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DEPARTMENT OF ENVIRONMENTAL PROTECTION

OFFICE OF WATER PROGRAMS
BUREAU OF CLEAN WATER

CONTAMINANTS OF EMERGING CONCERN IN SURFACE WATER USING PASSIVE WATER SAMPLERS, PENNSYLVANIA (2013 – 2017)

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1. EXECUTIVE SUMMARY

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. Due to the unknown nature of CECs in Pennsylvania's surface waters, an extensive study was initiated by the Pennsylvania Department of Environmental Protection (DEP) to evaluate the presence and concentrations of various CECs in Pennsylvania's streams and rivers. CECs were collected from 68 sites throughout Pennsylvania from 2013 through 2017 using passive water samplers – Polar Organic Chemical Integrative Samplers (POCIS) and Semi-Permeable Membrane Devices (SPMDs).

Over 300 contaminants were tested for, including hormones, pharmaceuticals, pesticides, wastewater indicator compounds, polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). While 70.4% of final environmental results were non-detected, 283 out of 395 compounds were detected at least once. PAHs – notably fluoranthene, chrysene, benzo(b&j)fluoranthenes, and pyrene – were among the most frequently detected compounds, with these PAHs detected in more than 97% of the samples in which they were analyzed.

Concentrations in passive samplers can be converted from raw values (i.e., ng/POCIS or ng/SPMD) to time-weighted average (TWA) concentrations (i.e., ng/L). Table 1 below shows the highest TWA concentrations of CECs documented in this study for each category of CECs:

Table 1. Highest CEC time-weighted average (TWA) concentrations for each CEC category.

CEC Category	CEC	Highest TWA Concentration (ng/L)	Location
hormones	total estrogenicity	2.4	Conodoguinet Creek (Cumberland County)
	cholesterol	325.0	Delaware River (Bucks County)
PAHs	fluoranthene	37.0	Chester Creek (Chester County)
PBDEs	PBDE-183	1.4	Quittapahilla Creek (Lebanon County)
pesticides	atrazine	863.0	Mahoning River (Lawrence County)
pharmaceuticals	carbamazepine	1044.0	Chester Creek (Chester County)
wastewater indicator	diethyl phthalate	3088.0	Little Beaver Creek (Lancaster County)

Land use variables and other variables (i.e., drainage area, flow) were tested against percent contaminants detected per site using spearman correlation analyses to determine if any environmental variables influenced the presence of CECs.

In small drainage areas, percent detected compounds increased as percent low-intensity developed land use and percent high-intensity developed land use increased. Percent compounds detected decreased with increased percent forested land use.

Percent compounds detected was significantly higher at sites downstream of sewage treatment plants (STP) versus upstream. In addition, percent detected compounds was significantly higher in near-shore locations versus main channel sites in large rivers. Percent compounds detected was not higher in smaller tributary sites versus main channel sites in large rivers. There was also no significant difference in percent compounds detected among seasons (i.e., winter, spring, and fall).

For this study, many sites were sampled across multiple years and seasons. For example, three sites across a transect of the Susquehanna River at Harrisburg were sampled over three years. Analyzing the percent detected wastewater compounds at these sites over time showed that detections remained consistent across the transect but changed over the years and seasons, possibly dependent on stream discharge at the time of sampling.

Overall, this study provides a window into the extent of CEC contamination in surface waters across the state, using passive samplers to quantify TWA concentrations of more than 300 CECs at 68 sites.

2. INTRODUCTION

Contaminants of emerging concern (CECs) are a growing threat in surface waters (Kolpin et al. 2002, Wilkinson et al. 2017). These contaminants are either compounds newly introduced into the environment or those that may have been in the environment for years but were only recently able to be analyzed with current laboratory analytical methods. CECs can be grouped into many categories of compounds, including hormones, pharmaceuticals and personal care products, various compounds found in wastewater, flame retardants, per- and polyfluoroalkyl substances (PFAS), and pesticides. Both natural compounds, such as hormones, and man-made compounds, such as pharmaceuticals, can be considered CECs. Many of these compounds are unregulated in both drinking water and surface waters. In Pennsylvania's water quality standards regulations at 25 Pa. Code Chapter 93, most CECs do not have numeric criteria established in § 93.7 or in Table 5 in § 93.8c, which contains water quality criteria for toxic substances; however, CECs are covered by Pennsylvani's general, narrative water quality criteria in § 93.6, which provide that, "Water may not contain substances attributable to point or nonpoint source discharges in concentration or amounts sufficient to be inimical or harmful to the water uses to be protected or to human, animal, plant or aquatic life." In addition, CECs are not routinely sampled during stream surveys. As a result, information on the prevalence of CECs in Pennsylvania's waters is generally somewhat limited; this study aims to provide more information on CECs in Pennsylvania surface waters. For additional information on CECs in Pennsylania surface waters, visit the Pennsylvania Department of Environmental Protection (DEP) webpage on Contaminants of Emerging Concern webpage. For additional information on CECs in drinking water, visit DEP's Emerging Contaminants webpage.

CECs can be hard to measure in surface waters using traditional discrete water sample collection methods because many CECs are often present in very low concentrations and may only be present in higher concenrations during relatively short time periods (e.g., immediately following an intense rainfall). Passive samplers are useful for detecting compounds that occur only occasionally or in very low concentrations that traditional discrete water sampling would not capture in measurable concentrations. Consequently, most of the CEC sampling done in surface water by DEP was completed using passive water samplers. There are many types of passive samplers, but the types used in these DEP studies were Polar Organic Chemical Integrative Samplers (POCIS) and Semi-Permeable Membrane Devices (SPMDs). These devices employ a combination of membranes and media to retain chemicals from water or air. They are deployed for extended periods of time, normally for an interval of 30 days. While very useful, passive samplers have their limitations. A time-weighted average (TWA) concentration can be calculated for many sample results from passive samplers, but it is difficult to compare these directly with discrete sample results, which are more commonly used to assess water quality status.

CECs can enter the water in a variety of ways, including via runoff from the surrounding landscape or as discharge from wastewater facilities, although modern wastewater treatment often removes many CECs (Hamid & Eskicioglu 2012). One of the first

comprehensive studies of CECs in Pennsylvania was a study conducted by the United States Geological Survey (USGS) in partnership with DEP to look at the concentrations of pharmaceutical compounds, antibiotics, hormones and natural sterols, and various organic wastewater compounds in water. Sampling for this USGS-DEP study occurred from 2006 to 2009 at a variety of locations: at locations upstream and downstream from wastewater treatment plant discharges and animal feeding operations; at groundwater wells; at sites within five miles of drinking water intakes; and at sites used to evaluate fish health (Reif et al. 2012). Generally, Reif et al. (2012) found higher concentrations and a greater number of compounds downstream of wastewater treatment plants. Reif et al. (2012) also found compounds more frequently in sediment than surface water, but only a few compounds were detected in groundwater wells.

A subcategory of CECs of particular concern is estrogenic compounds that act as endocrine-disrupting compounds (EDCs). Endocrine disruptors are compounds that can affect the endocrine system and often produce adverse effects in reproduction, the immune system, and development (National Institute of Environmental Health Sciences 2016). Very low concentrations of EDCs have been demonstrated to have non-lethal effects on fish, such as reproductive issues, reduced egg fertilization success, and intersex conditions (Caldwell et al. 2008, Caldwell et al. 2012, Parrott & Blunt 2005). A study of nine river basins in the United States found intersex fish at many sites, mainly by observing testicular oocytes, with the greatest incidence in the southeastern United States, but an intersex smallmouth bass was found in the Allegheny River at Natrona, Pennsylvania (Hinck et al. 2009). Blazer et al. (2014) found male fish in Pennsylvania rivers with testicular oocytes and plasma vitellogenin, both indicators of possible exposure to EDCs. These effects can occur at very low EDC concentrations. It can be difficult to measure EDCs at such low concentrations. Additionally, it can be difficult to determine at what EDC concentrations harms can occur because chemicals other than estrogenic compounds, such as triazine pesticides, can also have endocrine-disrupting effects (Faust et al. 2001) and because mixtures of estrogenic chemicals can cause synergistic, or combined, effects (Silva et al. 2002).

Routine monitoring efforts to establish trends and concentrations of these chemicals in waterways are not commonplace. To address this issue and to expand on the work by Reif et al. (2012), DEP began collecting surface water samples for CEC analyses in 2012 with samples from four sites analyzed for total estrogenicity and androgenicity. After this initial phase, the study expanded to include approximately 20 sites per year, with many sites sampled over multiple years and seasons. In addition, the analyte list expanded to include over 300 compounds per site. This work was initiated in response to a decrease in young-of-year smallmouth bass (SMB) and SMB lesions that were documented in the Susquehanna River basin. Since 2012, the population of young SMB has rebounded, with signs of disease also decreasing (PFBC 2018). Because of the SMB study efforts, most passive sampler sites have been in the Susquehanna River basin; however, sample coverage across the state slowly increased during the course of this study. Currently, DEP CEC sampling efforts have continued across the state to determine the occurrence and extent of CECs in Pennsylvania’s surface waters and to report findings to both the public and government bodies. Objectives of this work included reporting the most commonly detected CECs and their concentrations, and to

understand how abiotic parameters may influence the presence or concentrations of CECs. This information may assist in determining the necessity of future sampling efforts and help refine locations of future sampling. Although this report encompasses data from 2013 through 2017, work is ongoing each year to facilitate the establishment of CEC trends both spatially and through time.

3. METHODS

3.1. Field Study Sites and Collection

For this study, samples were collected from 68 sites throughout Pennsylvania from 2013 through 2017 (Figure 1, Appendix A-Site Info). Long-term sites were normally sampled for several years during multiple seasons; targeted, impacted sites were often collected only two or three times in one year, over multiple seasons.

