

CONTAMINANTS OF EMERGING CONCERN WITHIN THE MAINSTEM OF THE OHIO RIVER AND ITS TRIBUTARIES



Marc A. Mills¹, Erich Emery², Shoji F. Nakayama¹, John Spaeth²
¹ US Environmental Protection Agency, National Risk Management Laboratory
26 West Martin Luther King Drive., Cincinnati, OH 45268, USA.
² Ohio River Valley Water Sanitation Commission
5735 Kellogg Ave., Cincinnati, OH 45230, USA.



Introduction

Contaminants of emerging concern such as PPCPs, akyphenols, EDCs, and PFCs in waterways have been of increasing public concern. The extent and persistence of their occurrence in surface waters remains unclear. Though there are many sources of these contaminants, research has focused primarily on WWTPs and CAFOs. Kolpin et al. (2002) surveyed downstream of major municipal, industrial or agri-cultural centers for organic wastewater contaminants. They found that steroid hormones were present at varying levels in 86% of the streams surveyed. A national survey by USEPA NERL of 50 WWTPs found 26% to contain estrogenic endocrine disrupting activity levels high enough to induce vitellogenesis in male fathead minnows (Lazorchak & Smith 2004). However, these were grab samples and effluents change depending on influent characteristics, therefore this may not provide an accurate estimate as to the problem extent.

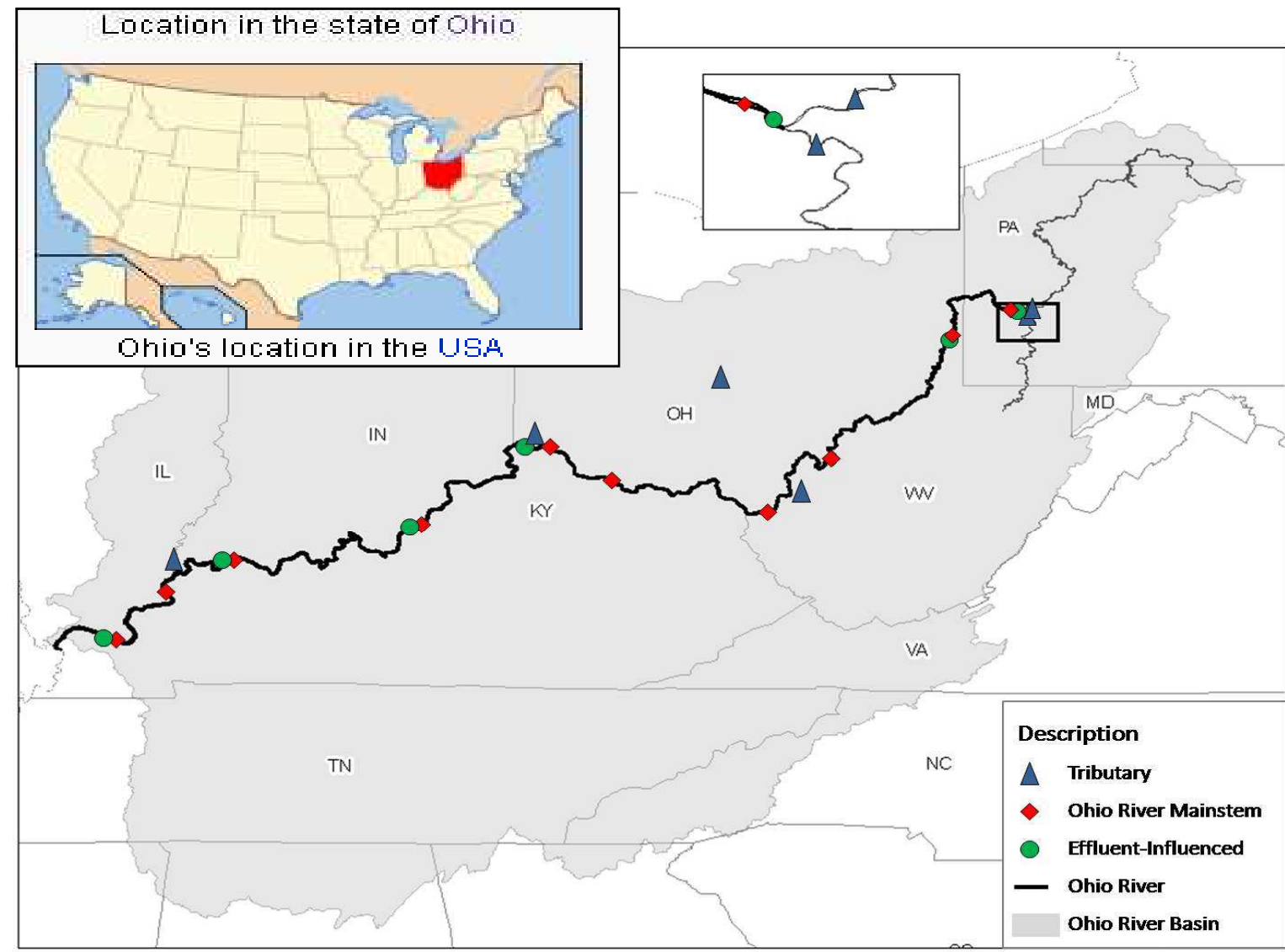
These studies provided valuable information about the presence of CECs in surface waters, however; the longitudinal occurrence and concentrations of these compounds within a large river system are unknown. Identifying CECs and their concentrations in surface waters of the Ohio River and its tributaries is essential to protecting the public health of the 25 million people who live within the basin and depend on the water for drinking water, irrigation, and recreation. The existence, extent of and persistence of PPCPs, APs, EDCs, and PFCs in the Ohio River and selected tributaries are reported. The primary focus is to document the occurrence and concentrations of CECs in the main-stem of the Ohio River and several of tributaries.

