figure 2. Steroids, nonprescription drugs, and an insect repellent were the three chemical groups most commonly detected in susceptible streams. Detergent metabolites, steroids, and plasticizers generally were found at the highest concentrations. (Kolpin et al., ES&T, 2002)

A USGS study in 2000 monitored 47 groundwater sites, including sites in southeastern Pennsylvania for 134 organic wastewater compounds (OWC). Preliminary results indicate that organic contaminants were detected at 80% of the sites. Fewer compounds and lower concentrations were found than in surface water. The five most frequently detected compounds in groundwater were cholesterol, bisphenol A, estriol, N-Ndiethyltoluamide, and nonylphenol monoethoxylate (NPEO1). (Studies Examine Contaminants: Pharmaceuticals, hormones an other organic wastewater contaminants in ground water resources <u>http://toxics.usgs.gov/pubs/contaminant_studies_article.pdf</u>) The USGS also monitored sources of drinking water in 2001 for 124 compound at 25 ground water and 45 surface water sites. Monitoring was conducted in 25 states and Puerto Rico. The site map indicates a site in the Delaware River Basin. Results are yet to be published. (http://www.clw.csiro.au/video_html/danakolpinSep04.html)

In 2002 the USGS monitored 10 WWTP by upstream, effluent and downstream sampling including a site in the Delaware River Basin. Preliminary unpublished results indicate the most frequently detected contaminants were cotinine, cholesterol, carbamazepine, tonalide, tri(dcp)phosphate, tri(2-ce)phosphate, 3,4-dcp isocyanate, b-sitosterol, codeine, ethyl citrate, sulfamethoxazole, caffeine, N-N-diethyltoluamide, tributylphosphate, tris (2-butoxy-ethyl)phosphate, benzophenone, diltiazem, NPEO2, NPEO1, triclosan, 3b-coprostanol, and trimethoprim.

(http://www.clw.csiro.au/video html/danakolpinSep04.html)

The USGS has also conducted studies on emerging contaminants in streambed sediment, municipal biosolids and landfill leachate. The results of these studies are unpublished and it is unclear from available information if Delaware River Basin sites were included in these studies.

Assinpink Creek was also used in methods development work by the USGS comparing standard depth and width water-column sampling to a passive in situ sampler for the detection of organic wastewater-related contaminants. The passive sampler was able to integrate the sampling of dissolved compounds over a longer time period but was not quantitative and did not sample particulate bound compounds. Some differences in compounds detected was observed between the standard sampling and passive sampler. The Assinpink Creek was selected because it receives agricultural, municipal and industrial wastewater. Out of 96 target analytes, the compounds detected included pharmaceuticals (acetaminophen, carbamazepine, dehydronifedipine, diltiazem, diphenhydramine, sulfamethoxazole, thiabendazole), herbicides (atracine, bromacil, metolachlor, and prometon, 3,4-dichlorphenyl isocyanate), flame retardants (tri-(2chloroethyl)phosphate, tri(dichloroiosopropyl)phosphate and tri(2-butoxyethyl phosphate), plasticizers (bisphenol A, diethylhexyl phthalate, and triphenol phosphate), alkyl phenols (cumylphenol, 4-tert-octylphenol, NPEO2, and OPEO1), insecticides (diazinon and pentachlorophenol), ingredients from personal care and consumer products (anthraquinone, benzophenone, caffeine, cotinine, DEET, HHCB, indole, methyl salicylate, tonalide (AHTN), triclosan, and triethyl citrate). Also found were bromoform, 5-methyl-1-H-benzotriazole, p-cresol, and 3-methyl-1H-indole. The concentrations of the individual OWC are between 1 to 500 ng/L (ppt). (Alvarez et al. 2005 Chemosphere)

4.0 United States Environmental Protection Agency (http://www.epa.gov/ppcp)

The USEPA ongoing studies and initiatives focusing on pharmaceutical and personal care products (PPCP) including steroids and hormones are listed below (Octavia Conerly, USEPA, ASIWPCA Conference Call).

