



**OFFICE OF WATER PROGRAMS  
BUREAU OF CLEAN WATER**

**CONTAMINANTS OF EMERGING CONCERN IN STREAMBED SEDIMENT,  
PENNSYLVANIA (2013 – 2017)**

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## 1. EXECUTIVE SUMMARY

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Contaminants of emerging concern (CECs) are contaminants either newly introduced into the environment or ones that may have been in the environment for many years but were only recently able to be analyzed with modern laboratory methods. Very little information has been collected on CEC streambed sediment contamination in Pennsylvania. As a result, the Pennsylvania Department of Environmental Protection (DEP) began sampling streambed sediment in 2013 for a variety of emerging contaminants. Between 2013 to 2017, DEP sampled streambed sediment at 87 sites and had those samples analyzed for contaminants in a variety of CEC categories – pesticides, polychlorinated biphenyls (PCBs), hormones, and wastewater indicator compounds – and for various metals.

In these samples, 202 CECs and metals were analyzed, with 115 CECs and metals detected, although 72% of all environmental sample results were non-detect. Most metals were detected every time they were tested for. Commonly detected CECs were fluoranthene and pyrene, which are common polycyclic aromatic hydrocarbons (PAHs). Cholesterol was the most commonly detected hormone. Pesticides and PCBs were rarely detected. The highest concentration of a currently-used pesticide was cis-permethrin at 5,985 µg/kg. The legacy pesticides with the highest concentrations were DDT and its metabolites. The highest concentration of PCB was Arochlor-1254 at 362 µg/kg.

Canonical correspondence analyses (CCAs) were completed to assess the influence of various environmental variables on streambed sediment CEC and metal concentrations. In large drainage areas in 2013-2015 samples, percent agricultural land use in the upstream watershed was the strongest predictor of streambed sediment hormone concentrations. Out of the anthropogenic variables, percent agricultural land use was the strongest predictor of streambed sediment wastewater compound concentrations in larger watersheds while percent agricultural land use and percent forested land use were the strongest predictors of streambed sediment wastewater compound concentrations in smaller watersheds. Significant natural predictors of hormone and wastewater concentrations in streambed sediments for the 2013-2015 data were flow and drainage area. The most significant anthropogenic predictor of streambed sediment metal concentrations in larger drainage areas was percent developed land use. For streambed sediment metals concentrations, drainage area and ecoregion were the most significant non-anthropogenic predictors.

This study was able to quantify CEC concentrations in streambed sediments across Pennsylvania. This information could assist DEP in determining causes of impairment in stream aquatic life use assessments. In the future, streambed sediment sampling could prove to be useful and commonplace in DEP work.

## 2. INTRODUCTION

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Streambed sediment (referred to hereafter simply as sediment) is often a reservoir for hydrophobic chemical contaminants that adsorb to sediment particles rather than disperse in the water column (USGS 2020). Areas with substantial anthropogenic activity tend to have detectable levels of hydrophobic contamination in sediment, while remote areas do not (Antonic & Heath 2007). Some examples of contaminants in sediment include currently-used and legacy pesticides, polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), metals, pharmaceuticals, and wastewater indicator products. Some of these contaminants are termed contaminants of emerging concern (CECs). These contaminants were either not detected or not able to be detected in the past or are now found in higher concentrations than in the past. They are not necessarily “new” chemicals, although some may be.

Persistent chemicals can remain for years in sediment, which can be dangerous for aquatic life, such as macroinvertebrate larvae, that spend much of their time in sediment (Moran et al. 2017, Fairbairn et al. 2015). As an example, reduced abundance, biomass, and richness of macroinvertebrates have been seen in sediment contaminated with bifenthrin, a common insecticide (Rogers et al. 2016).

Unlike samples collected to analyze chemistry in the water column, samples to analyze chemistry in sediment are collected much less frequently by state and federal agencies. In addition, far fewer criteria are developed for chemicals in sediment compared to water. The Pennsylvania Department of Environmental Protection (DEP) is no exception to this and has historically conducted very little sediment sampling. More recently, and as part of [DEP’s contaminants of emerging concern \(CEC\) monitoring program](#), sediment sample collection has increased for a variety of hormones, pesticides, PCBs, metals, and wastewater indicator compounds.

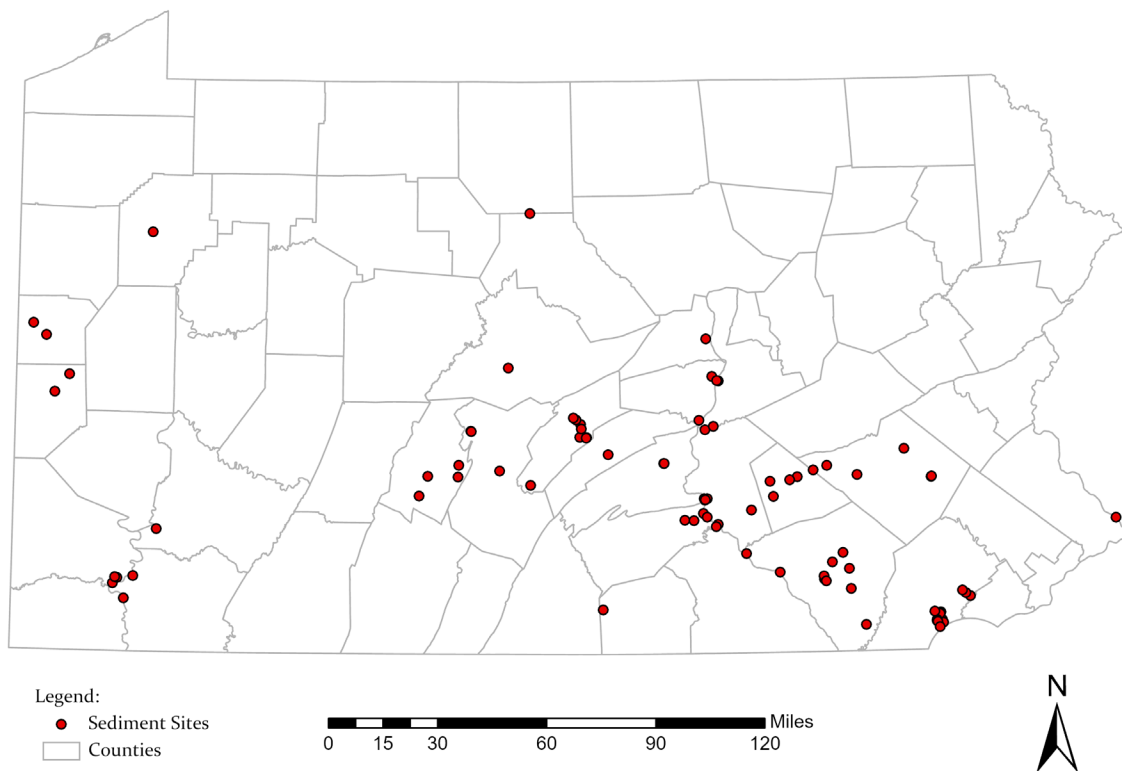
The original intent of DEP’s collection of sediment samples for CEC analysis was aimed at determining if any CECs were found at higher concentrations in sediment in the Susquehanna River and Juniata River basins than in other river basins. Preliminary results of this study were included as part of the causal analysis investigation for the population decline of smallmouth bass (*Micropterus dolomieu*) in the Susquehanna River and Juniata River (Shull and Pulket 2015).

Even more recently, DEP conducted CEC studies to assess overall occurrences and concentrations of CECs in Pennsylvania. The purpose of this report is to catalog the work that DEP has completed to this point and to report the findings of DEP’s sediment contaminant work across Pennsylvania. Results in this report are from data collected and analyzed from 2013 through 2017. Through this study DEP hopes to build upon the technical reports and understanding that ultimately lead to defensible assessment methods and regulatory criteria for sediment.

### 3. METHODS

#### 3.1. Data Collection Protocols and Study Locations

Surficial sediment was collected according to methods established in Chapter 4 of DEP’s Water Quality Monitoring Protocols for Streams and Rivers, *Sediment Chemistry Data Collection Protocol* (Shull and Lookenbill 2018). Briefly, sediment samples were collected within littoral, backwater habitats. Sediment was collected from the surficial layer using trowels and composited in bowls before being transferred to collection jars. Between 2013 to 2017, DEP sampled sediment at 87 sites (Figure 1). Sediment collection sites were often co-located with passive water samplers to obtain a larger perspective of CECs at each site. A full list of sites is in Appendix A-Sites.



**Figure 1.** Sediment sites, 2013 through 2017

#### 3.2. Laboratory Processing

Several analytical laboratories were used for sediment analyses. In 2013 and 2014, sediment samples were analyzed for historical pesticides and PCBs by DEP’s Bureau of Laboratories (BOL). From 2013 to 2017, sediment samples were analyzed for metals, hormones, and wastewater indicator compounds. For these analyses, in 2013 through 2015, hormones, wastewater, and currently-used pesticides were analyzed by the United States Geological Survey (USGS) National Water Quality Laboratory (NWQL). From 2016 to 2017, hormone samples were analyzed by SGS AXYS Analytical

Services Ltd., and wastewater samples were analyzed by USGS NWQL. Specific lab analytical methods used by each laboratory are provided in Appendix B-Methods.

### **3.3. Quality Control (QC)**

Analytical QC varied among laboratories. While field blanks were not completed for SGS AXYS and USGS analyses, SGS AXYS did conduct laboratory QC blanks using ultrapure water. Ultrapure water is ASTM Type 2 water, which has been distilled to a conductivity < 1.0  $\mu\text{S}/\text{cm}$  at 25°C (ASTM D1193-06). Field blanks were conducted in the field for samples sent to DEP's BOL. These consisted of ultrapure water run over cleaned sediment equipment prior to sampling. Field blank contamination is indicative of equipment and/or sampling protocol sources of contamination (USGS 2015). Blank data are provided in Appendix C-Blanks.