This study was designed to generate data as preliminary survey by the Commission and results would be used to guide future actions.

Sites Description

Study Overview: In September and October, 2009, single grab samples were collected from 22 locations on the mainstem Ohio River and the lower reaches of tributaries. Target analytes included 158 compounds considered to be contaminants of emerging concern or emerging contaminants.

- 118 - Pharmaceutical and Personal Care Products
- 27 - Hormones and Sterols
- 13 - Perfluorinated Compounds



Sample Number	Location	River	River Mile*	Date
1	Tributary	Allegheny	9.5	9/14/2009
2	Tributary	Monongahela	5.0	9/14/2009
3	Ohio River Mainstem (EI)	Ohio	3.1	9/14/2009
4	Ohio River Mainstem	Ohio	9.7	9/14/2009
5	Ohio River Mainstem (FB)	Ohio	462.9	9/16/2009
6	Ohio River Mainstem	Ohio	86.7	9/14/2009
7	Ohio River Mainstem (EI)	Ohio	91.3	9/14/2009
8	Ohio River Mainstem	Ohio	220.3	9/15/2009
9	Tributary	Kanawha	4.1	9/15/2009
10	Ohio River Mainstem	Ohio	306.8	9/15/2009
11	Tributary	Scioto	105.8	10/20/2009
12	Ohio River Mainstem	Ohio	394.9	9/15/2009
13	Ohio River Mainstem (FB)	Ohio	220.3	9/15/2009
14	Ohio River Mainstem	Ohio	462.9	9/16/2009
15	Ohio River Mainstem (EI)	Ohio	478.0	9/16/2009
16	Tributary	Mill Creek	0.2	9/16/2009
17	Ohio River Mainstem	Ohio	600.5	9/21/2009
18	Ohio River Mainstem (EI)	Ohio	612.2	9/21/2009
19	Ohio River Mainstem	Ohio	791.5	9/21/2009
20	Ohio River Mainstem (EI)	Ohio	791.8	9/21/2009
21	Tributary	Wabash	0.8	9/21/2009
22	Ohio River Mainstem	Ohio	889.1	9/21/2009
23	Ohio River Mainstem	Ohio	934.4	9/22/2009
24	Ohio River Mainstem (EI)	Ohio	935.9	9/22/2009
25	Tributary (FB)	Scioto	105.8	10/20/2009
26	PFC Field Spike 1 (Low)	Scioto	105.8	10/20/2009
27	PFC Field Spike 2 (High)	Scioto	105.8	10/20/2009