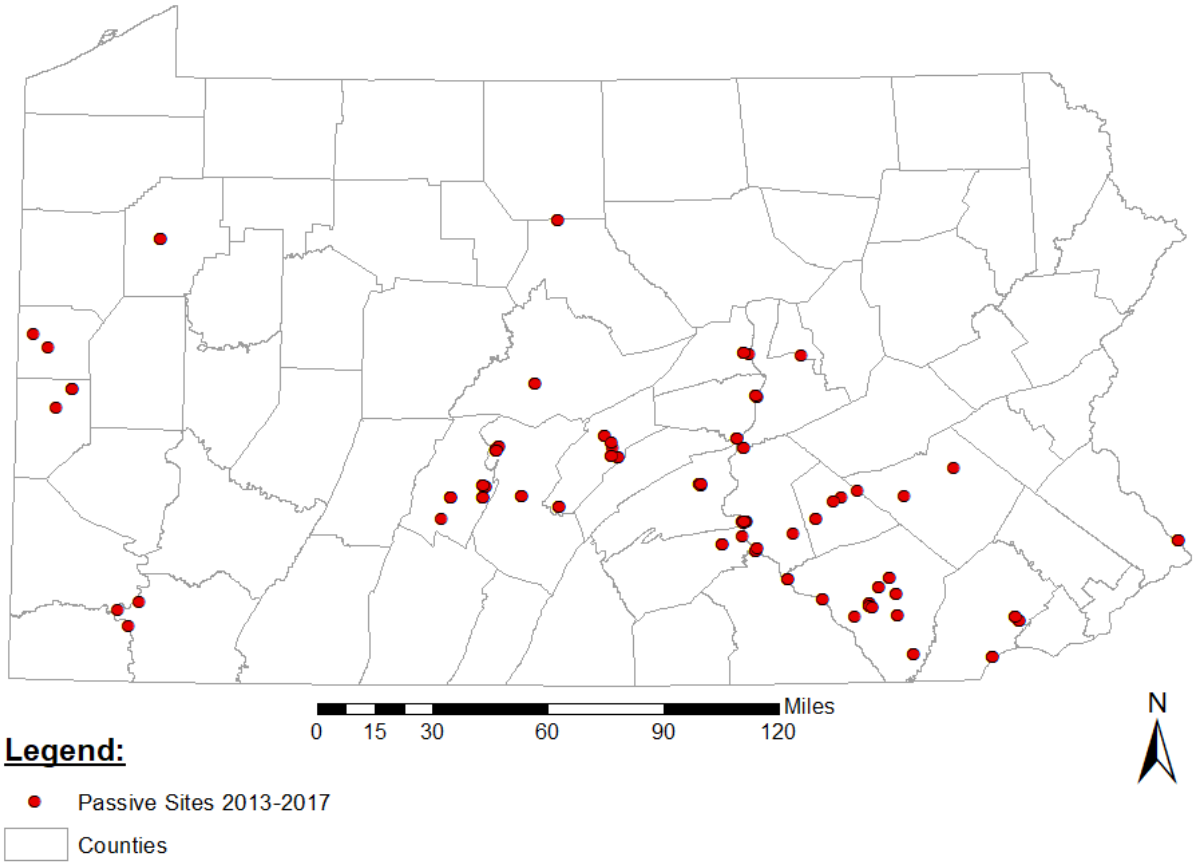


Figure 1. Passive sampler sites, 2013 through 2017

Passive water samples were collected according to the Passive Water Chemistry Data Collection Protocol found in Chapter 4 of Shull and Lookenbill (2018). For each sample, the samplers were deployed in water for at least 30 days to allow enough time for CECs to accumulate on the filters and membranes.

3.2. Laboratory Processing

Environmental Sampling Technologies (EST) in St. Joseph, Missouri provided sampling equipment and processing of the samplers. After processing by EST, the sample extracts were sent to a variety of laboratories for sample analyses. Laboratories that were used for analysis of CEC samples were: the DEP Bureau of Laboratories (BOL) in Harrisburg, Pennsylvania; the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado; the USGS Eastern Ecological Science Center in Kearneysville, West Virginia; the USGS Columbia Environmental Research Center in Columbia, Missouri; and SGS-AXYS Analytical Services Ltd in Sidney, British Columbia, Canada. Over 300 compounds were analyzed from many CEC categories. From 2013 through 2015, all samples were analyzed by USGS laboratories. From 2016 onward, USGS, DEP, and SGS-AXYS labs were used. For a list of lab analysis methods used per test suite, see Appendix B-Methods.

3.3. Concentration Calculations

Results from passive sampler analyses are reported to DEP from the laboratories as concentrations per sampler (i.e., ng/SPMD, ng/POCIS); however, it is possible to estimate the concentration of certain compounds. Raw SPMD results were converted to estimated concentrations (i.e., ng/L) using performance reference compound (PRC) loss data (described below in Section 3.4 Quality Control (QC)), experimentally-derived chemical sampling rates (*Rs*) when available from the literature, and length of time deployed (Alvarez 2010). SPMD concentrations were calculated using the SPMD Calculator version 5.1 (USGS 2011). Raw POCIS results were converted to estimated concentrations using experimentally-derived *Rs* values and time deployed (Alvarez 2010). These raw values were converted to time-weighted average concentrations where *Rs* values were available – if unavailable in the literature, concentrations remained as concentrations per sampler (i.e. ng/SPMD, ng/POCIS).

Raw results and TWA concentrations are shown in Appendix C-Results and sampling rates are shown in Appendix D-Sampling Rates. Recommended sampling rates can be updated through time based on new laboratory studies. This can make comparisons with previously calculated data inaccurate. Therefore, the most current *Rs* were used and if any *Rs* were republished during this study period, results were recalculated to maintain comparable analyses. Depending on how much the *Rs* values changed based on new laboratory studies, new TWA results using new *Rs* values may be significantly different than old results. It is important to be mindful of this when interpreting and analyzing TWA concentrations here and in other sources. Also, it is important to remember that, in the end, TWA concentrations are averages, which also presents a challenge when comparing TWA concentrations to discrete water samples.

3.4. Quality Control (QC)

3.4.1. Performance reference compounds (PRCs)

PRCs and photolysis surrogates were added to SPMDs to aid in accounting for the site-specific effects that may impact sampler performance. PRCs are chemicals that are added to passive samplers at known concentrations during assembly and can be measured after deployment to quantify loss of chemicals in the field due to various environmental conditions. A photolysis marker can also be added to SPMDs, which can indicate whether potential photodegradation of certain chemicals, such as polycyclic aromatic hydrocarbons (PAHs), may have occurred. The membrane of the SPMD is transparent to ultraviolet radiation; therefore, photodegradation of some analyte compounds may occur in clear, shallow waters. PRCs are not typically added to POCIS as the POCIS mechanisms for retaining chemicals typically do not allow for loss (Alvarez 2010). Although some chemicals have been proposed as possible PRCs for POCIS in the literature, they work only for a very small subset of similarly structured chemicals. Photolysis markers are not needed for the POCIS as the membrane of the POCIS provides adequate photodegradation protection of sampled chemicals.

PRCs used to calculate concentrations of polybrominated diphenyl ethers (PBDEs) and PAHs were anthracene-d10, fluoranthene-d10, phenanthrene-d10, and pyrene-d10. PRCs used to calculate concentrations of pesticides and polychlorinated biphenyls (PCBs) were 3,5-dichlorobiphenyl (PCB-14), 2,4,5-trichlorobiphenyl (PCB-29), and 2,2,',4,6-tetrachlorobiphenyl (PCB-50). The photolysis marker used was dibenz(a,h)anthracene-d14. PRC and photolysis marker concentrations are shown in Appendix E-PRCs-Photolysis and photolysis marker percent recoveries are shown in Appendix F-Photolysis Pct.

3.4.2. Lab QC

Baseline SPMD blanks, also known as fabrication or day zero blanks, were created by EST labs along with the field equipment and stored until the field samplers were processed (Alvarez 2010). Baseline samples were also spiked with PRCs and results were used as the “baseline” value for TWA SPMD concentrations (Appendix G-Lab QC). Baseline blanks also determine the “baseline” level of contamination present from equipment, storage, or sampler processing prior to laboratory analysis. Extraction blanks from POCIS, prepared similarly as baseline blanks from SPMDs, were also included in the QC results (Appendix G-Lab QC). Extraction blanks were used to determine if contamination occurs from equipment, storage, or sampler processing. Labs also performed their own QC, such as lab blanks and spikes. Lab blanks use a matrix analogous to field samples and are analyzed at the same time as field samples using the same procedures. These show any contamination in the sample processing and analysis process. Spiked matrix samples are similar to lab blanks, except they are first fortified with known concentrations of analytes, then reported as percent recovery to monitor the performance of lab methods. Surrogates were also used and can quantify interferences and losses (Alvarez 2010). See Appendix G-Lab QC and Appendix H-

Spikes-Surrogates for the QC results from laboratories. More information on types of QC used with POCIS and SPMDs can be found in Alvarez (2010).

If there were detections in the baseline SPMD blanks, extraction blanks, or lab blanks, these results were averaged and, if the blank detection average was >10% of the environmental result, the blank detection average was subtracted from the raw final amount, prior to any calculations. The 10% method of blank correction is used by DEP BOL and has been used by the United States Environmental Protection Agency (USEPA). Dialysis blanks were corrected with lab blank detections, then averaged with the lab blank to obtain final blank correction values for environmental data. In some cases, the lab blank was extremely low compared to the dialysis blank detection (e.g., 1 ng/SPMD versus 50 ng/SPMD). In these cases, the lab blank was subtracted from the dialysis blank, but then the two were not averaged – the dialysis blank value was used in further corrections. Since the dialysis blanks were conducted in the equipment processing laboratory and the lab blanks in the analysis laboratories, they represent different locations where sample contamination occurred. In some DEP BOL lab blanks, two concurrent lab blanks displayed widely differing results, some of which were high – indicating random matrix interference. In these cases, the lab blanks were removed from analyses and any dialysis blank detections were used on their own. Lab blanks were always associated with the samples with which they were batched – SGS AXYS samples were run in “batches” of 20 samples, with some seasons having a few batches. Care was taken to account for dialysis, extraction, and/or lab blank detections because there was a large quantity of lab blank detections >10% of sample results, which had the potential to greatly impact sample results and interpretation.