- Fish tissue study On August 23, 2006, the first PPCP Fish Tissue Pilot Study sample collection was completed in the vicinity of West Chester, PA. (email from Leanne Stahl, EPA –OST (202)566-0404, stahl.leanne@epamail.epa.gov)
- POTW study No POTWs in the Delaware River Basin are included in this study. (email Woody Forsht EPA OST (202)566-1025 forsht.elwood@epa.gov)
- 2006 Targeted National Sewage Sludge Survey (Biosolids) Pottsville, PA Main Sewage Treatment Plant is included in this study. (Rick Stevens EPA-OST- personal communication, (202)566-1135, stevens.rick@epa.gov)
- Literature database OST
- Prioritization of Drinking Water Contaminants (Contaminant Candidate List CCL) OGW and DW
- Interagency Task Group on Pharmaceuticals in the Environment

The USEPA also continues to develop new water quality criteria. In 2006, final aquatic life ambient water quality criteria were released for two substances, nonylphenol and diazinon,that are often listed as ECOC (Table 2). The USEPA also announced that a new criteria would not be released for another ECOC, methyl tertiary-butyl ether (MTBE), because the chemical is typically found in aquatic environments at levels that are not toxic to aquatic life.

	Freshwater µg/L		Saltwater µg/L	
	acute	chronic	acute	chronic
diazinon	0.17	0.17	0.82	0.82
nonylphenol	28	6.6	7.0	1.7

 Table 2. USEPA Ambient Water Quality Criteria: 2006 Release

http://www.epa.gov/waterscience/criteria

5.0 Basin States

5.1 Delaware

• The main emerging contaminant initiative that DNREC has underway is the collection of PBDE data as a part of a Toxics in Biota monitoring program. So far, DNREC has analyzed PBDEs in 80 fish and shellfish samples collected over the period of fall 2003 through fall 2005. DNREC will be analyzing PBDEs in 33 additional samples during the 2006 monitoring cycle. However, only a fraction of the samples were collected from the main stem tidal Delaware River. Several samples were collected from the Delaware Bay or tributaries that flow into the Delaware Bay. • DNREC has consistently analyzed for dioxins and furans in fish and shellfish for over a decade (300+ samples). Even though dioxins and furans aren't exactly emerging contaminants, this monitoring program is collecting a unique data set for the Delaware River Basin (email dated Aug 22, 2006 from Rick Greene, DNREC).

5.2 New Jersey

As part of the 2004 Routine Monitoring Program estuarine-marine fish/shellfish (striped bass, bluefish, white perch, white catfish, American eel, blue crab and lobster) that are under current consumption advisories on a statewide, regional and/or waterway-specific basis for PCB and/or dioxin contamination were collected. In addition, several other species of recreational or commercial importance were collected. These included weakfish, porgy and Atlantic croaker. Sampling included alongshore-coastal areas, Delaware Bay and Estuary, and Barnegat Bay. Unless specified, all coastal estuarine and marine species were analyzed for PCBs, pesticides and total mercury, as well as lipids. A limited number of samples were also analyzed for PBDEs (flame retardants). All fish species were analyzed as individual fillets (skin off) and all blue crab were analyzed for both muscle meat and hepatopancreas tissues. In the Delaware Estuary, the emerging contaminant PBDE was detected in striped bass at concentrations between 6.17 to 21.22 ng/g and in American eel at concentrations between 12.19 to 290.68 ng/g. (http://www.state.nj.us/dep/dsr/2004data.htm)

5.3 New York

- New York Department of Health undertook sampling in 2003 and 2004 to determine if detectable levels of selected pharmaceutical analytes are present in the NYC watershed. The project characterized input to the watershed from effluents of four wastewater treatment plants (WWTPs) and monitored major inputs and outputs of key reservoirs. In the WWTP, atenol was found in every sample and ibuprofen was found at every site. Also found was trimethoprim, caffeine, estrone, and 17β-estradiol. In reservoirs, caffeine, trimetoprim and ibuprofen were detected in a few samples but not confirmed in duplicate samples. (Lloyd Wilson, Center for Environmental Health, NYS Department of Health presentation to EPA Region 2 Science Day on Non-Regulated Pollutants on October 25, 2005, Survey of the New York City Watershed for the Presence of Pharmaceuticals at http://www.mass-awma.net/files/2006-04 Wilson Presentation.pdf)
- A partial and informal list of emerging compounds of concern for New York State includes PBDE, brominated dioxins, perchlorates, pharmaceuticals, endocrine disruptors, and nanotechnology (Scott Stoner, NYSDEC, ASIWPCA Conference