**Laboratory control samples (LCS)** were performed at SGS AXYS. These are samples spiked with a known quantity of an analyte and are also called spiked matrix material (SPM) or on-going precision and recovery (OPR) samples. In addition, SGS AXYS also did a duplicate analysis with each batch of up to 20 field samples (personal communication, SGS AXYS, October 2020). **Matrix spikes** are samples spiked with known concentrations of analytes of interest and analyzed along with the environmental samples. The recovery results of these samples show how well analytes of interest will be recovered in the environmental samples. Matrix spike samples were conducted in USGS samples.

**Surrogates** are compounds that are structurally similar to the analytes of interest, but typically contain one or more isotopically labeled atoms giving them a slightly different mass and are not found in natural settings. Surrogates are added to environmental samples and blanks in known concentrations, so their recovery can quantify how accurate the environmental sample analyses are. Before extraction, each SGS AXYS environmental and QC sample was spiked with known concentration(s) of surrogate(s). Surrogate recoveries were compared to acceptance criteria developed for the hormone suite.

USGS and SGS AXYS surrogate and spike data are in Appendix D-Surrogates\_Spikes. LCS samples are in Appendix E-AXYS Lab QC. USGS matrix spike data are in Appendix F-Matrix Spikes.

Split replicate samples were collected in the field once per sampling season. The replicates were collected at the same locations, composited, processed in the field, and placed into separate sampling containers. This method of replication is used to assess variability with splitting the sample and variability in laboratory environment and analysis (USGS 2015). Split replicates were compared to each other. Non-parametric Spearman correlation analyses were conducted on each analyte (see Section 4.1.3 for details). Replicate results, in addition to all other environmental results, are in Appendix G-Results. Lab replicates from SGS AXYS were also compared (see Section 4.1.4 for details) and are in Appendix H-Lab Duplicates. For more details on QC design and interpretation, please see Mueller et al. 2015.



Sample results from any laboratory were flagged by DEP if there were detections in associated lab or field blanks. If blank results were greater than ten times the environmental result, environmental results were blank corrected by subtracting the blank concentration from the environmental result. If blank results were less than ten times the environmental result, the original environmental result was retained. In addition, some detected results were below reporting levels but above detection levels, below detection levels, detected in laboratory blanks, or some combination of these. If this occurred, the data were flagged by the analysis laboratory; this is noted in the 'Original LAB\_FLAG' column in the data in Appendix G-Results. If no lab flag was noted, a description of a comment qualifier was noted in the Comment column of Appendix G-Results. Additional lab comments may be in the Notes column. If a blank-corrected result was below the detection limit and no LAB\_FLAG existed, the result was corrected to the detection level and the necessary LAB\_FLAG was added in the 'Corrected LAB\_FLAG' column (i.e. flagged as "U" (non-detect) if less than the detection level). Increasing a blank-corrected value to the noted detection limit was necessary for 74 results. If a non-corrected detection was below the detection limit it was not raised to the detection limit. Any results that were zero but not labeled as non-detect were also flagged as non-detect. Definitions of all lab flags used in the data and definitions of comment codes in the Comment column are located in Appendix I-Lab Flags & Comments.

### **3.4. Land Cover Calculations**

Fourteen categories of land cover were quantified for inclusion in data analyses (Table 1). In addition, dominant bedrock lithology (Bedrock-Lith1), Level IV ecoregion (US\_L4NAME), drainage area, flow, and season were included for data analyses. Land cover of the upstream watershed was calculated for each site with a watershed smaller than 1000 mi<sup>2</sup>. Watershed polygons were created using the ArcGIS Online watershed tool (Scopel 2014). Watershed land cover for sites with larger drainage areas, such as sites on the lower Susquehanna River, are not very useful for correlation analyses because such large watersheds encompass large quantities of every type of land cover, which makes it difficult to ascertain the effect of any particular land cover category, or combination of land cover categories, on sample results. Therefore, for each site with a watershed larger than 1000 mi<sup>2</sup>, a five-mile-radius circular buffer was created for each sample site point location, the circular buffer area was cut in half to encompass only the area upstream of each site, and the extent of each of the 14 land cover categories were measured within the resulting buffer area. This decision was based on best professional judgment. For these sites with larger drainage areas, buffers with five-mile radiuses were chosen to assess the effects of localized land cover on sample results. The five-mile radius was chosen based on best professional judgment. The dominant lithology (Bedrock-Lith1) at the sampling site was obtained from a Bedrock Geology layer from the Pennsylvania Department of Conservation and Natural Resources, Bureau of Topographic and Geologic Survey. Level IV Ecoregion (US\_L4NAME) was obtained from the Ecoregions of Pennsylvania Level IV layer (USEPA 2012).

Watershed polygons (for sites with watersheds smaller than 1000 mi<sup>2</sup>), buffered polygons (for sites with watersheds larger than 1000 mi<sup>2</sup>), and the 2011 National Land Cover Database (NLCD, Homer et al. 2015) were then imported into R, version 3.5.0 software (R Core Team 2018) to calculate land cover percentages. Land cover categories were calculated as percent cover for: open development, low intensity urban development, medium intensity urban development, high intensity urban development, deciduous forest, evergreen forest, mixed forest, woody wetlands, emergent wetlands, barren land, open water, shrub vegetation, herbaceous vegetation, hay/pasture, and cultivated crops. Percent open water was removed from any further analyses because, for the larger rivers, the river itself was included as open water land cover. In addition, drainage area was calculated for each site. Because land use percentages for sites with larger drainage areas (>1000 mi<sup>2</sup>) were calculated very differently than for sites with smaller drainage areas (<1000 mi<sup>2</sup>), the larger and smaller sites were divided into two separate groups for analyses.

### **3.5. Flow Calculations**

A streamflow metric was included in this analysis as an explanatory variable for CEC detections. Using R, version 3.5.0 software (R Core Team 2018), a streamflow metric was calculated for each sample finding the percent of the average flow from the 30 days (Q30) prior to sampling divided by the long-term monthly median. Daily mean streamflow was obtained from the nearest stream gage representing each waterbody from USGS Current Water Data for the Nation (USGS 2019). Most gages were on the sampled streams themselves, but a few gages were on nearby streams of comparable size. DEP protocols, as described in Chapter 4 of DEP's Water Quality Monitoring Protocols for Streams and Rivers, *Sediment Chemistry Data Collection Protocol* (Shull & Lookenbill 2018), specify sediment collection of the surficial 1 to 6 cm targeting grain sizes less than 0.06 mm with the assumption that these materials would have been deposited just prior to data collection (e.g., 30 days). After daily discharge data was downloaded, the long-term monthly median flow and long-term monthly mean flow was obtained. The average daily flow from the 30 days prior to sampling as a percent of the long-term monthly median flow at the site was then calculated.

### **3.6. Data Analysis**

Due to the large dataset and varieties of analytical requirements, the analyses were divided into the following three subsections, each of which has a corresponding subsection in the Results section (Section 4) of this report. Each of these subsections explore several core questions in the data. The following is a breakdown of the analyses in each subsection:

#### **3.6.1. Quality Assurance (QA) and Quality Control (QC) Results**

In this section, blank, replicate, surrogate, and spike results were examined.

### **3.6.2. Occurrence and Distribution Analyses**

The most common contaminants, rare contaminants, and sites with the highest concentrations were examined and summarized. Analytes detected by category were also investigated and summarized.

### **3.6.3. Explanatory Variable Analyses**

Nineteen abiotic explanatory variables (Table 1) were considered for statistical analyses and compared to detected concentrations of CECs in sediment. Additional variables of soil types, rock types, and ecoregions were also considered for inclusion for metals. Multicollinearity between variables was tested. If an explanatory variable was highly correlated with another explanatory variable, it was removed, or, in some cases, the correlated variables were combined, such as in the case of percent developed land use. If a variable needed to be removed, the variable determined to be most relevant was retained.

**Table 1.** Explanatory variables considered for data analyses

Category	Variable	Min	Median	Max	Details
Land Cover	% Hay/Pasture	0.9	17.2	45	Grasses for livestock grazing or crops
	% Herbaceous	0	0.1	3.5	Short, herbaceous vegetation >80% of total
	% Barren	0	0	1.4	Bedrock, strip mines, little vegetation
	% Shrub	0	0.1	7.6	Shrub/young trees cover >20% of vegetation
	% Cultivated Crops	0	11	52.3	Annual crop production
	% Emergent Wetlands	0	0	1.2	Wetlands with herbaceous vegetation >80% of total
	% Woody Wetlands	0	0.3	6	Wetlands with forest/shrub cover >20% of vegetation
	% Deciduous Forest	0	45.8	74.4	More than 75% of tree species shed foliage annually
	% Mixed Forest	0	0.7	14.1	Mix of deciduous and evergreen tree species
	% Evergreen Forest	0	0.8	17.8	More than 75% of tree species keep leaves all year round
	% Developed - Open	0.9	8.5	40.2	Some construction, mostly lawn
	% Developed - High Intensity	0	0.3	19.3	Highly developed, most is impervious surface
	% Developed - Low Intensity	0	4.9	38.3	Some construction & vegetation, commonly homes
	% Developed - Medium Intensity	0	1.5	31	Some construction & vegetation, commonly homes
Rock	Bedrock-Lith1	N/A	N/A	N/A	Dominant lithology
	US_L4NAME	N/A	N/A	N/A	Level IV ecoregion
Natural	Drainage Area	N/A	N/A	N/A	Area drained to sample site (square miles)
	Flow	0.5	1.1	3.8	Calculated as percent of average flow from last 30 days to long-term monthly median
	Season	N/A	N/A	N/A	Sample collected in winter, spring, or fall *

\*Winter: February - March

Spring: May - June

Fall: August - October

### 3.6.3.1. Explanatory Variable Data Preparation

Sediment analyte groups available for analyses were hormones, wastewater compounds, metals, pesticides, and PCBs. Data were broken into two subsets: 2013 through 2015 and 2016 through 2017. After 2015, lab analysis of hormones moved from USGS to SGS AXYS.