3.4.3. Field blanks

Field blanks were used while deploying and retrieving passive samplers based on recommendations in Alvarez (2010) and via personal communication (David Alvarez, USGS). Field blanks were exposed to the air during the time passive samplers were being deployed and retrieved from the water. This allowed any external contamination due to the shipment and/or contamination during field handling to be quantified. Although not field blanks in the traditional sense, given that they are not exposed to any water, air field blanks are commonly used in passive sampler water studies. Due to the quantity and cost of utilizing blanks, one blank was used per every three to four sites sampled. The downside to this is that any field blank contamination was unable to be traced to a specific site.

Because the passive sampler field blanks sample air, the possibility of contamination from highly industrial or urban areas is possible. If contamination occurred in field blanks at a higher concentration than the environmental sample result, the result was deleted from further analyses. These were included in the final dataset (Appendix C-Results) as “BlankHigher” in the FIELD_BLANK_FLAGGED column. Other samples that had field blank detections less than the environmental sample result were flagged in the final dataset as “BlankLower” in the FIELD_BLANK_FLAGGED column.

3.4.4. Field Replicates

Field replicates were not deployed due to the high cost of samplers; however, some compounds were tested multiple times in the same sample because the compounds were in multiple analysis suites. These acted as split replicates for quality assurance. There were also two sites, Conodoguinet Creek near Hogestown, PA and Yellow Breeches Creek near Camp Hill, PA, sampled in Fall 2015, that had field replicates collected for some compounds. However, field replicates or the aforementioned split replicates were not included in the data analysis sections 4.2.2 or 4.2.3 to avoid pseudoreplication. The split replicates were not included in sections 4.1.2 through 4.1.4 or section 4.3.

3.4.5. A Note on Detection and Quantitation Limits

When necessary, the method detection limits (MDLs) and method quantitation limits (MQLs) were also calculated from raw values. The MDL was defined as the mean of the blanks plus three times the standard deviation of the blanks and the MQL was defined as the mean of the blanks plus ten times the standard deviation of the blanks (Alvarez 2010). Types of reporting limits or detection limits varied between labs and years. The reporting limits and types are noted in the final dataset (quantitation limit, method quantitation limit, verified instrument reporting level, reporting limit, sample detection limit, method detection limit, lowest calibration level equivalent, or contract defined limit). After correcting for lab blanks, any changed results were compared to the detection limit and accordingly set to non-detect if the new result was less than the reported detection limit. Results that were originally flagged as less than the lower method calibration limit (LMCL), MQL, or similar ("J" values) were left as reported but noted with the comment "Original result less than defined detection limit - result not edited" in the Comment column. This comment could refer to any of the above scenarios. Blank-corrected data that were substantially less than the original result were accounted for in this fashion. Various lab flags for the data and their meanings are listed in Appendix I-Lab Flags.

3.5. Data Preparation

3.5.1. Land Cover

Fourteen categories of land cover were quantified for inclusion in data analyses (Appendix A-Site Info, Table 1). Land cover of the upstream watershed was calculated for each site with an upstream watershed smaller than 1000 mi^2. This was based on best professional judgement. Watershed polygons were created using the ArcGIS Online watershed tool (Scopel 2014). Watershed land cover for sites with upstream watersheds larger than 1000 mi^2 (e.g., sites on the Susquehanna River) is not very useful for correlation analyses. Such large drainage areas have large quantities of every type of land cover and, consequently, the effect of any particular land cover category, or combination of land cover categories, on sample results becomes more difficult to ascertain during analyses. Therefore, for each site with a large watershed (i.e., >1000 mi^2), 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. 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 DEP best professional judgment.

Watershed polygons (for sites with watersheds smaller than 1000 mi^2), buffered polygons (for sites with watersheds larger than 1000 mi^2), 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, the drainage area was calculated for each site. Because land use percentages for sites with larger drainage areas (greater than 1000 mi^2) were calculated very differently than for sites with smaller drainage areas (less than 1000 mi^2), the larger and smaller sites were divided into two separate groups for analyses in Section 3.6.2 to determine if larger versus smaller drainage areas affected percent CEC compounds detected per sample.

3.5.2. Flow

A streamflow metric was included as an abiotic parameter that could affect CEC detections. Using R, version 3.5.0 software (R Core Team 2018), a streamflow metric was calculated for each sample by averaging the flow from the 30 days prior to sampler retrieval and dividing that 30-day averaged flow by the long-term monthly median flow at the site, resulting in a streamflow metric of the 30-day (i.e., short-term) averaged flow as a percent of the long-term monthly median flow. 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. 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 sampler retrieval as a percent of the long-term monthly median flow at the site was then calculated. Because passive samplers are deployed for approximately 30 days, this metric provides a measure of the relative streamflow during each sampling period.

3.5.3. CEC Data

For parts of the Results section (Section 4), percent CEC compounds detected per sample were used as final endpoints. Because TWA concentrations are an estimate, the data was complex, and there were many non-detects, which complicates meaningful analyses; for this reason, percent CEC compounds detected per sample, rather than TWA concentration, was used as the outcome variable of interest in most analyses. Depending on the analysis, individual percent compounds detected were also

summarized into percent compounds detected per CEC category. Analyses in Section 4.1 of the Results investigated the concentrations of compounds.

3.6. Data Analysis

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

3.6.1. Quality Control, Occurrence, and Distribution Analyses

Quality control results are described here. A summary of the most common contaminants, rare contaminants, and sites with the highest concentrations are examined. Summaries of compounds detected by group are also investigated.

3.6.2. Explanatory Variable Analyses

With several hundred compounds and dozens of sample sites comprising many types of locations and seasonal situations, this passive sampler dataset is rather complex. In addition, calculating the estimated concentration for each compound based on lab-defined sampling rates has its limitations, and many compounds have no sampling rates developed and, therefore, do not have TWA calculations. Therefore, as outcome variables of interest, the larger statistical analyses used percentage of compounds detected per sample, and percentage of compounds detected per category per sample. See Appendix N-Pct Per Category for percent detections of all compounds sampled and percent detections of different CEC groups.

As noted in Section 3.5.1, for purposes of analysis, samples were divided into large drainage areas (greater than 1000 m^2) and small drainage areas (less than 1000 m^2) since land use variables were calculated differently in large versus small drainages. Then, results from both large and small drainage areas were combined to analyze correlation of percent compounds detected per sample with the drainage area of each site. All samples except field replicates and blanks were used in these analyses.

Abiotic explanatory variables were considered for the analyses (Table 2). These variables were used to determine if any abiotic variables explained percent detections of various CEC categories. Variable correlation was tested, and some variables were combined or removed to eliminate multicollinearity. Multicollinearity was tested by calculating the variance inflation factor (VIF), which measures how much variance of a parameter is inflated because of collinearity. A VIF of one indicates no multicollinearity, while the higher the VIF gets, the more influential the collinearity is. A VIF of 10 and above (as recommended by Penn State 2018) was used as indicative of multicollinearity. Normality testing was first completed to determine if parametric or non-parametric tests were appropriate. Correlation analyses between abiotic explanatory

variables and percent compounds detected were then done using R, version 3.3.2 software (R Core Team 2018) to quantify the relationship between pairs of variables.

Correlation analyses were also conducted to compare relationships between total estrogenicity concentrations, also known as the estradiol equivalent factor (EEQ), to explanatory variables. EEQ measures an estimate of the concentration of 17β-estradiol equivalent to the amount of chemicals that can bind to estrogen receptors in a sample (Morace 2012). This is computed using a yeast estrogen screen (YES) assay.

Table 2. Explanatory variables considered for data analyses.

Category	Parameter	Min	Median	Max	Details
Land Use	% Developed-Open	0.9	8.3	32.2	Some construction, mostly lawn
	% Developed-Low Intensity	0	4.9	30.8	Some construction & vegetation, commonly homes
	% Developed-Medium Intensity	0	1.6	31.0	Some construction & vegetation, commonly homes
	% Developed-High Intensity	0	0.3	19.3	Highly developed, most is impervious surface
	% Barren	0	0	1.4	Bedrock, strip mines, little vegetation
	% Deciduous Forest	0.1	46.5	74.4	More than 75% of tree species shed foliage annually
	% Evergreen Forest	0	1.0	7.3	More than 75% of tree species keep leaves all year round
	% Mixed Forest	0	1.0	14.1	Mix of deciduous and evergreen tree species
	% Shrub	0	0.1	5.9	Shrub/young trees cover >20% of vegetation
	% Herbaceous	0	0.1	3.5	Short, herbaceous vegetation >80% of total
	% Hay/Pasture	0.9	15.9	43.7	Grasses for livestock grazing or crops
	% Cultivated Crops	0	13.9	52.3	Annual crop production
	% Woody Wetlands	0	0.2	6.0	Wetlands with forest/shrub cover >20% of vegetation
	% Emergent Wetlands	0	0	0.7	Wetlands with herbaceous vegetation >80% of total
Other	Drainage Area	1.8	302.7	26001.0	Area drained to sample site (square miles)
	Flow				Calculated as percent of average flow from last 30 days to long-term monthly median
	Season				Sample collected in winter, spring, or fall

3.6.3. Local-Scale Pattern Analyses

Analyses focused on more in-depth exploration of other factors that further divided the data into spatial components. Analyses included comparing upstream and downstream of wastewater treatment plants, main channel versus near-shore differences, and larger river systems versus tributary concentrations.

3.6.4. Temporal Analyses

Patterns over time (both years and seasons) were examined at sites repeatedly sampled.

3.6.5. Differences Between Laboratories

Analyses were completed of differences between percent detected compounds at different laboratories because labs changed from the 2013 – 2015 time period to the 2016 – 2017 time period. Percent compounds detected per sample were compared between USGS (2013 – 2015), DEP (2016 – 2017), and SGS AXYS (2016 – 2017).

3.6.6. Comparison to Sediment Samples

In many cases, sediment samples for CECs were collected at the same site as passive water samples. This section describes comparisons between passive water samples and corresponding sediment samples. Comprehensive analyses of sediment sample methods and results are in Williams (2022, In Review).

4. RESULTS

4.1. Quality Control, Occurrence, and Distribution Analyses

4.1.1. Quality Control (QC) Results

There were several detections in lab blanks, baseline/day zero values, and extraction blanks. Most of these were low-level detections close to non-detection, which shows the likelihood of contamination in these sample types. Detection may have not even occurred in a traditional grab sample, since these are less likely to detect low-level contaminants at a single point in time. A few groups of chemicals, such as PBDEs and PAHs, had higher level contamination in the lab QC samples. Samples were corrected for these QC samples. Accounting for blanks corrected 6.5% of results (including environmental, dialysis blanks, extraction blanks, and field blanks, because all were analyzed together in labs). Out of all samples, 0.8% resulted in a detection changed to a non-detect when lab blank-corrected.