Call). NYSDEC has also developed a more formal list of chemical substances that need ambient surface water quality criteria for human health and/or aquatic life (letter to Dr. Edward Ohanian, Director, Health and Ecological Criteria Division, USEPA from Sandra Allen, Director, Division of Water, NYSDEC date Dec 17, 2004). The list includes acenaphthylene, alachlor, tert-amyl methyl ether (TAME), benzo(ghi)perylene, benzothiazole, bromine, tert-butyl alcohol, carbaryl, carbon tetrachloride, chlorendic acid, 2-chloroethyl vinyl ether (mixed), 4-chlorophenyl phenyl ether, cyanazine, desethyl atrazine (DEA), desisopropyl atrazine (DIA), dibenzofuran, 2,6-dinitrotoluene, 1,4-dioxane, disulfoton, EDTA, endosulfan, sulfate, eptam (EPTC), ethanol, hexamehtylbenzene, hydrogen peroxide, iron, lead, linuron, malathion, manganese, methanol, methoxypropylamine, methylene chloride, metolachlor, octachlorocyclo-pentene, napropamide, pendimethalin, pentachlorphenol, permethrin, polybrominated dioxins and furans (PBDDs and PBDFs), polybrominated diphenyl ethers (PBDE), polychlorinated naphthalenes (PCN), polyhalodioxins and polyhalofurans, polymethacrylic acid, potassium permanganate, prometon, resmethrin, selenium, silver, simazine, sumithrin, tebuthiuron, terbacil, 1,1,2,2tetrachloroethane, tetrachloroethylene (PCE), 1,1,1-trichloroethane, trichloroethylene, and trifluralin.

5.4 Pennsylvania

- A committee on non-regulated contaminants is working to develop a list of potential contaminants in drinking water source waters that are not currently regulated by PADEP. The committee is reviewing databases and considering the treatability of potential contaminants (Deborah Rotz, PADEP personal communication).
- A surface water survey of pharmaceuticals and antibiotics was conducted by USGS for PADEP in central Pennsylvania. None of the sites in this limited study are in the Delaware River Basin. A complete set of laboratory data has yet to be received as of August 2006. The next part of the survey may include analysis for hormones at USGS NAWQA sites. (Rhonda Manning, PADEP personal communication)

Table 3: List of Target Pharmaceutical Compounds to be Analyzed for thePA Study

Constituent	Minimum reporting limit	Reporting units	Analytical method
1,7-Dimethylxanthine	0.018	<i>u</i> g/L	HPLC
Acetaminophen	.009	<i>u</i> g/L	HPLC
Albuterol	.029	<i>u</i> g/L	HPLC
Caffeine	.014	<i>u</i> g/L	HPLC
Carbamazepine	.0107	ug/L	HPLC
Cimetidine	.007	ug/L	HPLC
Codeine	.24	<i>u</i> g/L	HPLC
Continine	.023	<i>u</i> g/L	HPLC
Dehydronifedipine	.01	<i>u</i> g/L	HPLC
Digoxigenin	.008	ug/L	HPLC
Diltiazem	.012	<i>u</i> g/L	HPLC
Diphyenydramine	.0148	ug/L	HPLC
Fluoxetine	.018	<i>u</i> g/L	HPLC
Gemfribrozil	.015	<i>u</i> g/L	HPLC
Ibuprofen	.018	ug/L	HPLC
Miconazole	.0175	ug/L	HPLC
Rantidine	.01	ug/L	HPLC
Sulfamethoxazole	.023	ug/L	HPLC
Thiabendazole	.0108	ug/L	HPLC
Trimethoprim	.014	ug/L	HPLC
Warfarin	.001	ug/L	HPLC

Table 4: List of Target Antibiotics to be Analyzed for the PA Study

Class of antibiotics	Constituent	Minimum reporting limit	Reporting units	Analytical method
Beta				
Lactams				
	Amoxicillin	0.010	<i>u</i> g/L	LC/MS
	Ampicillin	0.010	<i>u</i> g/L	LC/MS
	Cefotaxime	0.010	<i>u</i> g/L	LC/MS
	Oxacillin	0.010	<i>u</i> g/L	LC/MS
	Penicillin G	0.010	<i>u</i> g/L	LC/MS
	Penicillin V	0.010	<i>u</i> g/L	LC/MS