* - Tributary river miles are assigned by the number of miles upstream of the confluence with the Ohio River proper.
FB - Field blank taken at this location
EI - Effluent influenced

Methods/Approaches

Field Methods

Sampling protocols and analytical methods specific to the type of analytes to be collected are summarized in Table 2. Since each compound required each different sampling procedure, the appropriate SOPs were followed. Especially for PFCs, conventional water sampling technique can't be applied due to their chemical/physical properties. Since AXYS method does not include sampling procedure, the method developed by NERL (SOP EMAB-113.0) was used.

Between sampling locations, collecting equipment was rinsed with river water, then ultrapure water for proper decontamination of equipment. Latex/nitrile gloves were worn during water collection to minimize sample contamination. Sample storage and handling are also defined in each specific SOP.

Field blanks were also prepared to further account for potential sampling error. Preparation and handling of field blanks for each class of analytes are described in their respective SOPs. Travel spike samples were also prepared for PFCs as described in the SOPs.

Type of compound	Analytical Laboratory	Sampling protocol	Container/ preservation/storage/ holding time	Analytical method	Appendix
ORSANCO (AXYS and)					
Pharmaceuticals	Waters	Waters-Agents-Analysis Method	20 ml glass/NA/dark < 6°C/7 d	Waters-Agents-Analysis Method	A
PPCPs	AXYS	EPA Method 1694 with modification	1 L HDPE/NA/dark < 6°C/7 d	EPA Method 1694 with modification	B
PFCs	AXYS	EPA-NERL SOP EMAB-113.0 with modification	1 L HDPE/5 mL 3% nitric acid/ambeim 28 d (avoid PTFE or Teflon materials)	AXYS MLA-060	C, D
Hormones and Steroids	AXYS	EPA Method 1698	1 L amber glass/NA/dark < 6°C (field), frozen (lab)/7 d	AXYS MLA-068	E, F
NERMRL					
Steroid Hormones	NERMRL	EPA Method 1698	1 L amber aluminized glass/NA/dark < 6°C (field), frozen (lab)/7 d	NERMRL Draft SOP	G
Region 5 CRL					
APs	Region 5 CRL	ASTM Standard Test Method D7065-6	1 L glass/H ₂ SO ₄ pH 2/iced or 0-4°C (avoid freezing)/28 d (avoid Tygon tubing)	ASTM Standard Test Method D7065-6	H
APEOs	Region 5 CRL	CRL SOP # HS004	1 L amber glass/bottle/iced or 4°C (field), -10°C (lab)/7 d (avoid Tygon tubing)	CRL SOP # HS004	I
NPECs	Region 5 CRL	CRL SOP # MS002	250 mL or 1 L amber glass/-1% w/v formaldehyde/4°C/NA (avoid Tygon tubing)	CRL SOP # MS002	J