Pesticides and PCBs were very rarely detected. Therefore, these datasets were very small and not amenable to large-scale ordination analyses. As a result, pesticides and PCBs were excluded from explanatory variable analyses (Table 1).

Hormones and wastewater compounds were analyzed independently with anthropogenic variables. Since the hormones were analyzed by a different lab using different analyses after 2015, the data for hormones were grouped into two temporal subsets – data collected 2013-2015 and 2016-2017. The data for wastewater compounds was analyzed as one set (2013-2017) because the lab and analyses did not change. Although beta-stigmastanol and beta-sitosterol are hormones, they were included in the wastewater category because they are plant hormones rather than animal hormones. Although all categorized with the wastewater indicator compound “suite”, in some analyses that follow, PAHs and PBDEs were divided into their own groups since they are so different than other wastewater compounds. Otherwise, they were categorized with wastewater indicator compounds. Metals results were analyzed as a separate set and no temporal sub-setting was necessary because the same metals were tested by the same lab using the same analytical methods throughout the entire study.

In addition to grouping data into the temporal subsets described above, data were grouped into sites with smaller (0.4 - 963 mi<sup>2</sup>) and larger (>1000 mi<sup>2</sup>) drainage areas for land use analyses due to the differences in calculating land use percentages described above.

Any non-detect results (LAB\_FLAG = U) were set to zero, due to the high variability of detection limits across tests and sample results. Concentrations of sediment contaminants, including the non-detect results that were set to zero, were used in the analyses.

Abiotic explanatory variables (Table 1) were first tested for multicollinearity. If any explanatory variables were highly correlated, some of the highly correlated variables could potentially be removed from the analyses. Multicollinearity was tested by calculating the variance inflation factor (VIF), which measures how much the variance of a variable's data is inflated because of collinearity. A VIF of one indicates no multicollinearity, and the greater the VIF, the more influential the collinearity becomes. A VIF of 10 and above should be addressed (Penn State 2018). Removing variables that are highly collinear with others or combining collinear variables will lower the VIF and reduce multicollinearity. Multicollinearity results are described in Section 4.3.1. Preliminary analyses failed to produce any discernable patterns or significant results in the data if all sediment analyte categories (hormones, wastewater

compounds, and metals) were combined. Therefore, analyte categories were analyzed separately where necessary to produce discernable patterns or significant results.

Anthropogenic variables (land use), natural variables (drainage area, flow, and season), and rock/ecoregion (dominant lithology and ecoregion) were analyzed as separate variable groups due to their differing influences on contamination. Natural variables were not grouped per watershed since those variables were site specific (flow, drainage area) or independent of watershed boundary (season).

The final explanatory variable analyses framework is shown in Table 2.

**Table 2.** Framework for explanatory variable analyses

<b>Analyte Category</b>	<b>Years</b>	<b>Watershed Size</b>	<b>Explanatory Variable Type</b>
Hormones	2013 - 2015	Small	Anthropogenic
		Large	Anthropogenic
Hormones	2016 - 2017	Small	Anthropogenic
		Large	Anthropogenic
Hormones, Wastewater Compounds	2013 - 2015	Small, Large	Natural
Hormones, Wastewater Compounds	2016 - 2017	Small, Large	Natural
Wastewater	all years	Small	Anthropogenic
		Large	Anthropogenic
Metals	all years	Small	Anthropogenic
		Large	Anthropogenic
		Small, Large	Natural
		Small, Large	Rock/Ecoregions

### 3.6.3.2. Canonical Correspondence Analyses

Canonical correspondence analyses (CCAs) were conducted using the R package ‘vegan’ (Oksanen et al. 2020) to explore influences of the explanatory variables on sediment contaminant concentrations. CCAs isolate multivariate relationships between outcome variables and explanatory variables – in this case, sediment analyte concentrations and environmental variables – but do not assume linear relationships or normal data distributions, which are often violated in environmental data. CCA is a very common analysis method for ecological/species data and has been used with abiotic data as well and can determine relationships of environmental variables with water or sediment chemistry (Bo-Jie et al. 2006, Bodaghabadi et al. 2011, Faye et al. 1997).

Some sediment contaminants were infrequently tested for in this study. These rarely tested contaminants were removed from analyses because they have little influence on the CCA. Only detected results were used in the CCAs; non-detects were omitted. This reduced the samples and analytes available for analyses but allowed for more meaningful results. Reported CCA metrics include: constrained inertia (the variability explained by the CCA); the proportion of the inertia explained by the constrained inertia;

unconstrained inertia (correspondence analysis of the residuals of the CCA); the proportion of the inertia explained by the unconstrained inertia; and model significance. Inertia helps explain how good the “fit” of the CCA is (Buttigieg & Ramette 2014).

## 4. RESULTS

### 4.1. Quality Assurance (QA) and Quality Control (QC) Results

#### 4.1.1. Laboratory and Field Blanks

There were very few detections in laboratory blanks (Table 3). While many blank-corrected results did not change significantly, some blank corrections caused several analytes' results for a season to be corrected from a detected value to non-detect, due to blank results being greater than environmental results.

**Table 3.** QC blank detections in sediment samples (µg/kg)

Collected	Analyte	Result	QC Type
Fall 2016	androstenedione <sup>#</sup>	1.03	Lab Blank
Fall 2016	androstenedione <sup>#</sup>	2.14	Lab Blank
Fall 2017	androsterone	K 17.6	Lab Blank
Fall 2017	androsterone	K 24.7	Lab Blank
Spring 2017	androsterone <sup>#</sup>	41.6	Lab Blank
Winter 2017	androsterone	14.8	Lab Blank
Fall 2017	desogestrel	TIC 31.3	Lab Blank
Spring 2017	desogestrel	TIC 191	Lab Blank
Fall 2017	mestranol	K 38.9	Lab Blank
Fall 2017	mestranol	K 41.2	Lab Blank
Spring 2017	mestranol <sup>#</sup>	K 65.9	Lab Blank
Winter 2017	mestranol	K 39.7	Lab Blank
Spring 2013	potassium <sup>*</sup>	5000	Field Blank
Fall 2016	progesterone	K 0.694	Lab Blank
Fall 2016	progesterone	1.44	Lab Blank
Spring 2017	progesterone <sup>#</sup>	2.22	Lab Blank
Spring 2013	strontium <sup>*</sup>	250	Field Blank
Fall 2016	testosterone	K 0.2	Lab Blank

<sup>#</sup> Blank corrections resulted in entire analytes being non-detect

<sup>\*</sup> Result not blank-corrected because <10x result value

K = Peak detected, but did not meet qualification criteria, result reported represents the estimated maximum possible concentration.

TIC = Analyte identity and concentration are estimated.

#### **4.1.2. Matrix and Surrogate Spikes**

SGS AXYS laboratory control samples/spiked matrix material samples were all within acceptable percent recoveries. SGS AXYS surrogate spikes had several results outside the desired percent recovery range – called the ongoing precision and recovery (OPR) – for D6-Norethindrone, D6-Norgestrel, and D6-Progesterone (Appendix D-Surrogates\_Spikes). These surrogate results are labeled with a 'V' LAB\_FLAG. If no other qualifiers were applied to the environmental data, the quantification did not affect surrogate spike results outside desired percent recovery thresholds. If quantifications were affected, the result was labeled 'NQ' for not quantifiable, which occurred for 28 individual environmental results.

USGS surrogate recoveries ranged from 0% to 2708%. Generally, the category most out of range was hormones and the category with the most acceptable recoveries was pesticides. Low recoveries can indicate that environmental results were potentially biased low and high recoveries indicate they could be biased high (Mueller et al. 2015). Several matrix spikes from the USGS sampling QA were above or below the expected recoveries.

#### **4.1.3. Split Replicates**

Field-split replicate samples were compared to original field samples to quantify variability with splitting the sample and also variability in laboratory environment and analysis. Non-parametric Spearman correlation analyses showed results for many analytes to be fairly similar between original field samples and replicate samples, although this was not the case for some analytes (Table 4). The Spearman rho result ranges from -1 to 1, with a rho of -1 indicating a perfect negative correlation, a rho of zero indicating no correlation, and a rho of 1 indicating a perfect positive correlation. The Spearman correlations for 54% of the replicate analyte samples had significantly similar correlations measured as p-values  $\leq 0.05$ . The largest percentage of these similar correlations were among metals replicates. Because of replicate differences, the replicate samples were not included in analyses except when indicated in this report. Replicates were included in analyses examining percent detected analytes and concentrations of analytes.