Field-split replicate results were often very dissimilar. These results likely demonstrate a high degree of error in detection between different tests. If there were multiple non-detect results per compound per sample, only one was retained for analyses. In addition, for presence/absence analyses, if multiple detects of the same compound were in a sample, only one was retained for analyses. If one result was a detection and

one was non-detect, the results were omitted from analyses. If there were multiple detections, Wilcoxon sign rank tests were performed on the paired observations (significance level of $p = 0.05$). In most cases, results were statistically different, except for caffeine and atrazine. Consequently, it was decided not to average or retain duplicate detected results. Instead, the highest concentration of a replicated chemical was kept for each sample.

Most field blank results were non-detect. From 2013 through 2017, 6% of samples had a detection in a field blank. Out of these, 1% of field blank results were higher than the environmental sample; these environmental results were deleted from final data analyses. Five percent of samples had a detection in a field blank that was less than a corresponding detected environmental result. For reasons described in Section 3.4.3, it was impossible to determine which site(s) contributed to these field blank detections. Where a field blank result was lower than the relevant environmental result, the envirionmental sample results were retained in the analyses. Where a field blank result was higher than the relevant environmental result, the environmental sample results were flagged in Appendix C-Results in the FIELD_BLANK_FLAGGED column. Note that several passive sampler environmental results do not have a corresponding field blank result due to not having a field blank for that site or due to the inability to analyze for a particular compound. Any sample that had a non-detect environmental or field blank result were flagged as “None” in the FIELD_BLANK_FLAGGED column.

Several of the surrogate results were out of range (Appendix H-Spikes-Surrogates). Any surrogate recovery out of range are notated with a “V” in the LAB_FLAG column (surrogate recovery is not within method/contract control limits). Most of the surrogate results out of range were above the surrogate recovery range for each compound. If the surrogate recovery result was above the range, this indicated that there may have been interferences during analyses and data may be over-reported in those samples (Udesky et al. 2019). These situations are something to keep in mind when viewing the results.

Dibenz(a,h)anthracene-d14 was added to SPMD samples as a photolysis marker and subsequent percent recoveries were calculated. Available photolysis marker recoveries ranged from 45% to 123% (Appendix F-Photolysis Pct). Some of the lower recoveries, present mainly in the fall, indicate that photodegradation may have affected some results, with some concentrations likely biased low.

4.1.2. Common and Rare Compounds

From 2013 through 2017, 395 compounds were tested from various CEC groups (Appendix J-Compounds). Although many chemicals were detected, 70.4% of final environmental passive sampler results were non-detect. There were 283 compounds detected at least once during this time, 22 of which were detected in more than 90% of the samples in which they were analyzed (Table 3), and 51 of which were detected in less than 5% of the samples in which they were analyzed (Table 4).

Table 3. Compounds detected in more than 90% of the samples in which they were analyzed – 2013 through 2017.

Compound	Description
Hormone	
Androstenedione	natural & artificial steroid hormone
Estrone	weak, natural form of estrogen
Pesticide	
Atrazine	herbicide
Metolachlor	herbicide
N,N-Diethyl-meta-toluamide (DEET)	insecticide
Polycyclic Aromatic Hydrocarbon (PAH)	
Benzo(b&j)fluoranthenes	formed from variety of combustion sources
Benzo[e]pyrene	formed from variety of combustion sources
Chrysene	formed from variety of combustion sources
Fluoranthene	formed from variety of combustion sources
Pyrene	formed from variety of combustion sources
Pharmaceutical	
Carbamazepine	anticonvulsant /analgesic drug
Desvenlafaxine	treats depression
Erythromycin-H_2O	antibiotic
Fexofenadine	antihistamine
Fluconazole	anti-fungal
Lidocaine	pain reliever
Metoprolol	treats heart failure, high blood pressure
Nicotine	in cigarettes, supplements
Tramadol	used to treat pain
Triamterene	water pill
Venlafaxine	SSNRI; treats depression, anxiety; Effexor
Wastewater	
Methyl-1h-benzotriazole	deicing fluid

Table 4. Compounds detected in less than 5% of the samples in which they were analyzed – 2013 through 2017

Compound	% Detected	Compound	% Detected
Napropamide[P]	0.6	Beta-bhc[P]	2.5
Norethindrone[H]	0.6	17-alpha-ethynylestradiol[H]	2.5
4-cumylphenol[W]	0.6	Equilenin[H]	2.5
4-epianhydrochlortetracycline [eactc][PH]	1.2	1,2-dimethylnaphthalene[PAH]	2.6
Digoxin[PH]	1.2	Linuron[P]	2.6
Ormetoprim[PH]	1.2	Thiobencarb[P]	2.6
Oxytetracycline [otc][PH]	1.2	3-tert-butyl-4-hydroxyanisole (bha)[W]	2.7
Penicillin g[PH]	1.2	Propachlor[P]	3.1
Penicillin v[PH]	1.2	Heptachlor[P]	3.1
Tetracycline [tc][PH]	1.2	Famotidine[PH]	3.1
Pebulate[P]	1.2	n-desmethyldiltiazem[PH]	3.1
Bromacil[P]	1.3	PBDE-66[PBDE]	3.1
Biphenyl[PAH]	1.3	Carbazole[W]	3.1
Epitestosterone[H]	1.3	Metalaxyl[W]	3.1
Methyl azinphos[P]	1.3	Para-nonylphenol (total) (branched)[W]	3.2
Tebuthiuron[P]	1.3	Cloxacillin[PH]	3.5
Bupropion[PH]	1.3	Flumequine[PH]	3.5
Sulfamethizole[PH]	1.3	OP1EO[W]	3.7
NP1EO[W]	1.5	delta-benzenehexachloride[P]	3.7
Phendimetrazine[PH]	1.6	Endosulfan[P]	3.7
Alachlor[P]	1.7	cis-androsterone[H]	3.9
Chlordene[P]	2.3	Propanil[P]	3.9
Isochlortetracycline [ictc][PH]	2.4	Tefluthrin[P]	3.9
Norgestimate[PH]	2.4	Omeprazole + Esomprazole[PH]	4.7
Oxolinic acid[PH]	2.4	Clinafloxacin[PH]	4.7
Virginiamycin m1[PH]	2.4		

P = Pesticide
H = Hormone
W = Wastewater compound
PH = Pharmaceutical
PAH = Polycyclic Aromatic Hydrocarbon
PBDE = Polybrominated Diphenyl Ether

PAHs were among the most frequently detected compounds (fluoranthene, chrysene, benzo(b&j)fluoranthenes, and pyrene), with several detected in more than 97% of the samples in which they were analyzed. Carbamazepine was the most detected pharmaceutical, detected in 156 out of 160 samples in which it was analyzed. Estrone

was the most common hormone (156 detections out of 161 samples). Atrazine was the most common pesticide (141 detections out of 148 samples) followed by metolachlor (89 detections out of 94 samples). The PBDE with the highest number of detections was PBDE-47, with 143 detections out of 160 samples. PCBs as a whole, which were considered as their own CEC category, only had 16 detections out of 603 total analyses, all of which were very close to non-detection levels. Out of seven PCBs tested for, only Arochlor-1254 and Arochlor-1248 were detected (5 and 11 times, respectively).

Sites with the highest percent of CEC detections included: Quittapahilla Creek in Lebanon County (50.2%); Mahoning River in Lawrence County (47.3%); Chester Creek in Chester County, known locally as Goose Creek (47.2%); and Conestoga River downstream of Lancaster Sewage Treatment Plant (STP) (45.4%). Sites with the lowest percent of CEC detections included: Kettle Creek at Cross Fork (7.2%); Spruce Creek (10.9%); and Susquehanna River middle channel at Rockville (12.0%). A full list of percent CEC detections by sampling event (site and season/year sampled) is available in Appendix K–Pct Per Sample.

4.1.3. Notable Concentrations and Sites

As previously noted, TWA concentrations can be viewed as average concentrations, although care must be taken not to compare them directly to discrete water samples. Regardless, TWA concentrations can be analyzed.

The highest total estrogenicity TWA concentration was 2.4 ng/L EEQ in Conodoguinet Creek in Cumberland County (Appendix L-Max). The highest hormone concentration was cholesterol at 325 ng/L in the Delaware River in Bucks County. Fluoranthene had the highest concentration of any PAH, which was 37 ng/L in Chester Creek in Chester County. Although not a commonly detected PBDE, PBDE-183 had the highest concentration at 1.4 ng/L in Quittapahilla Creek in Lebanon County. Atrazine, the most commonly detected pesticide, also had the highest pesticide concentration at 863 ng/L (0.863 µg/L) in the Mahoning River in Lawrence County, which is below the USEPA fish chronic aquatic life use benchmark of 5 µg/L (USEPA 2019). Carbamazepine, one of the most commonly detected pharmaceuticals, also had the highest pharmaceutical concentration at 1044 ng/L in Chester Creek. The highest wastewater compound concentration was diethyl phthalate at 3088 ng/L in Little Beaver Creek in Lancaster County; while this TWA concentration should not be directly compared to discrete water sample criteria, it is worth noting that this concentration is lower than the aquatic life use criterion in 25 Pa. Code § 93.8c Table 5, which contains water quality criteria for toxic substances. Applicable Pennsylvania numeric aquatic life water quality criteria and recommended USEPA numeric aquatic life criteria continuous concentrations (CCC) and criteria maximum concentrations (CMC) and USEPA recommended aquatic life pesticide benchmarks are listed, when available, in Appendix L-Max. Although not directly comparable to those benchmarks and criteria, the passive water sample TWA concentrations found in this study were mostly well below those benchmarks and criteria. The pesticide fipronil had four occurrences above the USEPA

macroinvertebrate chronic benchmark of 11 ng/L and the pesticide metabolite p,p'-DDD occurred above the Pennsylvania aquatic life CCC of 1 ng/L one time.