Macrolide				
	Erythromycin	0.005	<i>u</i> g/L	LC/MS
	*Anhydro-erythromycin	0.005	<i>u</i> g/L	LC/MS
	Lincomycin	0.005	<i>u</i> g/L	LC/MS
	Ormetoprim	0.005	<i>u</i> g/L	LC/MS
	Roxithromycin	0.005	<i>u</i> g/L	LC/MS
	Trimethoprim	0.005	<i>u</i> g/L	LC/MS
	Tylosin	0.005	<i>u</i> g/L	LC/MS
	Virginiamycin	0.005	<i>u</i> g/L	LC/MS
Quinoline	S			
	Ciprofloxacin	0.005	<i>u</i> g/L	LC/MS
	Clinafloxacin	0.005	<i>u</i> g/L	LC/MS
	Flumequine	0.005	<i>u</i> g/L	LC/MS
	Lomefloxacin	0.005	<i>u</i> g/L	LC/MS
	Norfloxacin	0.005	<i>u</i> g/L	LC/MS
	Ofloxacin	0.005	<i>u</i> g/L	LC/MS
	Oxolinic acid	0.005	<i>u</i> g/L	LC/MS
	Sarafloxacin	0.005	<i>u</i> g/L	LC/MS
Sulfonami	des		-	
	Sulfachloropyridazine	0.005	<i>u</i> g/L	LC/MS
	Sulfadiazine	0.005	<i>u</i> g/L	LC/MS
	Sulfadimethoxine	0.005	ug/L	LC/MS
	Sulfamerazine	0.005	<i>u</i> g/L	LC/MS
	Sulfamethazine	0.005	<i>u</i> g/L	LC/MS
	Sulfamethoxazole	0.005	<i>u</i> g/L	LC/MS
	Sulfathiazole	0.005	<i>u</i> g/L	LC/MS
	Carbadox	0.005	ug/L	LC/MS
Tetracvcli	nes and Degradation			
Products	5			
	Chlorotetracycline	0.010	<i>u</i> g/L	LC/MS
	*Anhydro-chlorotetracycline	0.010	<i>u</i> g/L	LC/MS
	*Demeclocycline	0.010	<i>u</i> g/L	LC/MS
	Doxycycline	0.010	<i>u</i> g/L	LC/MS
	Minocycline	0.010	ug/L	LC/MS
	Oxytetracycline	0.010	ug/L	LC/MS
	Tetracycline	0.010	ug/L	LC/MS
	*Anhydro-tetracycline	0.010	ug/L	LC/MS
			;	

• The Fish Consumption Technical Workgroup chaired by Mike Webb, PADEP developed the following list of emerging contaminants. This list was provided to DRBC staff by John Arway, PA Fish and Boat Commission.

Emerging Contaminants – The Pennsylvania List (3/21/06)

Polybominated diphenyl ethers (PBDE) Phthalic acid esters Adipates Nonyl-phenols **Bisphenyl** A Perfluorinated compounds including perfluorinated octanoic acid (PFOA) Personal car products (PCP) Pharmaceuticals Antibiotics Polynuclear aromatics (PNA) Polycyclic aromatic hydrocarbons (PAH) Atrazine and other triazine herbicides Alachlor Sulfoureas Glyphosate Triclosan PCB congeners silver selenium

6.0 Other

• Dr. Rominder Suri, Villanova University, Villanova, PA - Initially measured estrogens, antibiotics and an anti-depressant in 21 stream sites in Chester County, PA and 3 WWTP in a USEPA sponsored study. He plans to expand the area of interest to the Schuykill watershed and include personal care products (PCP) and other emerging compounds. Future studies will examine sediments as well as water.

List of Initial Compounds of Interest 17 α -estradiol (1) 17 β -estradiol (1) 17 α -dihydroequilin (1) ethinyl estradiol (1) estriol (1) estrone (1) equilin (1) progesterone (1) medrogesterone (1) norgestrel (1) levonorgestrel (1) gestodene (1)

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sulfamethoxazole (2)
sulfamethazine (2)
trimethoprim (2)
norfloxacin (2)
ofloxacin (2)
lincomycin (2)
tetracycline (2)
oxytetracycline (2)
chlorotetracycline (2)
erythromycin (2)
roxithromycin (2)
tylosin tartrate (2)
venlafaxine (3)
 (1) estrogenic hormones
 (2) antibiotics
 (3) anti-depressant
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 Dr. Jeffrey Ashley, Philadelphia University, Philadelphia, PA – Conducted a NJDEP and Delaware Estuary Program sponsored study of PBDE flame retardants in American eels and sediment from sites in the Delaware River and tributaries of the Delaware Bay. Total PBDE concentrations in American eel were in the range of 10 to 5,652 ng/g lipid. The concentrations of total PBDE for sediments were in the 39 to 1,104 ng/g OC range (Ashley *et al.* in press).