**Table 4.** Correlations between replicate field sediment sample analytes

Analyte	Spearman Correlation Rho	p-value	Analyte	Spearman Correlation Rho	p-value
1,4-dichlorobenzene <sup>W</sup>	1	0.0833	Indole <sup>W</sup>	0.87	<b>0.0009</b>
4-androstene-3,17-dione <sup>H</sup>	1	0.0833	Chloride <sup>M</sup>	0.86	<b>0.0107</b>
4-nonylphenol (sum of all isomers) <sup>W</sup>	1	1	Calcium <sup>M</sup>	0.85	<b>0.0003</b>
4-tert-octylphenol <sup>W</sup>	1	1	Chromium <sup>M</sup>	0.85	<b>0.0003</b>
Androstenedione <sup>H</sup>	1	1	Potassium <sup>M</sup>	0.85	<b>0.0003</b>
Cadmium <sup>M</sup>	1	1	Barium <sup>M</sup>	0.85	<b>0.0004</b>
Chloroneb <sup>P</sup>	1	1	3-beta-coprostanol <sup>H</sup>	0.85	<b>0.0021</b>
cis-permethrin <sup>P</sup>	1	1	Strontium <sup>M</sup>	0.84	<b>0.0005</b>
Mestranol <sup>H</sup>	1	1	Naphthalene <sup>PAH</sup>	0.83	0.0583
Metolachlor <sup>P</sup>	1	1	Manganese <sup>M</sup>	0.82	<b>0.0011</b>
o,p'-DDD <sup>P</sup>	1	1	Acetophenone <sup>W</sup>	0.80	0.3333
p,p'-DDD <sup>P</sup>	1	1	HHCB <sup>W</sup>	0.80	0.3333
p,p'-DDE <sup>P</sup>	1	1	Phenanthrene <sup>PAH</sup>	0.79	<b>0.0098</b>
p,p'-DDT <sup>P</sup>	1	1	Nickel <sup>M</sup>	0.78	<b>0.0047</b>
Progesterone <sup>H</sup>	1	0.3333	Magnesium <sup>M</sup>	0.76	<b>0.0040</b>
2,6-Dimethylnaphthalene <sup>PAH</sup>	0.97	<b>7.4E-07</b>	Zinc <sup>M</sup>	0.75	<b>0.0044</b>
2-Methylnaphthalene <sup>PAH</sup>	0.96	<b>0.0028</b>	Benzo[a]pyrene <sup>PAH</sup>	0.75	<b>0.0082</b>
1-Methylnaphthalene <sup>PAH</sup>	0.95	<b>0.0004</b>	Pyrene <sup>PAH</sup>	0.73	<b>0.0150</b>
beta-stigmastanol <sup>W</sup>	0.95	<b>0.0004</b>	Fluoranthene <sup>PAH</sup>	0.69	<b>0.0231</b>
beta-sitosterol <sup>W</sup>	0.94	<b>2.2E-16</b>	Aluminum <sup>M</sup>	0.66	<b>0.0160</b>
Copper <sup>M</sup>	0.92	<b>2.2E-16</b>	Lead <sup>M</sup>	0.65	<b>0.0196</b>
3-methyl-1(h)-indole (Skatol) <sup>W</sup>	0.90	<b>0.0002</b>	Isophorone <sup>W</sup>	0.60	0.3500
Carbazole <sup>W</sup>	0.90	<b>0.0002</b>	Anthracene <sup>PAH</sup>	0.59	0.0974
Estrone <sup>H</sup>	0.90	0.0833	Iron <sup>M</sup>	0.55	0.0553
Anthraquinone <sup>PAH</sup>	0.89	<b>0.0014</b>	Bisphenol A <sup>W</sup>	0.40	0.7500
p-cresol <sup>W</sup>	0.88	<b>0.0007</b>	d-limonene <sup>W</sup>	0.40	0.5167
Arsenic <sup>M</sup>	0.88	<b>0.0072</b>	1-naphthol <sup>P</sup>	0	1
Cholesterol <sup>H</sup>	0.87	<b>2.2E-16</b>	trans-permethrin <sup>P</sup>	-1	1

W = Wastewater compound

H = Hormone

M = Metal

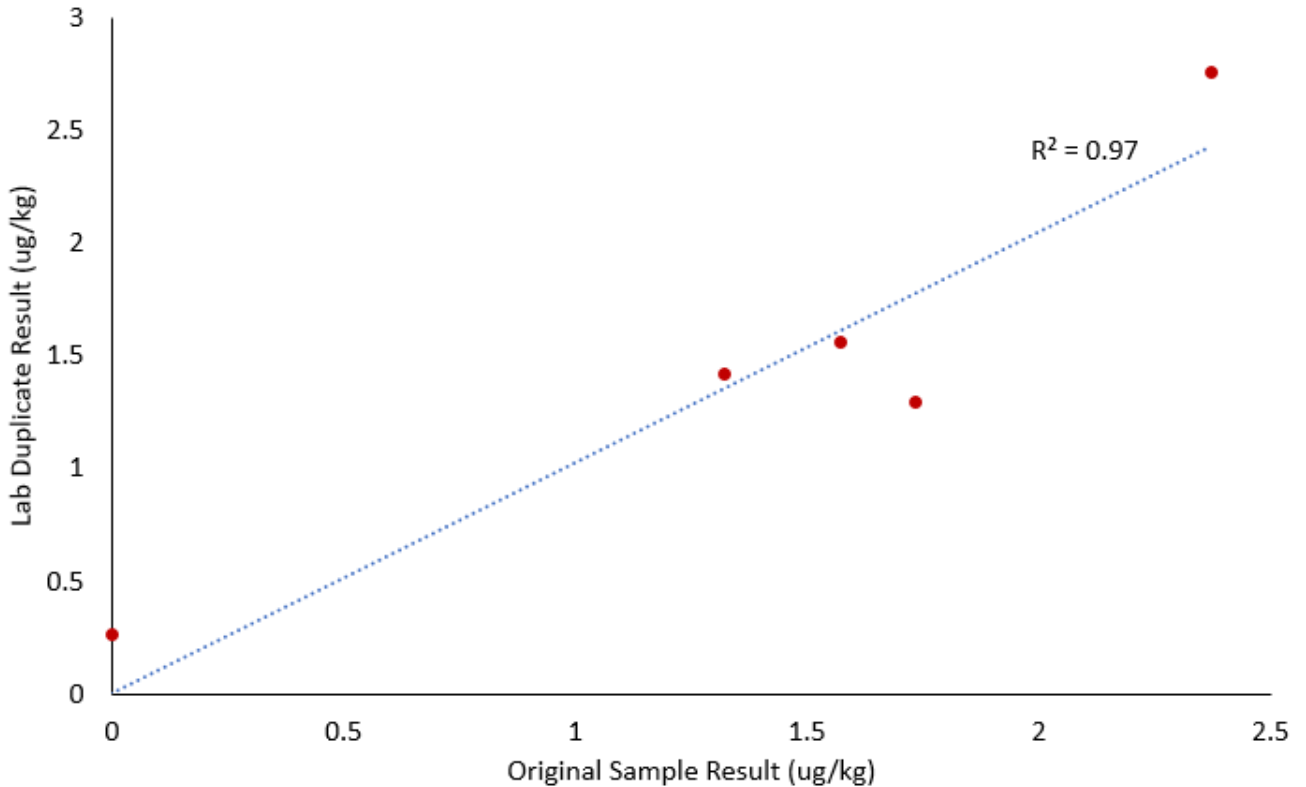
P = Pesticide

PAH = Polycyclic Aromatic Hydrocarbon

p-values ≤ 0.05 are bolded

#### 4.1.4. Lab Duplicates

SGS AXYS lab duplicate samples were compared to each other to evaluate reproducibility and precision (Figure 2). Most results for both the original and lab duplicate were non-detect. The five sample duplicates that were detected included equilenin, estrone, and progesterone. A linear regression of the detections showed a strong relationship between original and lab duplicates ( $R^2 = 0.97$  with intercept set to zero).



**Figure 2.** Original lab results versus lab duplicates

#### 4.2. Occurrence and Distribution Analyses

All chemical concentrations from sediment samples are presented in Appendix G-Results.

##### 4.2.1. Commonly Detected Analytes

A total of 115 of 202 analytes tested for from 2013 through 2017 were detected, although 72% of all individual sample results were non-detect (Appendix J-Analytes). Many of the 115 analytes that were detected were very infrequently detected. Detected analytes were detected from 0.6% to 100% of the time. Twenty-eight analytes were detected >90% of the time (Table 5), consisting mainly of metals, PAHs, and wastewater compounds. Total organic carbon and 4,4-bisphenol f were only tested for two and three times, respectively; each of these analytes was detected in all of the

samples tested, and are not on the list of analytes detected >90% of the time due to the infrequent testing of samples for these analytes. Most metals were detected nearly every time they were tested for in sediment. This is not uncommon since metals are naturally present in soils and sediment. Fluoranthene, a common PAH, was tested for 174 times and detected every time. Pyrene, another common PAH, was also detected nearly every time (173 out of 174 times). Cholesterol, a sterol that is found in all animals and in trace amounts in plants and some bacteria, was the most commonly detected hormone.

**Table 5.** Analytes detected >90% of the time (when tested for) – 2013 through 2017

Analyte	Description
<b>Current Pesticide</b>	
1-naphthol	metabolite of insecticide carbaryl and photooxidation of naphthalene; used in agrochemical production
<b>Hormone</b>	
Cholesterol	ubiquitous, natural sterol produced by animals & plants
<b>Metal</b>	
Aluminum	
Barium	
Calcium	
Chromium	
Copper	
Iron	
Lead	
Magnesium	
Manganese	
Nickel	
Potassium	
Strontium	
Zinc	
<b>PAH</b>	
2,6-dimethylnaphthalene	present in diesel/kerosene (trace in gasoline)
Anthracene	wood preservative, component of coal, tar, diesel, or crude oil
Benzo[a]pyrene	regulated PAH, found in coal tar, tobacco smoke
Fluoranthene	component of coal tar & asphalt (only traces in gasoline or diesel fuel)
Phenanthrene	manufacturing explosives, component of tar, diesel fuel, or crude oil
Pyrene	component of coal tar & asphalt (only traces in gasoline or diesel fuel)
Anthraquinone	coal, manufacturing of dye/textiles, seed treatment, bird repellent
<b>Wastewater</b>	
3-methyl-1(h)-indole (skatol)	odor in feces, coal tar; fragrance
Beta-sitosterol	plant sterol
Carbazole	insecticide; manufacturing of dyes, explosives, lubricants; tobacco; coal
Indole	fragrance compound (in coffee); inert ingredient in pesticide; coal
p-cresol	wood preservative; coal

#### 4.2.2. Rarely Detected Analytes

Of 202 analytes, 87 were tested for but never detected and 35 were detected <5% of the time (Table 6). Replicates were excluded from this analysis. Some sites were sampled multiple seasons/years. Interestingly, atrazine was only detected in sediment at a few Susquehanna River sites and a Swatara Creek site. However, these were very low-level detections. A full list of all analyte percent detections is located in Appendix K-Analyte Percents.