Analytical Methods

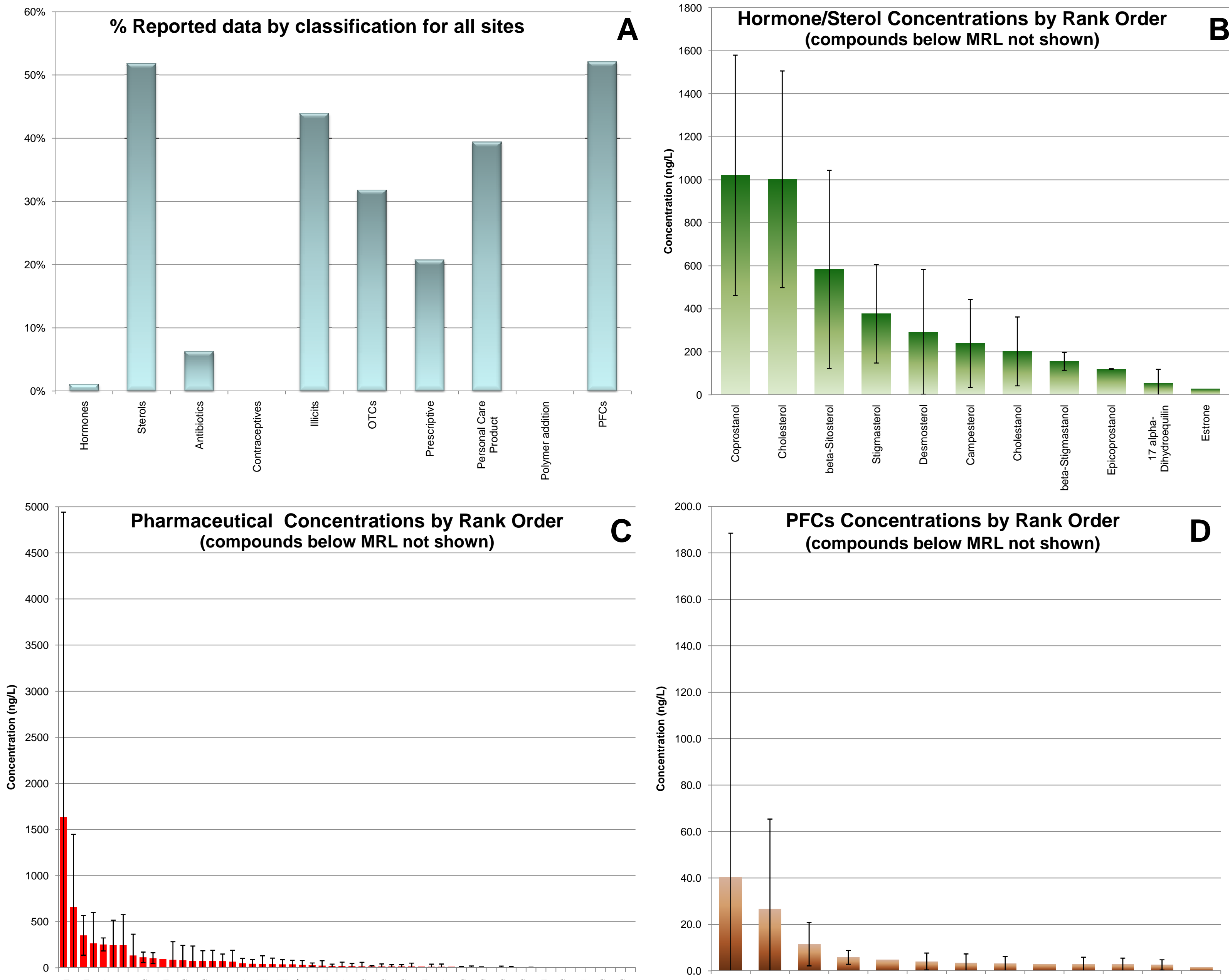
After proper preservation, samples were sent to the contract laboratory, AXYS Analytical, for extraction and analysis. The following three methods were used to measure three classes of target analytes.

- AXYS Method MLA-060 for PFCs (Table 3).Thirteen PFCs were analyzed by high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) by Axys Analytical T
- AXYS Method MLA-075 for PPCPs (Table 3). This method is technically equivalent to the EPA Draft Method 1964 released in 2007. The Method 1964 is a single laboratory validated method. A total of 118 PPCP analyte were measured using HPLC–MS/MS.
- AXYS Method MLA-068 for Hormones/Sterols (Table 3). AXYS' internal method MLA-068 is technically equivalent to the EPA draft Method 1698 which is a single laboratory validated method. A total of 27 hormones and sterols were analyzed by gas chromatography–high resolution mass spectrometry (GC–HRMS).

Results

All samples were successfully collected and analyzed for the target analytes following the SOPs and protocols as planned. Upon receipt of the chemistry data from the analytical laboratory, EPA followed a standard validation process for all data prior to any reporting.

In all sites, compounds were detected at some quantifiable levels (Graph A). The most common detected compounds was the pharmaceutical class of compounds. In all, every site had quantifiable concentrations of emerging contaminants. Sterol compounds were most often found in the highest concentrations of the compounds detected followed by pharmaceuticals, PFCs, and finally hormones were least commonly detected.