Figure 3. Polybrominated Diphenyl Ethers (PBDE) in American Eels from the Delware River, USA (Ashley et al. in press)

- A Pharmaceutical Assessment and Transport Evaluation (PhATE) model was developed by the Pharmaceutical Research and Manufacturers of America (PhRMA) as a tool to estimate concentrations of active pharmaceutical ingredients that result from patient use or consumption of medicines in surface waters in 11 watersheds including the Schuylkill River watershed. Simulations using three surrogate compounds showed that the PhATE model may be use to predict screening level concentrations of active pharmaceuticals and related compounds in the environment (Anderson *et al.* 2004, Environ Sci. Technol.)
- In a study of the effects of contaminant exposure on reproductive success of osprey nesting in the Delaware River and Bay, osprey eggs were analyzed for the emerging contaminants perfluorinated compounds (perfluorononanoic acid, perfluorodecanoic acid, perfluorodecanoic acid, perfluorodecanoic acid, perfluorodecanoic acid, perfluorodecanesulfonate, and perfluorodecanesulfonate) as well as PBDE congeners 47, 99, 100, 153, 154 and two unidentified PBDEs hexa-a and hexa-c. The study area was divided into four segments (Figure 4). The mean concentration of individual PFOAs in osprey eggs by study area ranged between 1 to 293 ng/g wet-weight. The mean PBDE congener concentrations by study area ranged from not detected to 276 ng/g with mean total PBDEs between 82 to 572 ng/g wet weight. The highest concentrations were observed between Trenton and the C&D canal for both PFOAs and PBEs. (Toschik et al., 2005)



Figure 4. Polybrominated diphenyl ethers (PBDE) in osprey eggs from the Delaware River Basin (Toschik et al., 2005)

7.0 Ecological Risk

Efforts to prioritize ECOC rely heavily on ecological risk assessment. Initial assessment of environmental risk consists of collecting available exposure and ecotoxicity data for a contaminant and determining both predicted environmental concentrations (PEC) and predicted no-effect concentrations (PNEC). The PEC is often difficult to estimate because of the scarcity of data on product usage and information on the environmental fate and effects of a product. The PNEC is usually determined from acute toxicity tests with an adjustment factor to predict chronic effects. However, chronic sublethal toxicity tests are increasing being considered. Sublethal toxic effects may include endocrine disruption and reproductive harm. Generally, if PEC/PNEC is < 1 the substance is considered environmentally safe and no further action is needed. If the PEC/PNEC is >1, additional risk assessment is needed. Based on various risk assessment methodologies, certain emerging contaminants have been identified to be priority concerns in aquatic environments (e.g., the pharmaceuticals carbamazepine, ethynylestradiol and sulfamethoxazole (Ferrari et al., 2004; Mitchell Kostich in USEPA Meeting on Pharmaceuticals in the Environment, http://es.epa.gov/ncer/publications/meetings/8-23-2005/finalsummary.pdf).

In addition, fate and effect studies and risk assessment of products have often focused on biodegradability to assure environmental safety. However, there is an emerging concern that chemical stability is not required for persistence in the environment. Continuous discharge of a pollutant into the environment can cause continual, multi-generational life-cycle exposures of sensitive species. (Daughton, 2004, <u>http://www.epa.gov/ppcp/pdf/daughton-needs.pdf</u>)

Currently, the USFDA has a "trigger' of 1 μ g/L environmental concentration for performing risk assessments on new pharmaceuticals. That value has been questioned as insufficiently conservative by Dr. Lynn Roberts, John Hopkins University in a USEPA Meeting on Pharmaceuticals in the Environment because some compounds exert chronic toxicity below that threshold value. (http://es.epa.gov/ncer/publications/meetings/8-23-2005/finalsummary.pdf) Following a precautionary principle, a lower threshold of 0.01 μ g/L has been proposed for surface water and drinking water. (Kummerer, 2004)

8.0 Summary

Advances in chemical analysis are allowing both the identification of different contaminants and the detection of substances at lower concentrations in the environment. Combine this enhanced analytical capacity with growing concerns over subtle long-term effects of exposure to low concentrations of contaminants or the effects of multiple contaminants and you start to understand the complexity of the ecotoxicology issues related to emerging contaminants. This report lists a number of efforts underway within the Delaware River Basin by the DRBC, Federal, and state agencies to monitor ECOC. At this time the results of many of the studies are not available for review. Upon review of the available information, a list of target ECOC for monitoring in the mainstem of the Delaware River Basin is proposed.

As an interstate agency entrusted with the management of water quality, the DRBC's response to public concerns about emerging contaminants should include:

- Compilation of within basin data on ECOC (non-regulated compounds);
- Identification of data gaps;
- Adapting monitoring program to current priorities;
- Partnering with EPA, USGS, states and stakeholders on ECOC initiatives; and
- Enhancing public awareness of managing pharmaceutical waste

9.0 References

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