**Table 6.** Analytes detected <5% of the time (when tested for) – 2013 through 2017

Analyte	% Detected	Analyte	% Detected
4-cumylphenol <sup>W</sup>	4.6	trans-nonachlor <sup>P</sup>	1.5
Estriol <sup>H</sup>	4.2	tris(2-butoxyethyl)phosphate <sup>W</sup>	1.2
Desogestrel <sup>H</sup>	3.8	4-n-octylphenol <sup>W</sup>	1.1
Atrazine <sup>P</sup>	3.4	PBDE-47 <sup>PBDE</sup>	1.1
alpha-chlordane <sup>P</sup>	3.1	Dieldrin <sup>P</sup>	1.0
Methoxychlor <sup>P</sup>	3.1	Trifluralin <sup>P</sup>	1.0
Equilenin <sup>H</sup>	2.9	Dihydrotestosterone <sup>H</sup>	1.0
Allyl trenbolone <sup>H</sup>	2.7	Hexachlorobenzene <sup>P</sup>	0.8
Androsterone <sup>H</sup>	2.7	Hexachlorocyclopentadiene <sup>P</sup>	0.8
NP2EO <sup>W</sup>	2.3	Aldrin <sup>P</sup>	0.8
Metribuzin <sup>P</sup>	2.1	Heptachlor epoxide <sup>P</sup>	0.8
OP1EO <sup>W</sup>	1.8	o,p'-DDE <sup>P</sup>	0.8
17-alpha-ethynylestradiol <sup>H</sup>	1.7	tris(dichloroisopropyl)phosphate <sup>W</sup>	0.7
DEET <sup>P</sup>	1.7	NP1EO <sup>W</sup>	0.6
Arochlor 1232 <sup>PCB</sup>	1.7	OP2EO <sup>W</sup>	0.6
Arochlor 1260 <sup>PCB</sup>	1.7	Tributyl phosphate <sup>W</sup>	0.6
Dacthal <sup>P</sup>	1.6	Triphenyl phosphate <sup>W</sup>	0.6
Pendamethalin <sup>P</sup>	1.6		

W = Wastewater compound  
H = Hormone  
P = Pesticide

PCB = Polychlorinated biphenyl  
PBDE = Polybrominated Diphenyl Ether

#### 4.2.3. Percent Detected Categories of Analytes by Sampling Event

Percent of analytes detected per sampling event (defined as site sampled per season/year) is best described by analyte category: metals and other elements, legacy pesticides, current pesticides, PCBs, hormones, and wastewater compounds (Appendix L-Pct Per Sample). This analysis does include field replicate samples.

While 100% was the highest percentage of hormones detected, these were from samples where only one or two hormones were tested for. When only including samples with numerous hormones tested for, the highest percentage of hormones were detected in the Spring 2015 sample at the Little Juniata River (LITTLEJ) site and in the Spring 2015 sample at the Juniata River at Newton-Hamilton (NEWTHAM) site, with 55% and 50% of hormones tested for detected, respectively. All other sampling events had

tested-for hormones detected at or below 48%. See Appendix A-Sites for the full site list.

Of the 20 individual metals tested for, 14 were detected in 99% or more of samples in which they were tested (see Appendix K-Analyte Percents). The metals percent detected ranged from 47% in the Winter 2017 sample at the Carbaugh Run (WQN0465) site to 95% in the Spring 2017 sample at the Chester Creek (locally known as Goose Creek and here after referred to as Goose Creek (GOOSEUP)) site and in the Spring 2017 sample at the Conestoga River site downstream of Lancaster Sewage Treatment Plant (CONESTOGADWS), with a median of 74% across 219 sampling events.

Currently used as well as historical/legacy pesticides were detected very infrequently. A range of only one to six current pesticides were detected across all samples, with a maximum of 30% detected in four sampling events at three sites. Historical/legacy pesticides were detected only slightly more frequently (one to seven detected across all samples). A tributary to West Branch Red Clay Creek (FQRBTRIB) had the most detections of historical/legacy pesticides (24% detected in three separate sampling events) but most sites had fewer detections.

PCBs were also infrequently detected, with a few sites having one PCB detected per sample but most sampling events having zero PCB detections. Because of this, sampling for pesticides and PCBs was largely discontinued after 2014.

Percent detections of wastewater compounds in each sampling event ranged from 61% down to 6.3%. In Fall 2015, Spruce Creek (SPRUCE) had one wastewater compound tested, which was detected. Out of the sites that had numerous wastewater compounds tested, the highest percent detections were: 61% in the Fall 2014 sample at the Juniata River (NEW\_2) site; 60% in the Winter 2017 sample at the Conestoga River downstream of Lancaster STP (CONESTOGADWS) site; and 60% in the Fall 2017 sample at the Mahoning River (MAHONING3) site. Similar to hormones, several samples only had a few wastewater compounds tested.

#### **4.2.4. Concentrations**

The currently used pesticide with the highest concentration was cis-permethrin, an anti-parasitic, at 5,985 µg/kg. The legacy pesticides with the highest concentrations were DDT and its metabolites. These were detected mainly in the Red Clay Creek watershed. PCBs were only detected a few times, with the highest concentration being 362 µg/kg of Arochlor-1254 in the Spring 2014 sample at the Elizabeth Run (ELIZABETH) site. Metals concentrations varied widely and likely were detected due to contributions from both natural (i.e., bedrock) and anthropogenic sources. Cholesterol, an animal sterol, and 3-beta-coprostanol, another natural sterol, had by far the highest concentrations of hormones detected, although both concentrations were estimated. Beta-stigmastanol, a plant sterol, and p-cresol, a wood preservative, had the highest concentrations of wastewater indicator compounds detected in sediment. Fluoranthene was the PAH with the highest concentration, 9,750 µg/kg in the Winter 2017 sample at the Goose Creek

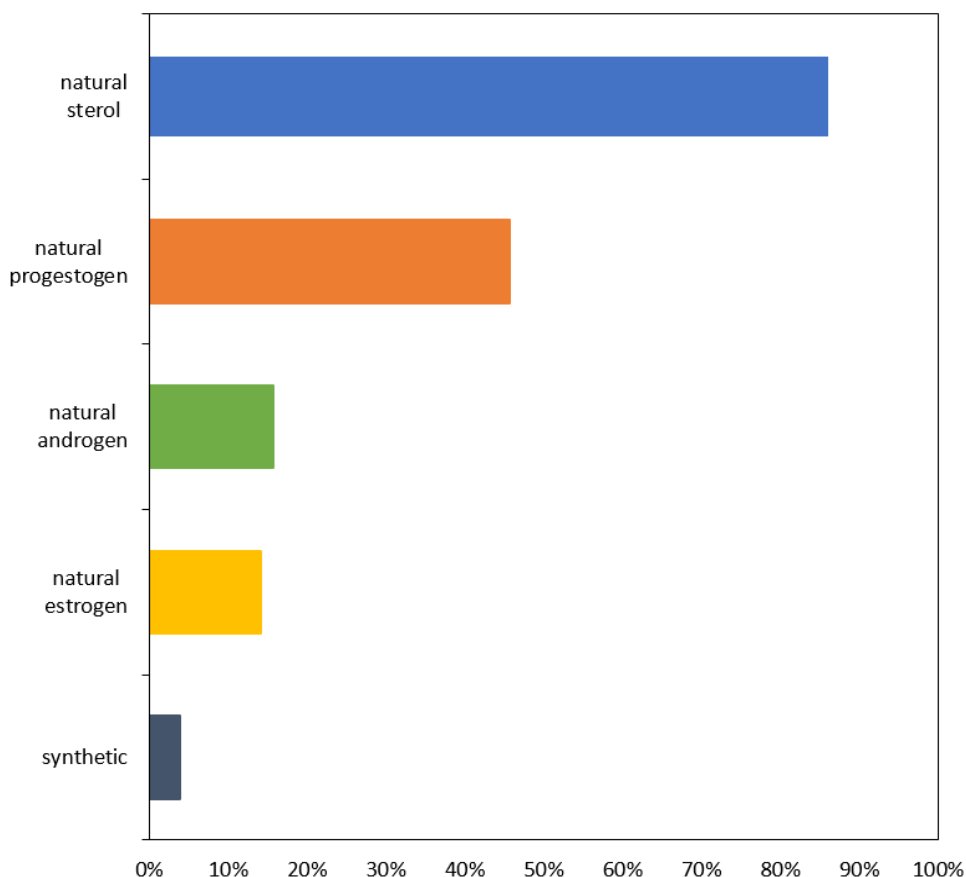
(GOOSEUP) site, although this was estimated. Field replicates were included in these analyses. A full list of maximum concentrations can be found in Appendix M-Max.

#### 4.2.5. Analyte Categories and Groups

Within each analyte category, the following analyses break out more specific groups of analytes in presenting percent detection results. For instance, within the hormone category, more specific groups of hormones include natural sterols, natural progestogens, natural androgens, natural estrogens, and synthetic hormones. The category and group for each analyte can be found in Appendix J-Analytes. Replicates were not included in the following analyses to avoid overestimating detections.