Conclusions

Detectable concentrations of selected contaminants of emerging concern were found through the Ohio River basin in this pilot survey. Significantly more data analysis and interpretation remains to be completed on this study. Additionally, all samples were collected as single grab samples, therefore no temporal or spatial relationship can be derived without further sampling and research. The study purpose was met by providing an initial view CECs in the basin and to inform further sampling and research efforts in the Ohio River basin.

Compound	General Use	MRL* (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Average (ng/L)	% Quant.
Classification - Endogenous (23)						
Androstenedione	Androgenic horm.	20.6	0.0	0.0	0.0	0
Androsterone	Androgenic horm.	8.32	0.0	0.0	0.0	0
Testosterone	Androgenic horm.	8.56	0.0	0.0	0.0	0
17 alpha-Dihydroequilin	Estrogenic horm.	8.08	9.1	100.0	54.5	9
Equilenin	Estrogenic horm.	8.31	0.0	0.0	0.0	0
Equilin	Estrogenic horm.	7.85	0.0	0.0	0.0	0
17 alpha-Estradiol	Estrogenic horm.	7.92	0.0	0.0	0.0	0
17 beta-Estradiol	Estrogenic horm.	8.16	0.0	0.0	0.0	0
beta-Estradiol 3-benzoate	Estrogenic horm.	8.64	0.0	0.0	0.0	0
Estril	Estrogenic horm.	7.92	0.0	0.0	0.0	0
Estrone	Estrogenic horm.	9.28	27.5	27.5	27.5	5
Mestranol	Estrogenic horm.	8.16	0.0	0.0	0.0	0
Progesterone	Progestin	20.5	0.0	0.0	0.0	0
Campesterol	Sterol	40.0	52.3	812.0	239.3	82
Cholesterol	Sterol	40.0	52.2	562.0	202.0	91
Cholesterol	Sterol	94.4	195.0	1830.0	1002.5	86
Coprostanol	Sterol	96.9	462.0	1830.0	1020.9	32
Desmosterol	Sterol	57.5	82.5	867.0	292.4	27
Epicoprostanol	Sterol	95.9	120.0	121.0	120.5	9
Ergosterol	Sterol	96.3	0.0	0.0	0.0	0
beta-Sitosterol	Sterol	94.5	98.0	1640.0	583.7	95
beta-Stigmasterol	Sterol	96.8	111.0	213.0	156.2	23
Stigmasterol	Sterol	40.5	90.9	119.0	377.4	73