Chester Creek in Chester County, Quittapahilla Creek in Lebanon County, and Conestoga River in Lancaster County downstream of Lancaster STP had the largest number of highest concentrations found of individual compounds, with 52, 36, and 29 individual compounds found at their highest concentrations at these three sites, respectively.

4.1.4. Compound Occurrence Overviews by Category

In the following subsections, each category of CECs is analyzed individually. These larger categories of pharmaceuticals, pesticides, and wastewater compounds/PBDEs were further broken down into smaller groups. The percentages displayed below are in Appendix J-Compounds and Appendix M-Chem Analyses.

4.1.4.1. Pharmaceuticals

Pharmaceutical compounds were first broken into major categories (Figure 2). Anticonvulsant drugs were detected most frequently at 95.1% followed by anesthetics (93.8%) and drug precursor compounds (90.6%).

Major groups of common pharmaceutical compounds were then analyzed further. Many types of antibiotics and related pharmaceutical compounds were detected across sites (Figure 3). Antibiotic prevalence in surface water is a growing concern due to antibiotic resistance (Baquero et al. 2008). In the class of antibiotics and related pharmaceutical compounds, erythromycin-H_2O, a breakdown product of the antibiotic erythromycin, was the most commonly detected compound at 91.8%, followed by the antifungal compound fluconazole (90.6%), and the antibiotic compound trimethoprim (85.0%).

Antidepressants and antianxiety drugs were also frequently detected (Figure 4). The antidepressant venlafaxine (brand name Effexor) was detected at 94.7%, followed by the antidepressant desvenlafaxine (93.8%), and the antianxiety drug meprobamate (89.1%). Meprobamate is now rarely prescribed (National Center for Biotechnology Information 2020) but is the most common metabolite of the muscle relaxant carisoprodol (Gonzalez et al. 2009), which may explain its prevalence.

Medications used to combat pain were also found frequently (Figure 5). Tramadol was the most common pain reliever, detected at 96.9%, followed by lidocaine (93.8%), and methocarbamol (89.1%).

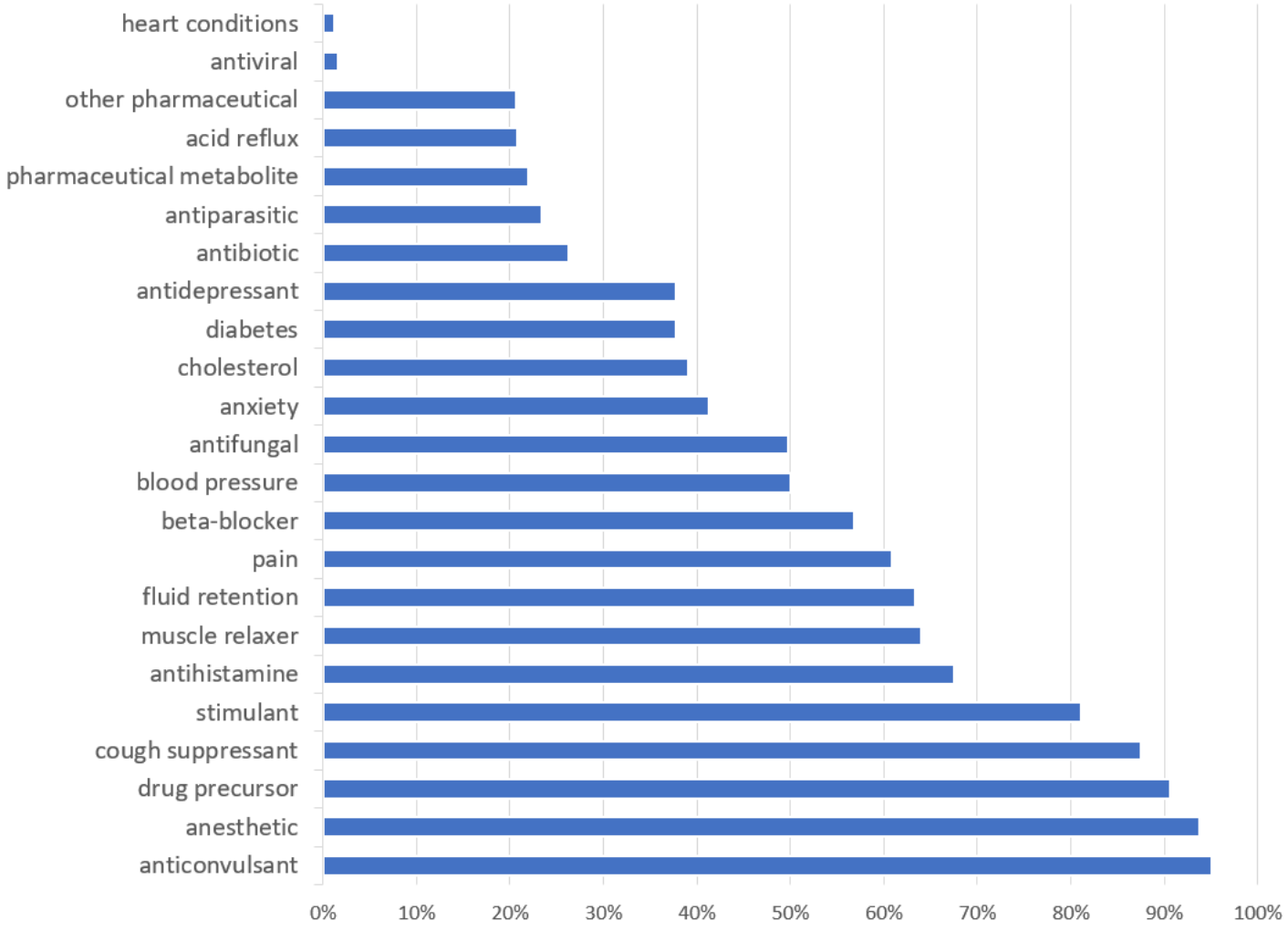


Figure 2. Percent detections of categories of pharmaceutical compounds – 2013 through 2017

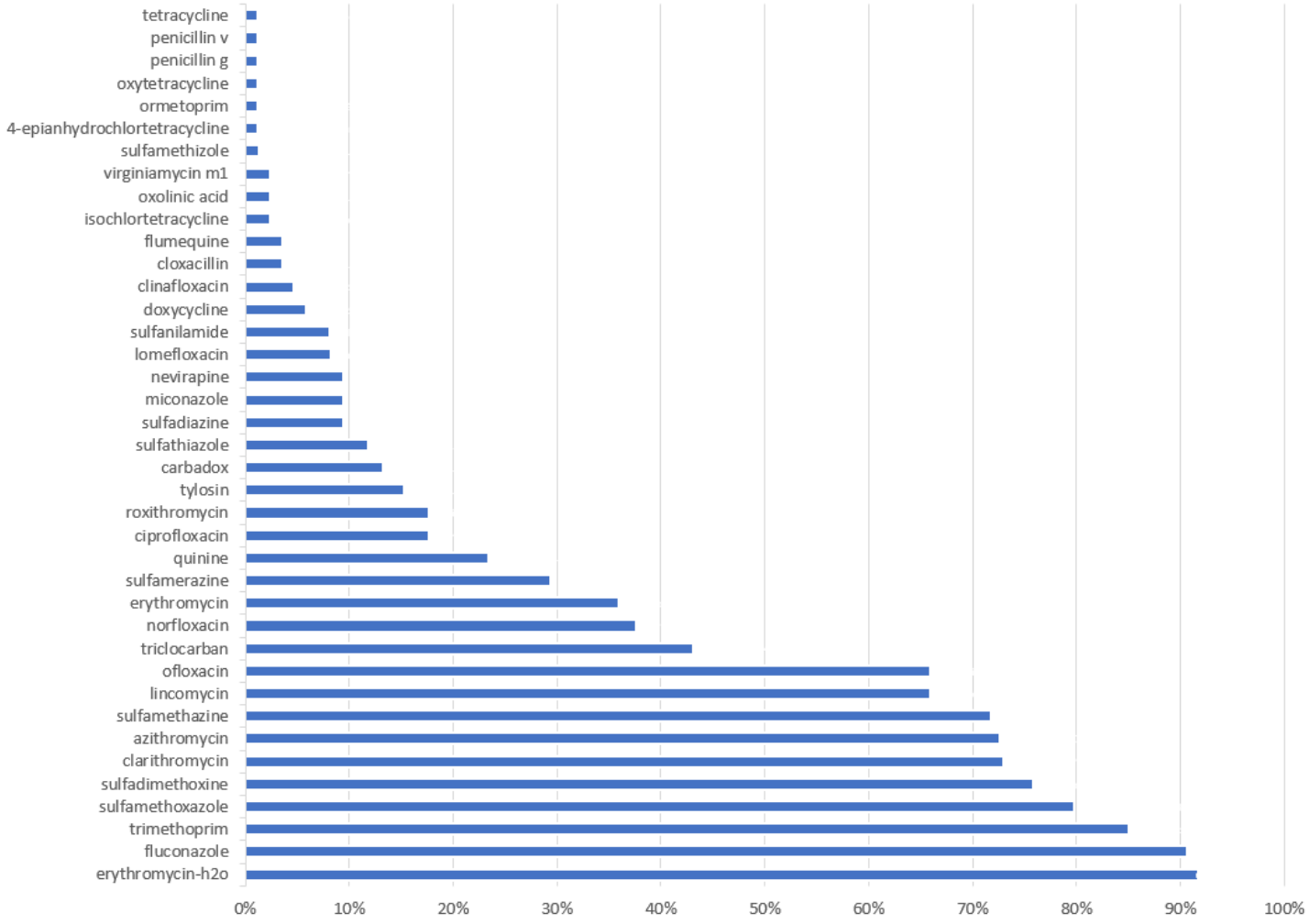


Figure 3. Percent detections of antibiotic, antifungal, antiparasitic, and antiretroviral pharmaceutical compounds – 2013 through 2017