##### 4.2.5.1. Hormones

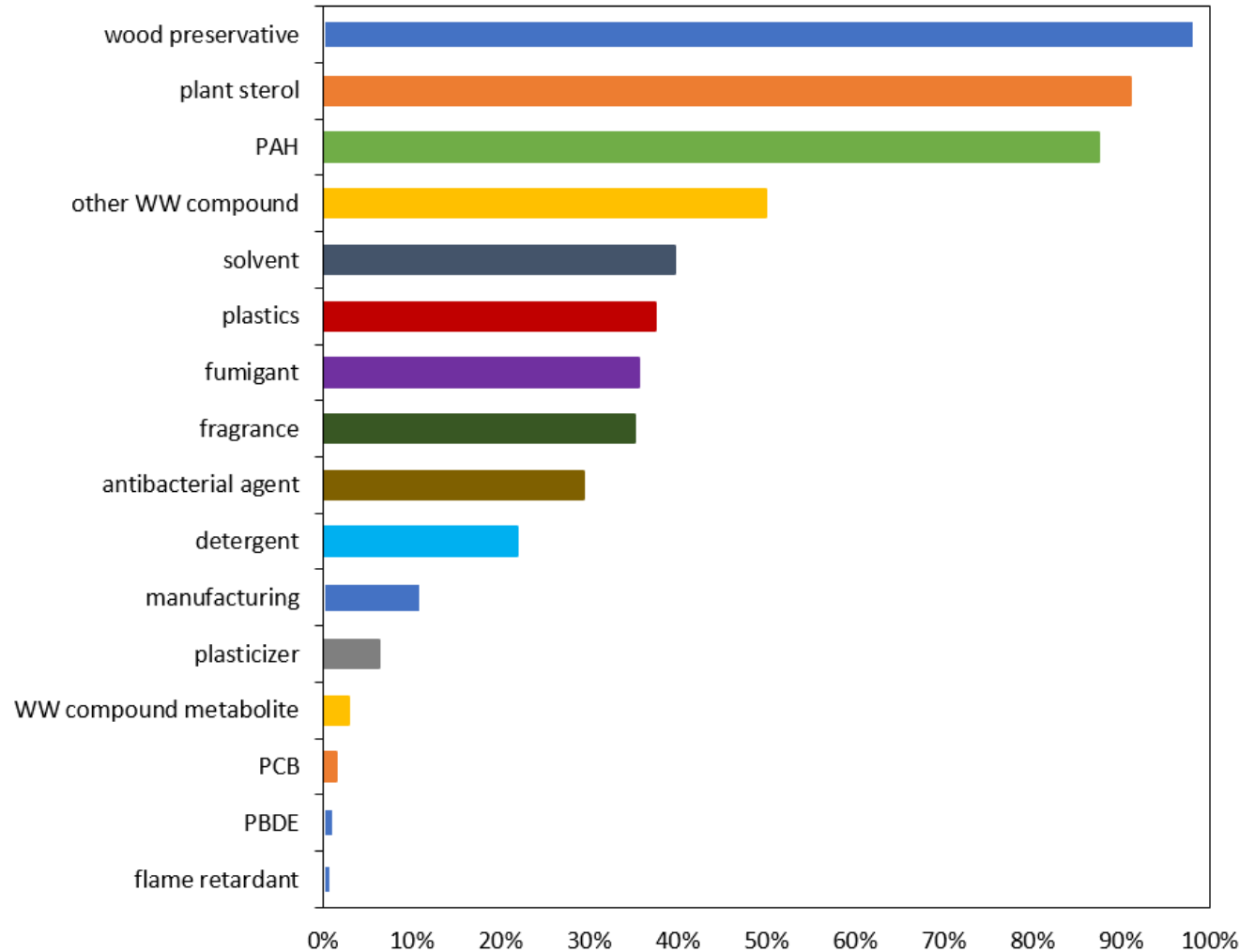
Natural sterols, which include 3-beta-coprostanol and cholesterol, were detected in 86% of sampling events, when tested for, making natural sterols the most common group of hormones detected (Figure 3). Progesterone, a natural progestogen, was detected in 44% of sampling events; because progesterone is the only compound in the natural progestogen group, it is not included in Figure 3. Hormones that are not naturally found in animals – synthetic hormones – were only detected in 4% of sampling events.



**Figure 3.** Percent of sampling events in which groups of hormones were detected in sediment samples, 2013 – 2017.

#### 4.2.5.2. Wastewater Indicator Compounds, PAHs, and PBDEs

Wood preservatives, plant sterols, and PAHs were detected the most frequently in the wastewater, PAHs, and PBDEs group (Figure 4).

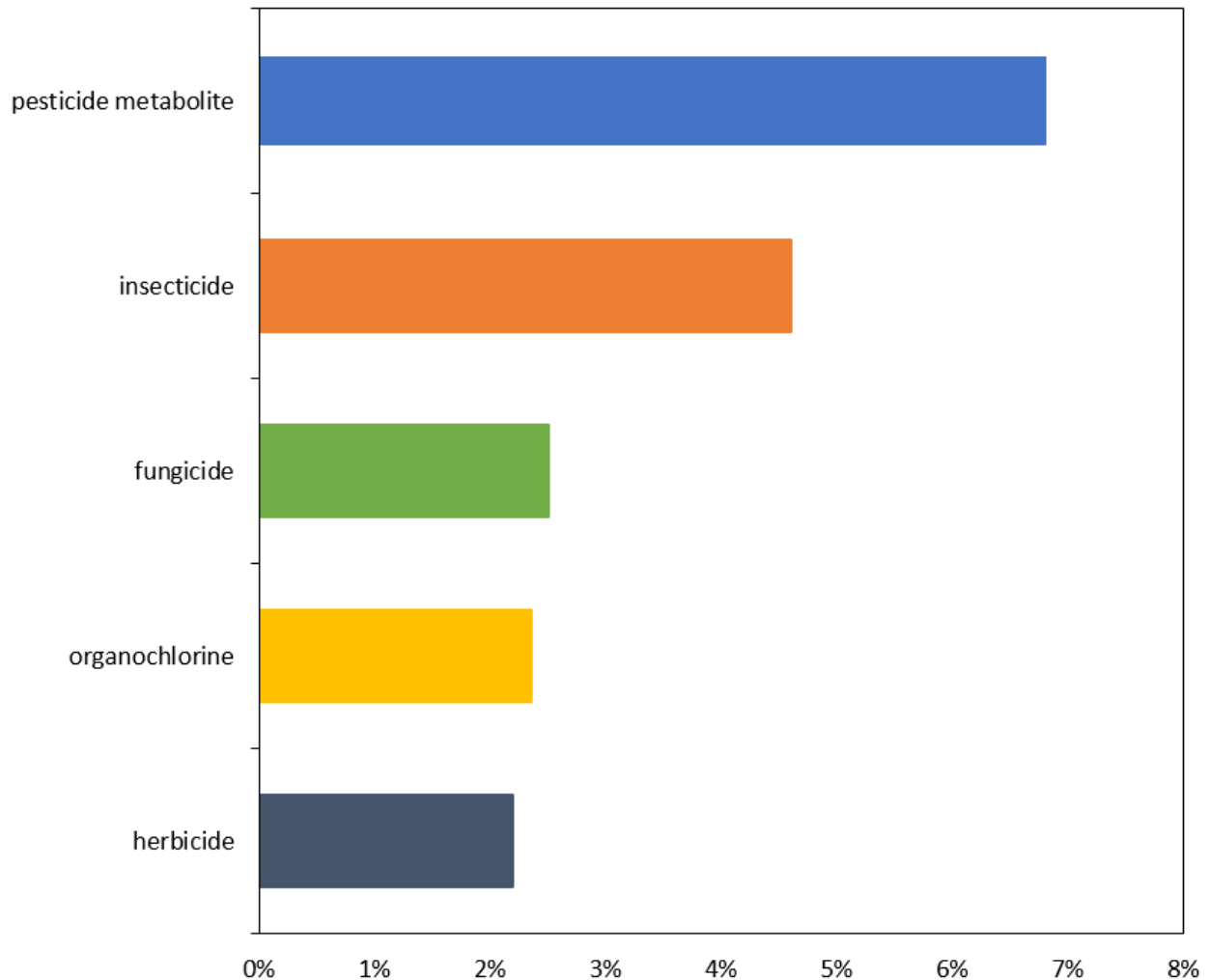


**Figure 4.** Percent of sampling events in which groups of wastewater indicator compounds, PAHs, and PBDEs were detected in sediment samples, 2013 – 2017.



#### 4.2.5.3. Pesticides

Pesticide metabolites, or breakdown products, were detected in 6.96% of sampling events, making pesticide metabolites the most detected group of pesticide compounds (Figure 5). This exemplifies how rarely pesticides and pesticide byproducts were detected in this study, which led to the ceasing of testing for pesticides in sediment samples collected for this project by the end of 2014.



**Figure 5.** Percent of sampling events in which groups of pesticides were detected in sediment samples, 2013 – 2017.

### 4.3. Explanatory Variable Analyses

#### 4.3.1. Tests for Variable Multicollinearity

All variables were included in the initial multicollinearity analyses and some were combined or eliminated as collinearity was detected. In the final analyses, forested land use variables were combined, agricultural land use variables were combined, and

developed (urbanized) land use variables were combined. The final anthropogenically influenced variables in the analyses were % forested land use, % agriculture land use, and % developed land use. VIFs were greatly reduced by combining these land use variables. Although the VIFs of % forested land use, % agriculture land use, and % developed land use were >10, they were all deemed too important to delete because they are major categories of land use variables. The final natural variables were flow, drainage area, and season collected (winter, spring, or fall). VIFs of the natural variables were all <10.

Rock type and ecoregion were retained for metals analyses; soil types were eliminated because of correlation with the other variables.

#### **4.3.2. Canonical Correspondence Analyses (CCA)**

CCAs were completed for several situations (Table 7). Replicates were not included in these analyses.