Classification - Pharmaceutical (118)						
Azithromycin	Antibiotic	1.50	41.2	834.0	245.9	23
Carbadox	Antibiotic	1.50	0.0	0.0	0.0	0
Cefotaxime	Antibiotic	6.00	0.0	0.0	0.0	0
Ciprofloxacin	Antibiotic	20.0	27.8	162.0	72.8	14
Clarithromycin	Antibiotic	1.50	1.9	530.0	88.6	32
Clinafloxacin	Antibiotic	6.00	0.0	0.0	0.0	0
Cloxacillin	Antibiotic	1.20	0.0	0.0	0.0	0
Demeclocycline	Antibiotic	15.0	0.0	0.0	0.0	0
Doxycycline	Antibiotic	20.0	0.0	0.0	0.0	0
Enrofloxacin	Antibiotic	3.00	0.0	0.0	0.0	0
Erythromycin-H2O	Antibiotic	1.00	1.1	15.2	15.2	91
Flumequine	Antibiotic	1.50	0.0	0.0	0.0	0
Lincomycin	Antibiotic	7.02	0.0	0.0	0.0	0
Lomefloxacin	Antibiotic	3.00	0.0	0.0	0.0	0
Miconazole	Antibiotic	1.50	0.0	0.0	0.0	0
Minocycline	Antibiotic	60.0	0.0	0.0	0.0	0
Norfloxacin	Antibiotic	15.0	14.3	14.3	14.3	5
Ofloxacin	Antibiotic	15.0	27.7	265.9	265.9	9
Ormetoprim	Antibiotic	0.600	0.0	0.0	0.0	0
Oxacillin	Antibiotic	3.00	0.0	0.0	0.0	0
Oxolinic Acid	Antibiotic	0.600	0.0	0.0	0.0	0
Oxytetracyclin [OTC]	Antibiotic	6.00	0.0	0.0	0.0	0
Penicillin G	Antibiotic	1.20	0.0	0.0	0.0	0
Penicillin V	Antibiotic	3.00	0.0	0.0	0.0	0
Roxithromycin	Antibiotic	0.300	0.0	0.0	0.0	0
Sarafloxacin	Antibiotic	50.0	0.0	0.0	0.0	0
Sulfachloropyridazine	Antibiotic	1.50	0.0	0.0	0.0	0
Sulfadiazine	Antibiotic	5.00	7.5	7.5	7.5	5
Sulfadimethoxine	Antibiotic	1.00	0.0	0.0	0.0	0
Sulfamerazine	Antibiotic	0.600	0.0	0.0	0.0	0
Sulfamethazine	Antibiotic	0.600	0.0	0.0	0.0	0
Sulfamethizole	Antibiotic	0.600	0.0	0.0	0.0	0
Sulfamethoxazole	Antibiotic	2.00	6.8	75.1	75.1	100
Sulfanilamide	Antibiotic	15.0	0.0	0.0	0.0	0
Sulfathiazole	Antibiotic	1.50	2.7	2.7	2.7	5
Anhydrochlortetracycline [ACTC]	Antibiotic	15.0	0.0	0.0	0.0	0
Anhydrotetracycline [ATC]	Antibiotic	15.0	0.0	0.0	0.0	0
Chlortetracycline [CTC]	Antibiotic	6.00	0.0	0.0	0.0	0
4-Epi-anhydrochlortetracycline [EACTC]	Antibiotic	60.0	0.0	0.0	0.0	0
4-Epi-anhydrotetracycline [EATC]	Antibiotic	15.0	0.0	0.0	0.0	0
4-Epichlortetracycline [ECTC]	Antibiotic	15.0	0.0	0.0	0.0	0
4-Epioxytetracycline [EOTC]	Antibiotic	6.00	0.0	0.0	0.0	0
4-Epitetracycline [ETC]	Antibiotic	6.00	0.0	0.0	0.0	0
Isochlortetracycline [ICTC]	Antibiotic	6.00	0.0	0.0	0.0	0
Tetracycline [TC]	Antibiotic	20.0	0.0	0.0	0.0	0
Trimethoprim	Antibiotic	15.0	50.0	187.0	105.5	18
Tylosin	Antibiotic	6.0	0.0	0.0	0.0	0
Virginiamycin	Antibiotic	3.00	0.0	0.0	0.0	0
Desogestrel	Contraceptive	8.56	0.0	0.0	0.0	0
17 alpha-Ethinyl-Estradiol	Contraceptive	8.56	0.0	0.0	0.0	0
Norethindrone	Contraceptive	8.59	0.0	0.0	0.0	0
Norgestimate	Contraceptive	3.00	0.0	0.0	0.0	0
Norgestrel	Contraceptive	8.16	0.0	0.0	0.0	0
Amphetamine	Illicit	5.00	5.1	13.0	7.7	18
Benzoylecgonine	Illicit	1.00	1.1	56.5	6.6	82
Cocaine	Illicit	0.150	0.2	7.6	1.6	32
Acetaminophen	OTC	2.00	201.0	506.0	353.5	6
Caffeine	OTC	5.00	57.8	243.0	114.4	64