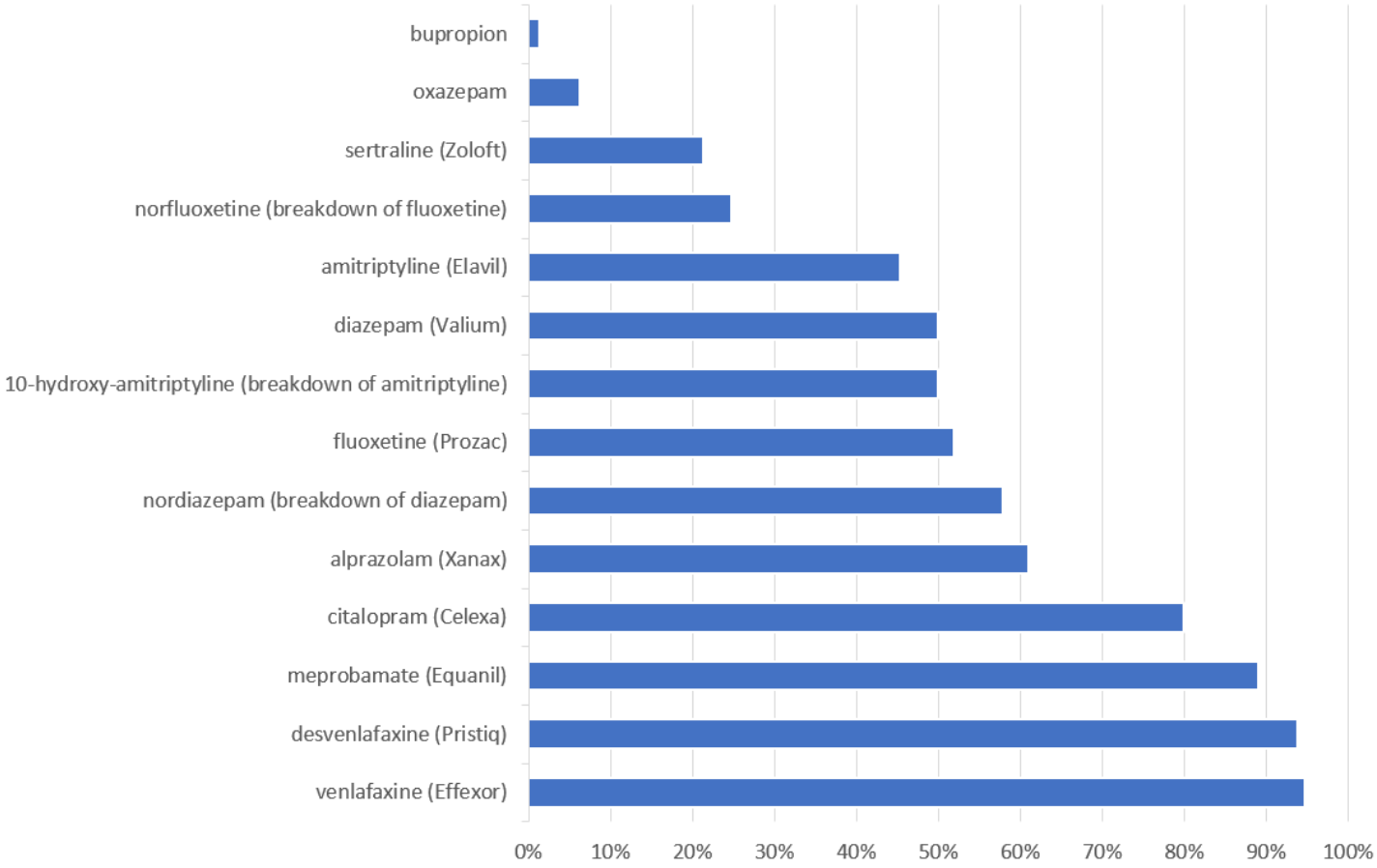


Figure 4. Percent detections of antidepressant and antianxiety pharmaceutical compounds – 2013 through 2017

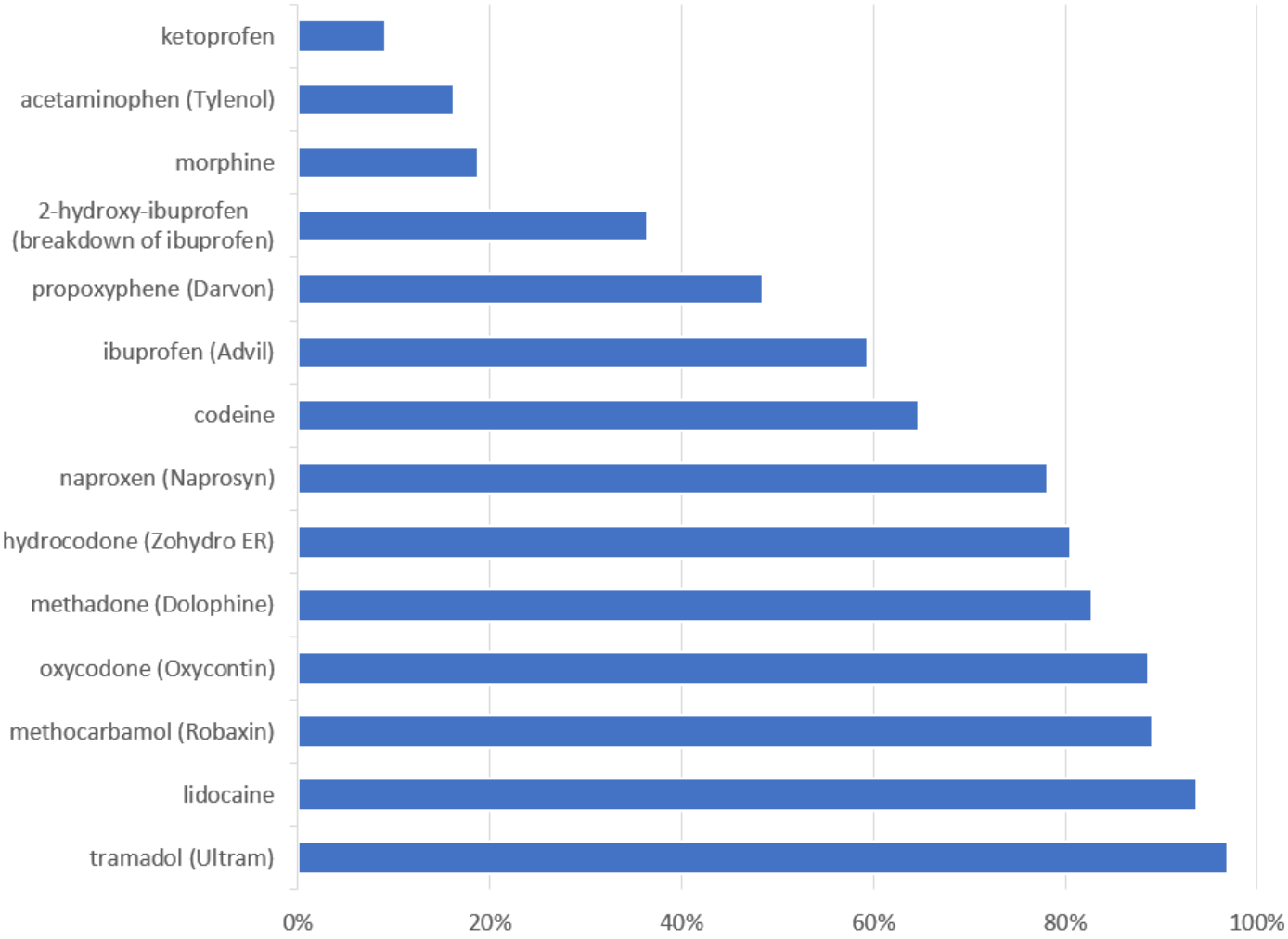


Figure 5. Percent detections of pain medications – 2013 through 2017

4.1.4.2. Pesticides

Most pesticides were not detected as frequently as other groups of compounds (Figure 6). Breakdown products, or metabolites, of pesticides were detected most frequently at 34.6%, followed by general insecticides (28.3%), organochlorine pesticides (18.6%), and herbicides (12.8%). Triazine herbicides, which are a group of commonly used herbicides, were broken down for further analysis (Figure 7). Atrazine was the most detected pesticide at 95.3%.