**Table 7.** CCA results – Inertia and model significance

Scenario	Years	Drainage	Data	Predictors	Constrained Inertia/Proportion	Unconstrained Inertia/Proportion	Model Significance (p-value)
1	2013-2015	Small	H	A *	0.0038/0.1432	0.0226/0.8568	0.228
2	2013-2015	Large	H	A *	0.0132/0.2308	0.0440/0.7692	<b>0.016</b>
3	2016-2017	Small	H	A *	0.0546/0.4185	0.0758/0.5815	<b>0.001</b>
4	2016-2017	Large	H	A *	0.0308/0.4306	0.0407/0.5695	0.358
5	2013-2015	Small, Large	H, W	N **	0.0831/0.1692	0.4081/0.8308	<b>0.001</b>
6	2016-2017	Small, Large	H, W	N **	0.0820/0.1301	0.5485/0.8699	0.151
7	All	Small	W	A *	0.2228/0.1960	0.9139/0.8040	<b>0.001</b>
8	All	Large	W	A *	0.0768/0.0799	0.8842/0.9201	<b>0.013</b>
9	All	Small	M	A *	0.0497/0.1810	0.2248/0.8189	<b>0.001</b>
10	All	Large	M	A *	0.0463/0.1609	0.2412/0.8391	<b>0.012</b>
11	All	Small & Large	M	N **	0.0212/0.0689	0.2863/0.9311	<b>0.005</b>
12	All	Small & Large	M	R ***	0.1295/0.4211	0.1780/0.5789	<b>0.001</b>

H = Hormones

W = Wastewater

M = Metals

A = Anthropogenic (land use)

N = Natural

R = Rock

\* Land use (% Agriculture, % Forest, % Developed)

\*\* Ptile30 (Flow), Season, Drainage Area

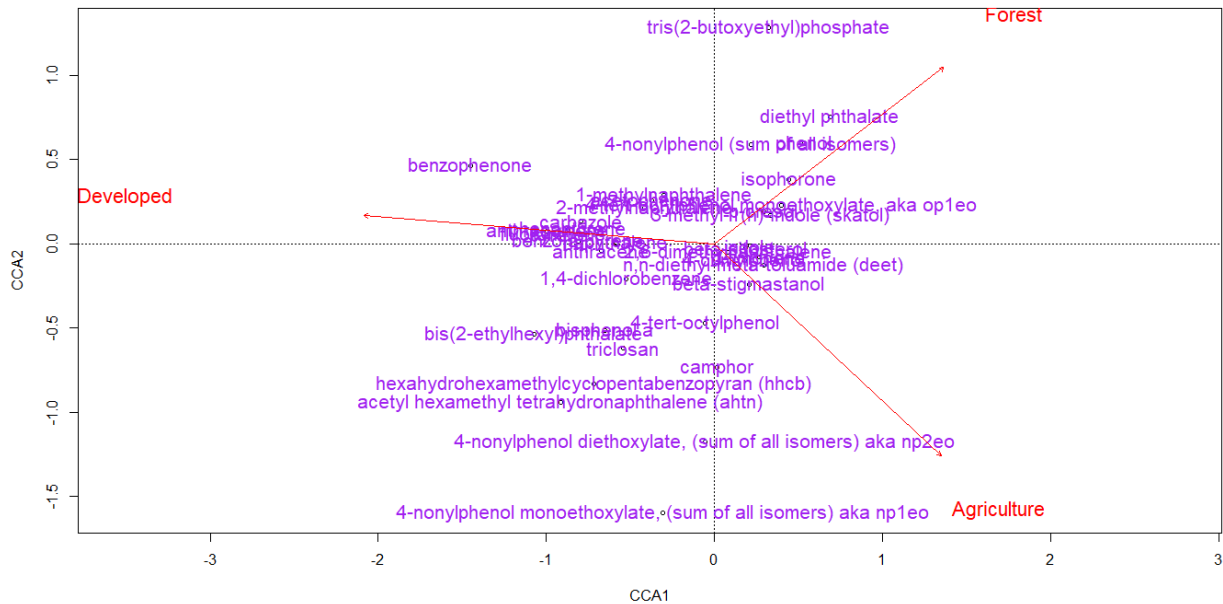
\*\*\*Bedrock-Lith1, US\_L4NAME

p-values bolded for models with p-values < 0.05

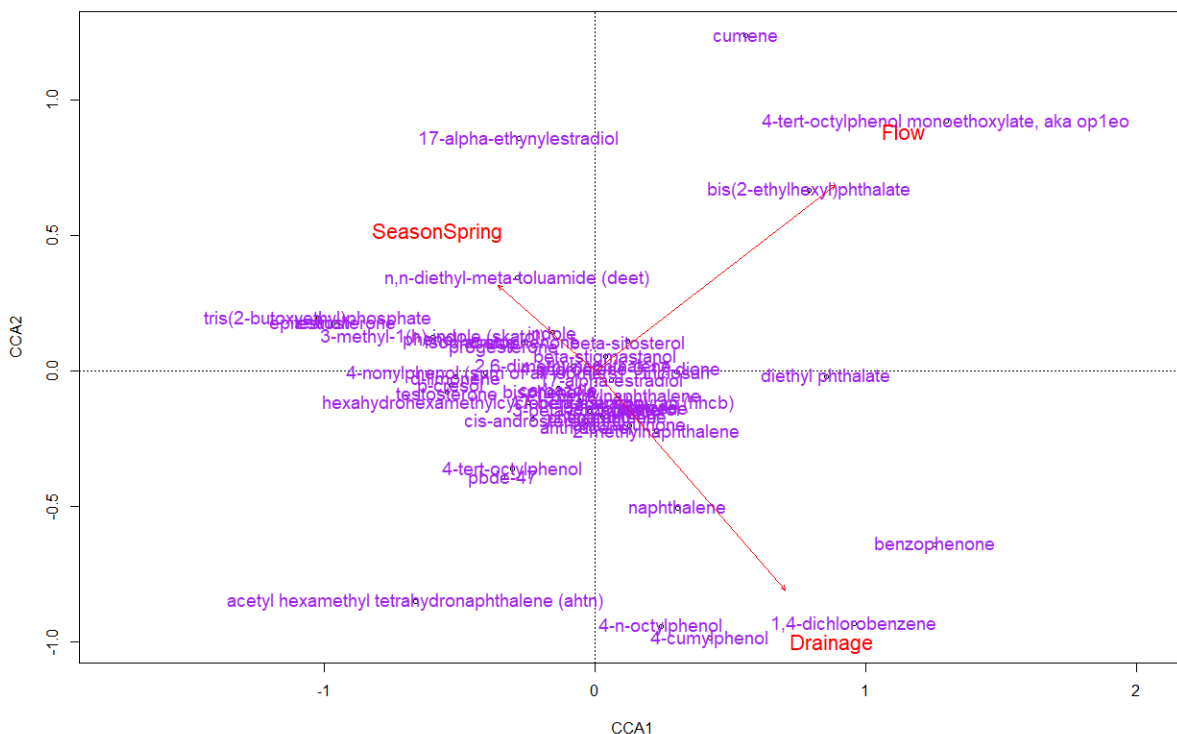
In large drainage areas in 2013-2015, % agricultural land use was the strongest predictor of hormone concentrations; there were no significant predictors of hormone concentrations for small drainage areas in the 2013-2015 data. In small drainage areas in 2016-2017, % forested land use was the strongest predictor of hormone concentrations; there were no significant predictors for large drainage areas in the 2016-2017 data. Out of the anthropogenic variables (% forested land use, % agricultural land use, and % developed land use), % agricultural land use was the strongest predictor of wastewater compound concentrations in large watersheds and % forested and % agricultural land use were the strongest predictors in small watersheds. Significant natural predictors of hormone and wastewater indicator compound concentrations for the 2013-2015 data were flow and drainage area; there were no significant predictors for the 2016-2017 data.

Many of the outlier analytes in ordinations, or CCAs, were the rarely detected analytes. Many analytes were detected only once or twice. Prior to running CCAs, analytes with no detections were removed, but the rare analytes were retained. Rerunning a CCA without these “rare species” did not affect the overall results substantially; this has also been demonstrated in the literature (Greenacre 2013). CCA plots showed these rare analytes as highly influenced by a particular predictor, while other analytes frequently detected were located in the center of the CCA plots, indicating they were not as influenced by any one variable. This can be seen in the CCA for wastewater compound concentrations and anthropogenic variables in sites with small drainage areas which had strong model significance ( $p = 0.001$ ) (Figure 6). Another plot of the CCA with 2013-2015 hormone and wastewater compound concentrations and natural variables also showed rarely detected analytes (for example, dihydrotestosterone, equilenin, mestranol) that did not affect overall CCA results (Figure 7).