Cimetidine	OTC	1.00	1.6	49.3	15.5	23
Cotinine	OTC	5.00	7.6	51.3	16.6	100
2-Hydroxy-ibuprofen	OTC	800	0.0	0.0	0.0	0
Ibuprofen	OTC	15.0	0.0	0.0	0.0	0
Naproxen	OTC	10.0	13.3	164.0	45.1	45
Ranitidine	OTC	2.00	4.2	203.0	76.7	14
Albuterol	Prescriptive	1.00	1.2	17.4	6.3	18
Aloprazolam	Prescriptive	1.00	1.5	7.7	3.9	14
10-Hydroxy-amitriptyline	Prescriptive	0.150	0.2	7.4	1.2	41
Amisulpride	Prescriptive	1.00	1.1	77.8	13.6	32
Amoxicillin	Prescriptive	1.50	3.5	3.5	3.5	5
Atenolol	Prescriptive	2.00	2.8	502.0	68.1	91
Atorvastatin	Prescriptive	15.0	0.0	0.0	0.0	0
Benzotropine	Prescriptive	0.300	0.0	0.0	0.0	0
Betamethasone	Prescriptive	1.50	0.0	0.0	0.0	0
Carbamazepine	Prescriptive	5.00	9.3	159.0	38.3	95
Clonidine	Prescriptive	1.50	0.0	0.0	0.0	0
Codeine	Prescriptive	10.0	11.8	88.2	50.0	9
Dehydronifedipine	Prescriptive	2.00	2.0	5.4	2.9	18
Desmethyldiltiazem	Prescriptive	0.500	0.7	79.6	13.6	36
Diazepam	Prescriptive	1.00	1.4	4.1	2.6	9
Digoxigenin	Prescriptive	6.00	0.0	0.0	0.0	0
Digoxin	Prescriptive	15.0	0.0	0.0	0.0	0
Diltiazem	Prescriptive	1.00	1.4	172.0	25.7	45
1,7-Dimethylxanthine	Prescriptive	15.0	0.0	0.0	0.0	0
Diphenhydramine	Prescriptive	2.00	3.3	42.2	13.2	29
Enalapril	Prescriptive	1.00	0.0	0.0	0.0	0
Fluocinonide	Prescriptive	6.00	0.0	0.0	0.0	0
Fluoxetine	Prescriptive	1.50	1.8	25.0	9.5	18
Fluticasone propionate	Prescriptive	2.00	2.0	2.0	2.0	5
Furosemide	Prescriptive	133	198.0	1570.0	660.0	14
Gemfibrozil	Prescriptive	5.14	6.5	366.0	40.6	68
Glipizide	Prescriptive	6.00	0.0	0.0	0.0	0
Glyburide	Prescriptive	3.00	13.0	13.0	13.0	5
Hydrochlorothiazide	Prescriptive	66.7	81.4	558.0	248.1	14
Hydrocodone	Prescriptive	5.00	5.2	159.0	39.4	23
Hydrocortisone	Prescriptive	600.0	0.0	0.0	0.0	0
Meprobamate	Prescriptive	13.3	13.6	646.0	82.6	68
Metformin	Prescriptive	300	324.0	15300.0	1633.9	91
Methylprednisolone	Prescriptive	40.0	0.0	0.0	0.0	0
Mefenoxol	Prescriptive	15.0	17.8	701.0	134.3	36
Norfloxacin	Prescriptive	1.50	2.2	2.2	2.2	5
Nifedipine	Prescriptive	5.14	6.5	366.0	40.6	68
Oxycodone	Prescriptive	2.00	2.6	66.1	15.7	45
Paroxetine	Prescriptive	4.00	5.5	5.5	5.5	5
Prednisolone	Prescriptive	6.00	0.0	0.0	0.0	0
Prednisone	Prescriptive	2.00	0.0	0.0	0.0	0
Promethazine	Prescriptive	0.399	0.0	0.0	0.0	0
Propoxyphene	Prescriptive	1.00	1.2	123.0	20.9	36
Propranolol	Prescriptive	6.67	10.1	146.0	38.9	14
Sertraline	Prescriptive	1.33	3.1	64.6	16.3	23
Sinvastatin	Prescriptive	20.0	0.0	0.0	0.0	0
Sulfinpyrazone	Prescriptive	2.00	204.0	304.0	254.0	9
Thiabendazole	Prescriptive	5.00	10.7	10.8	10.8	9
Trenbolone	Prescriptive	4.00	0.0	0.0	0.0	0
Trenbolone acetate	Prescriptive	0.300	0.0	0.0	0.0	0
Triamterene	Prescriptive	1.00	1.5	20.0	17.3	95
Valsartan	Prescriptive	13.3	17.6	625.0	77.8	64
Verapamil	Prescriptive	1.50	2.4	64.3	18.2	18
Warfarin	Prescriptive	1.50	3.9	3.9	3.9	3