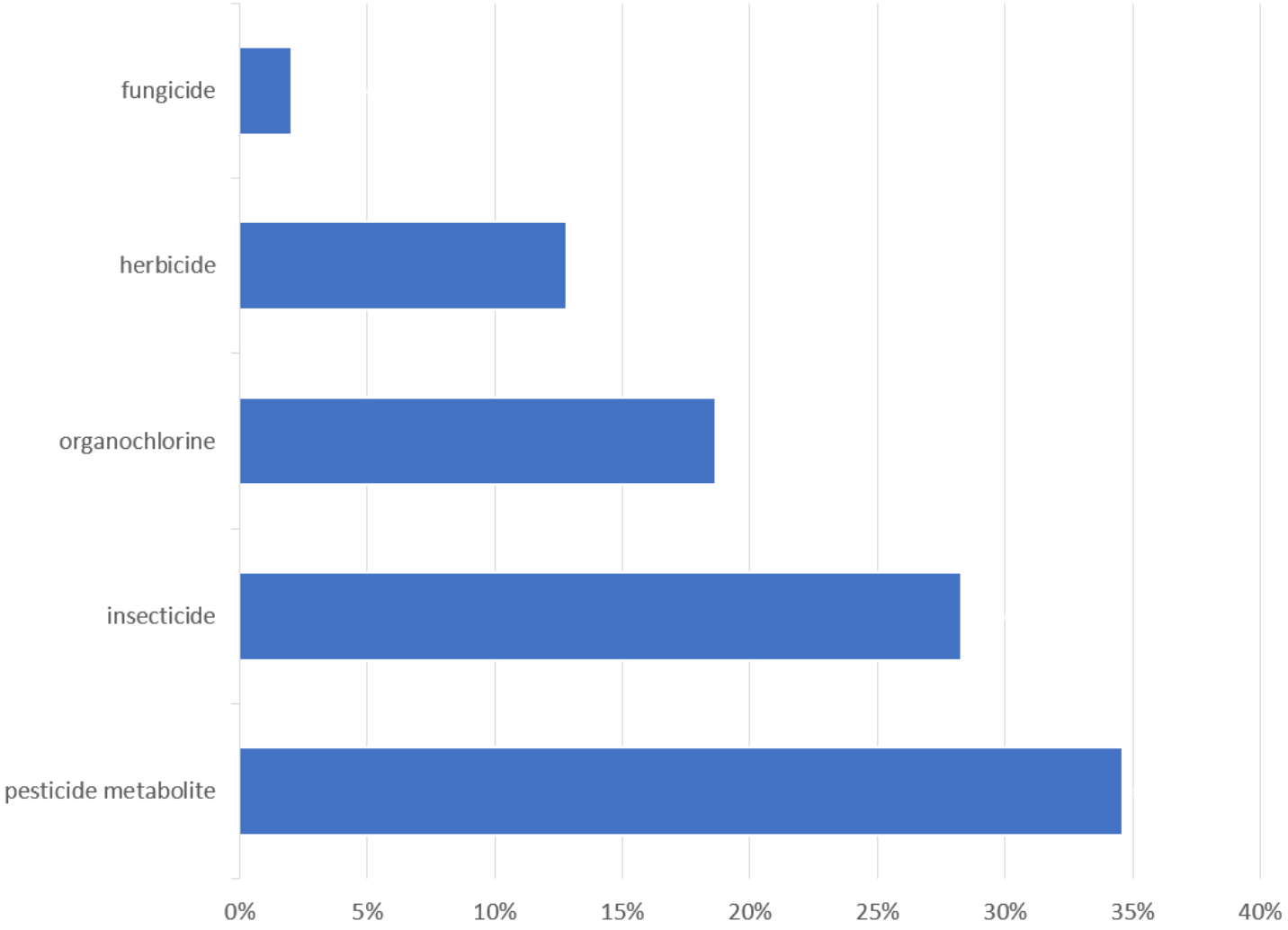


Figure 6. Percent detections of pesticide categories – 2013 through 2017

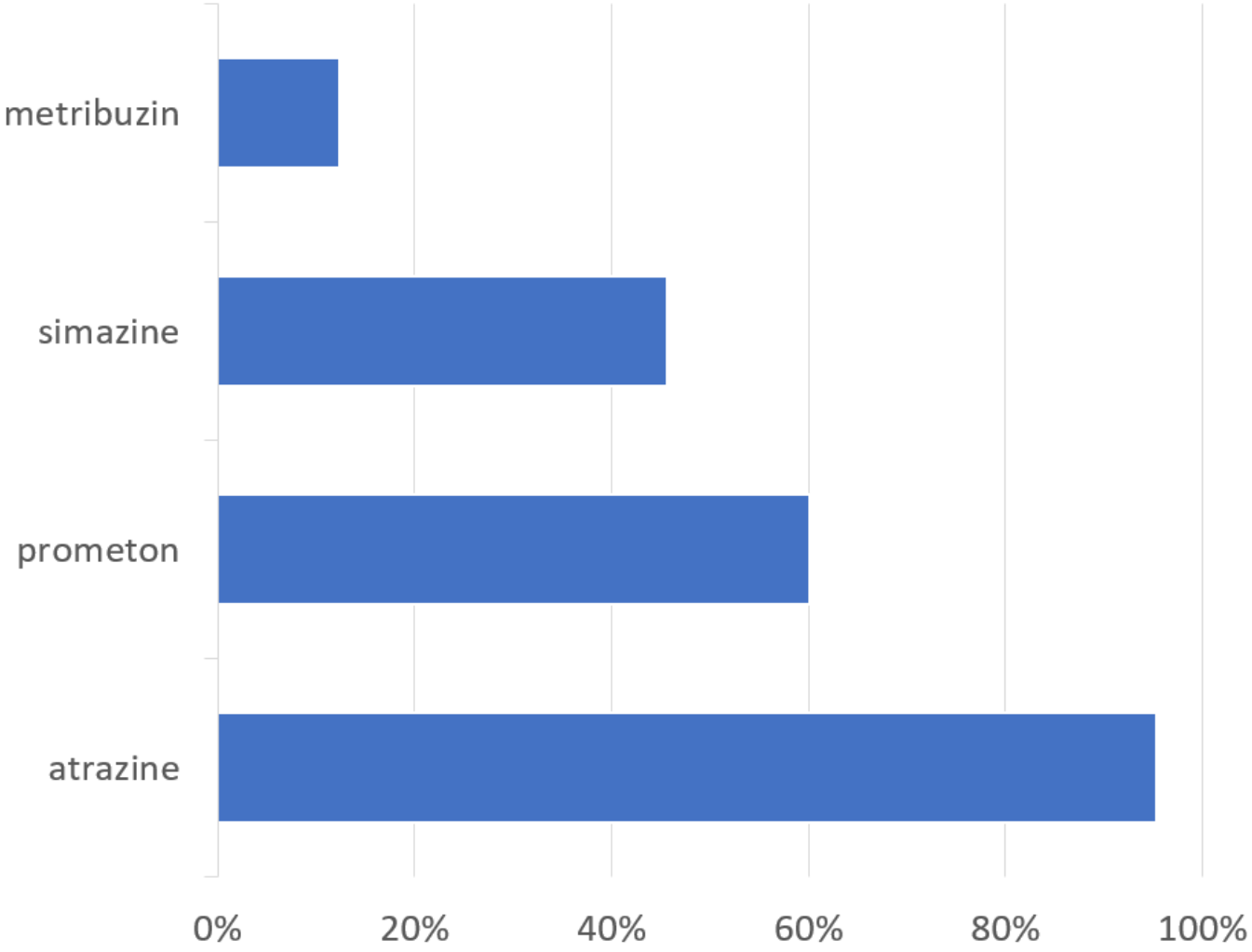


Figure 7. Percent detections of triazine herbicides – 2013 through 2017

4.1.4.3. Hormones

In the hormone category of CECs, natural sterols – 3-beta-coprostanol and cholesterol – were detected the most frequently at 32.0%, followed by natural androgens, such as testosterone (30.2%), and natural estrogens (23.4%) (Figure 8). Analyzed further by individual compound, estrone was the most commonly detected hormone at 96.9% (Figure 9). The next most common hormones were androstenedione at 94.1%, followed by 4-androstene-3,17-dione (82.9%), and cholesterol (60.3%).