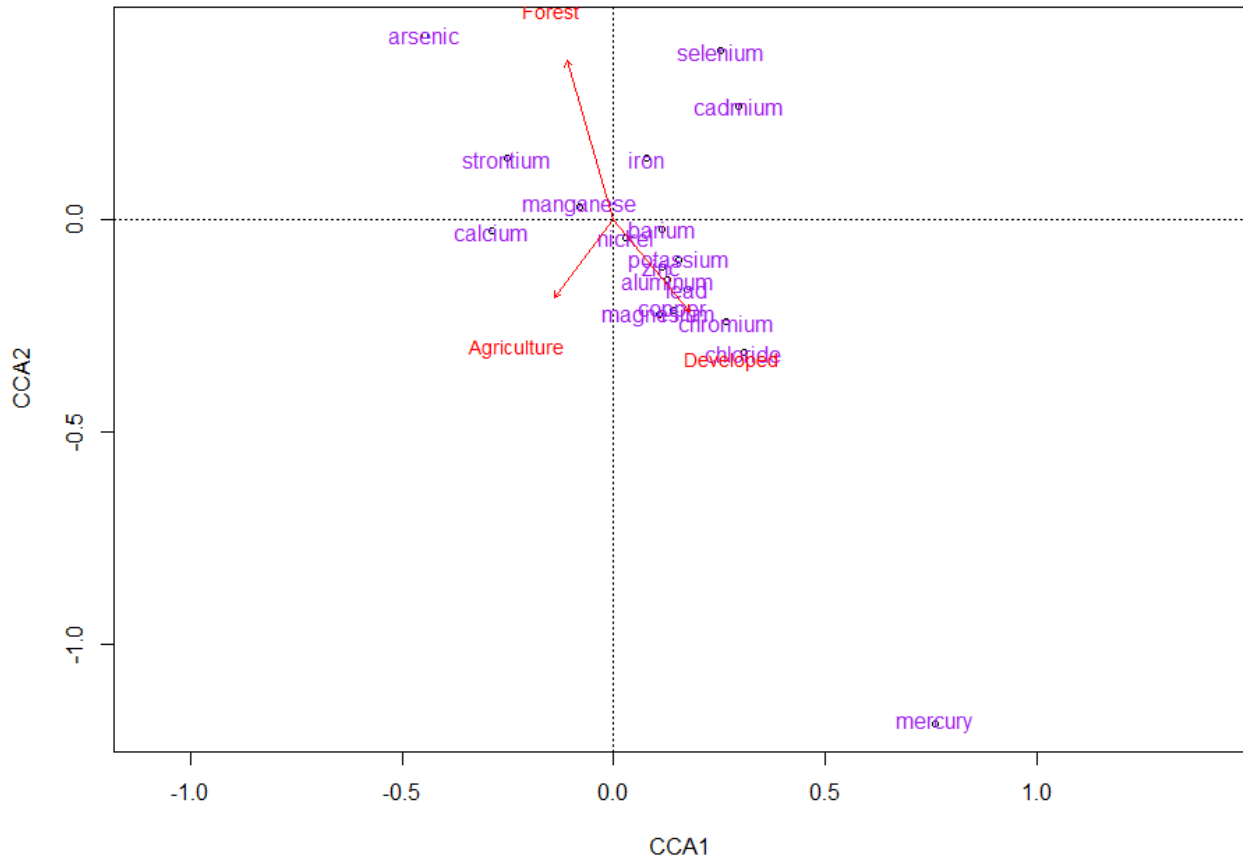
The most significant anthropogenic predictor of metals in sediment was % developed for large drainage areas, while specific metals were significant predictors in small drainage areas for particular land use categories, such as mercury being influenced by % developed land (Figure 8). Drainage area was the most significant natural predictor of metals and ecoregion was the most significant rock/ecoregion predictor. While drainage area, flow, and season were considered “natural” variables, anthropogenic actions can potentially affect all of these. For example, activities related to certain land covers such as row crops and grazing are season-dependent, flow can be altered through things such as channelization and dams, and drainage area, to an extent, can even be impacted by human activities such as urbanization and changing land use.



**Figure 6.** CCA with wastewater compound concentrations and anthropogenic (land use) variables (Developed = % developed land use; Forest = % forested land use; Agriculture = % agricultural land use); all years; small watersheds only; model significance  $p = 0.001$ ; Agriculture and Forest are significant predictors.



**Figure 7.** CCA with wastewater compound and hormone concentrations and natural variables; 2013 – 2015 data only; all watersheds; model significance  $p = 0.001$ ; Flow and Drainage are both significant predictors of wastewater compound and hormone concentrations.



**Figure 8.** CCA with metals and anthropogenic (land use) variables (Developed = % developed land use; Forest = % forested land use; Agriculture = % agricultural land use); all years; small watersheds only; model significance  $p = 0.001$ ; all land use variables are significant.

## 5. DISCUSSION

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Quality assurance analyses of samples and laboratory conditions were extensive during this study. This was important in order to understand outside influences on sediment sample contamination. Except for several low hormone detections in laboratory blanks, there were no systemic issues with detections in blanks. Laboratory blanks from SGS AXYS showed hormone samples had some contamination, although environmental results were corrected to reduce the impact of the contaminated lab blanks. This contamination would have come from some part of the laboratory preparation and/or analysis process.

Many lab and field replicates were in agreement, although some analytes exhibited inconsistency in replicates; these results should have been similar. Sediment can be very heterogeneous when collected, and that can complicate replicates if procedures are not properly followed in the field. In addition, laboratory contamination can occur.

Also, several of the surrogates and spikes were out of range, indicating an over- or under-estimation of the associated environmental sample results. If the resulting recovery percentage was lower than the lower range number, the environmental result could be underestimated. If the recovery percentage was higher than the upper range number, the environmental result could be overestimated. These issues will need to be investigated and understood better in the future.

A total of 115 of 202 analytes tested across 87 sites for the period of 2013 through 2017 were detected. Although 72% of all individual sample results were non-detect, the results indicate that sediment contamination for various analytes, including historical and currently used compounds, is a water quality concern that needs to continue to be monitored and evaluated. More specifically, wastewater compounds, PAHs, metals, and hormones were most frequently detected. Additional sediment data collection and comparisons to other media data, like water column or organism tissue, may be warranted to better understand and describe these contaminants in Pennsylvania surface waters. Pesticides and PCBs were least frequently detected. Some historical pesticides were detected, such as DDT and its metabolites, which reflects their persistence in the environment (Nowell et al. 2000). Historical pesticides and PCBs are currently assessed through the collection and analysis of fish tissue samples and data, and sediment collection efforts for these groups of compounds may not be as useful for monitoring and assessment purposes as fish tissue data collection efforts. Some currently used pesticides were still detected at low frequencies, even though they were designed to be less persistent in the environment. However, the currently used pesticide analyses in this study had reporting limits that were higher than other reported studies, which may have led to a lower number of detections. In other studies (Anim et al. 2017, Dias-Ferreira et al. 2016, Syakti et al. 2011, Wong et al. 2000, Yang et al. 2015), reporting limits for pesticides and PCBs in sediment were frequently lower than in DEP's study. Lower reporting limits may very well have resulted in more detections of pesticides or PCBs. However, unlike currently used pesticides, legacy pesticide reporting limits in this study were low (around 10 µg/kg) and there were few historical

pesticides detected. Future sediment data collection efforts for currently used pesticides should request lower reporting limits.

Over the years, management practices have focused on high-impact and highly publicized contaminants, such as PCB contamination. These management practices could be resulting in the lower detected frequencies of these compounds. Sampling design that includes areas of possible PCB accumulation, such as behind large dams, could increase the likelihood of detecting PCBs. In contrast, PAHs, hormones, and many wastewater compounds have generally not been the focus of extensive monitoring or control efforts. In addition, management of emerging contaminants has not traditionally focused on sediment quality. Consequently, more research into how chemical contaminants in sediment could affect aquatic biota that spend a significant portion of their lives in or on sediment, such as macroinvertebrates and some fish, may help direct future management practices. As an example, DEP completed a study on PAHs in sediment of Conodoguinet Creek that had concentrations exceeding recommended USEPA sediment benchmarks (Williams 2019). These areas of Conodoguinet Creek have an impaired aquatic life assessment based on low oxygen levels. However, because PAHs are present in concentrations that could harm aquatic life, sediment sampling could be used in the future to supplement or support aquatic life assessments such as this. In addition, where sources and causes of macroinvertebrate impairment are unknown, sediment sampling could provide insight. Future sampling should focus primarily on compound categories (pesticides, PAHs, etc.) that are suspected to be linked more to sediment than water. In addition, wastewater compounds and hormones were generally found to be present with some consistency, so they are worth continuing to investigate as well.

CCAs in this study showed varying influences of anthropogenic and natural variables on analyte groups in sediment. Agricultural land use was an explanatory variable that had poor explanatory capacity in this study, but results were significant for several analyses. Other studies have demonstrated correlations between CEC concentrations and land cover types. Blazer et al. (2014) found higher severity and presence of testicular oocytes in male Smallmouth bass in watersheds with higher % agricultural land use in the watershed. Severity of testicular oocytes was also higher downstream of wastewater treatment plants, although the presence was not higher. Water estrone concentrations also correlated with testicular oocytes. Compounds that can disrupt the endocrine system and stimulate or inhibit hormone processes are collectively called endocrine disrupting chemicals, and include many different compounds such as hormones, wastewater compounds, and various pesticides. These can cause male fish to display the female characteristics described above, which is called intersex. In the Blazer et al. (2014) study, estrone was the most common hormone detected in the sediment. Conversely, estrone was only detected in sediment in 50% of samples in this DEP study.

Additional concerns include the synergistic and additive effects of CECs on aquatic life and human health. A study on the combined estrogenic effects of estradiol, ethynylestradiol, nonylphenol, octylphenol, and bisphenol A in water on vitellogenin



induction in male fathead minnows showed an additive effect of these chemicals (Brian et al. 2005). Another study demonstrated mixture effects of water containing linuron, an herbicide, and di(2-ethylhexyl)phthalate, a plasticizer, on male fathead minnows and found greater estrogenic effects with the mixture as opposed to the individual chemicals (Crago and Klaper 2012). Although sediment data for this effort did not necessarily document widespread sediment contamination, which could be attributed to ongoing management efforts, results did document contamination at some sites for some groups of compounds that have been documented to have synergistic effects.

As documented by this study and others, sediment contamination should be considered a component of water quality protection. Consequently, it is recommended that sediment monitoring efforts continue and expand, and that steps are taken to better understand and acknowledge sediment contamination in the development and implementation of water quality standards. Sediment contamination could assist in determining impairment causes in stream aquatic life assessments. EPA Region III has published recommended freshwater sediment criteria benchmarks for many pesticides, metals, volatile organic compounds, and PAHs (Plata 2006). Without established numerical sediment criteria, narrative criteria could be applied to assist in assessments. Studies on sediment contaminants could be targeted and contaminant-specific, to determine the extent of contamination in surface waters. In addition, DEP should keep up with the current literature documenting effects of sediment contamination on aquatic biota. In the future, sediment sampling could prove to be useful and commonplace in DEP's work to monitor, assess, restore, and protect water quality in Pennsylvania.

## 6. LITERATURE CITED

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