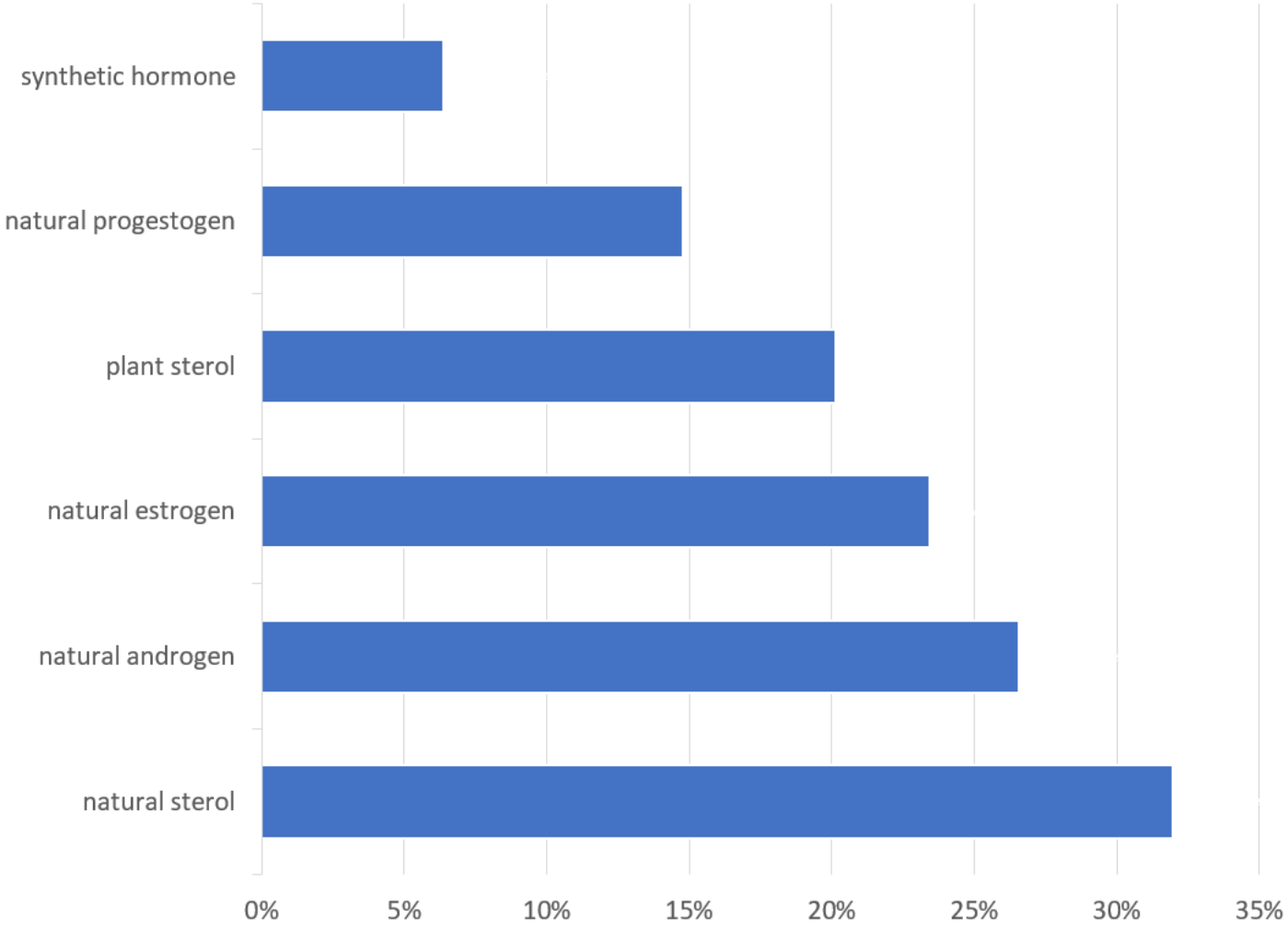


Figure 8. Percent detections of categories of hormones – 2013 through 2017

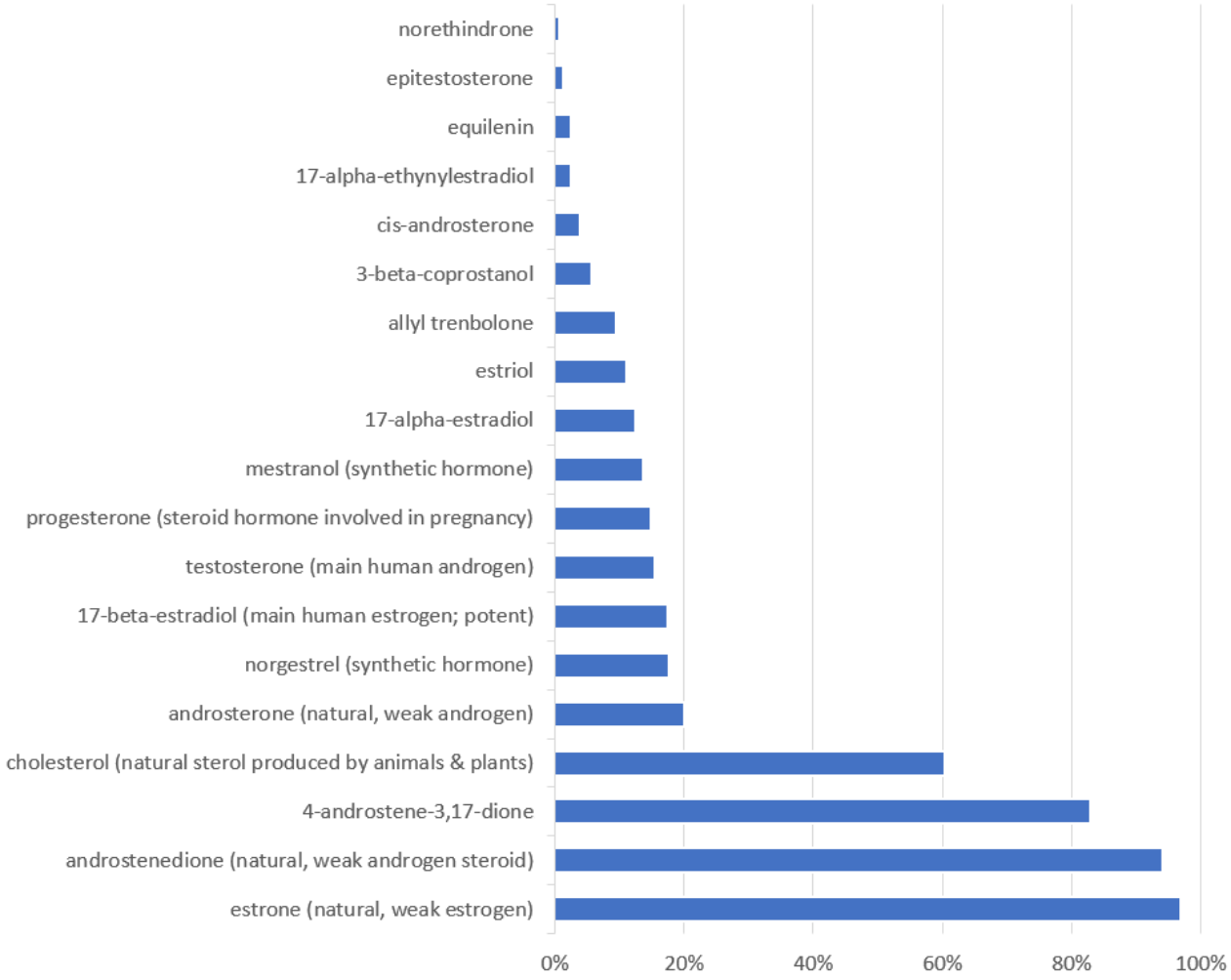


Figure 9. Percent detections of hormones – 2013 through 2017

4.1.4.4. Wastewater, PAHs, and PBDE Compounds

Wood preservatives were the most frequently detected group of wastewater indicator compounds at 70.4%, followed by PBDEs (57.3%), and flame retardants (54.7%) (Figure 10).

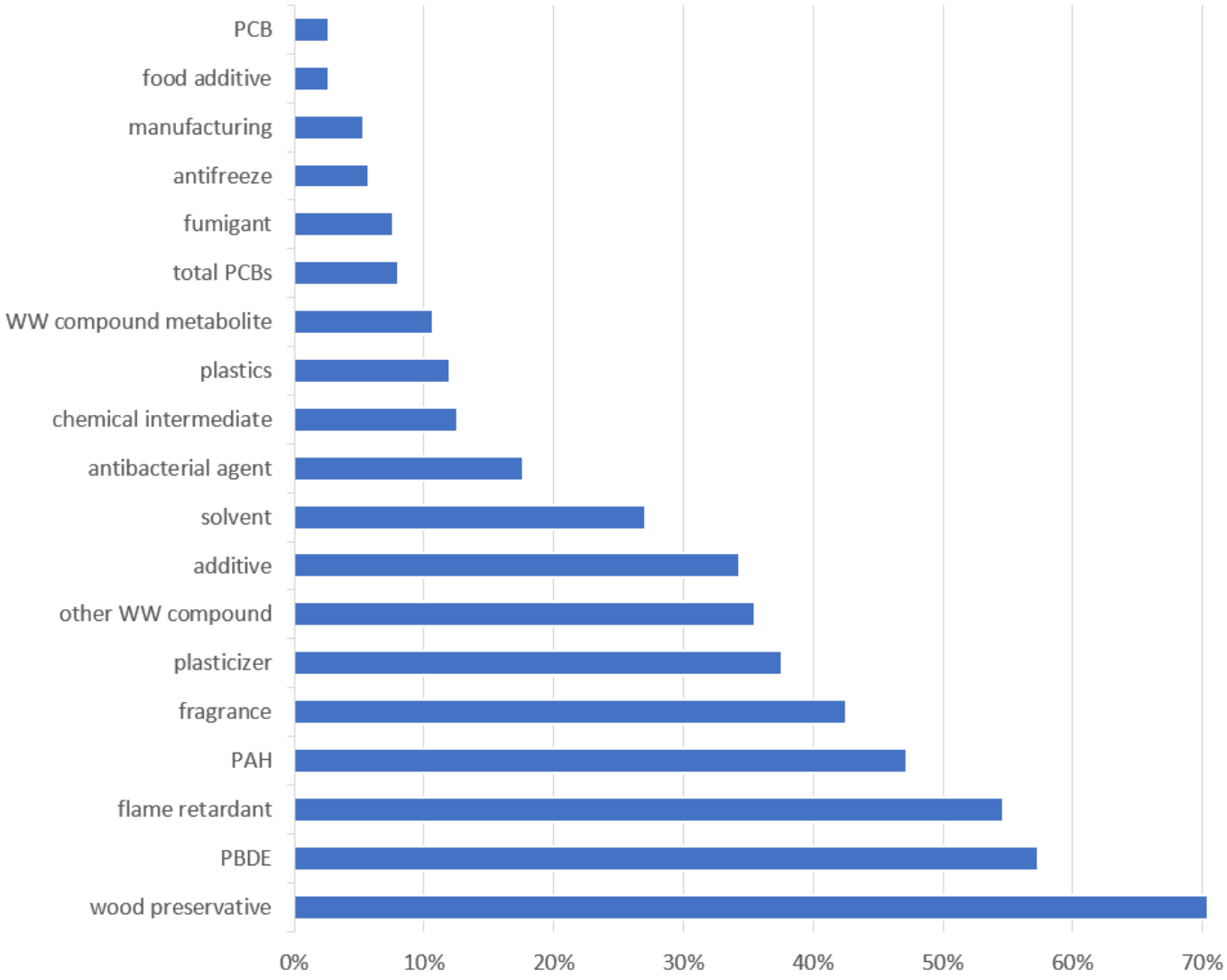


Figure 10. Percent detections of wastewater indicator & PBDE compound groups – 2013 through 2017

4.2. Explanatory Variable Analyses

4.2.1. Tests for Abiotic Parameter Collinearity

Multicollinearity tests showed significant relationships between explanatory variables. This can be attributed to percent land use variables increasing as others decrease and vice versa. The land use variables percent shrub, percent herbaceous, percent woody wetlands, and percent emergent wetlands individually ranged from 0% to a high of 6.1%, which means they composed very little of the land use in any watershed. Therefore, these variables were removed from correlation analyses. All forested land use categories were summed to obtain a single percent forested variable. Likewise, developed land use categories were consolidated by summing open + low development intensity into one low-intensity developed land use variable, and summing medium-intensity and high-intensity developed land use into a single medium/high-intensity land use variable (Table 5). VIF values were frequently >10 for the land use variables, but they were deemed too crucial to remove and collinearity issues will be demonstrated in the correlation analyses. Correlation was then tested between variables and percent detected compounds for both large and small drainage areas.

Table 5. Explanatory variables included in final data analyses

Category	Parameter	Details
Land Use	% LowDev	% Developed - Open + % Developed - Low Intensity
	% MedHighDev	% Developed - Medium Intensity + % Developed - High Intensity
	% Hay	% Hay/Pasture
	% Crops	% Cultivated Crops
	% Forested	% Evergreen Forest + % Mixed Forest + % Deciduous Forest
Other	Drainage Area	Area drained to sample site (square miles), large (>1000 mi^2) or small (<1000 mi^2)
	Flow	Calculated as percent of average flow from last 30 days to long-term monthly median flow

4.2.2. Correlation Analyses

Normality testing showed that most variables were not normally distributed, so non-parametric Spearman correlation analyses were performed. For large drainage areas, there were generally low correlations between percent detected compounds and the abiotic explanatory variables in Table 5; stronger correlations were found in smaller drainage areas (<1000 mi^2).

For smaller drainage areas, the percent of all compounds detected in all categories were first analyzed against the explanatory land use and flow variables (Figure 11). The Spearman rho correlation coefficient can range between -1 and 1, with -1 indicating a strong negative correlation, 0 indicating no association between the variables, and 1 indicating a strong positive correlation. In smaller drainage areas, percent detected

compounds increased as percent low-intensity development increased (rho = 0.75) and percent medium/high-intensity development increased (rho = 0.78). Percent compounds detected showed a slight negative correlation with percent forested (rho = -0.31), indicating that percent compounds detected decreased with increased percent forest.

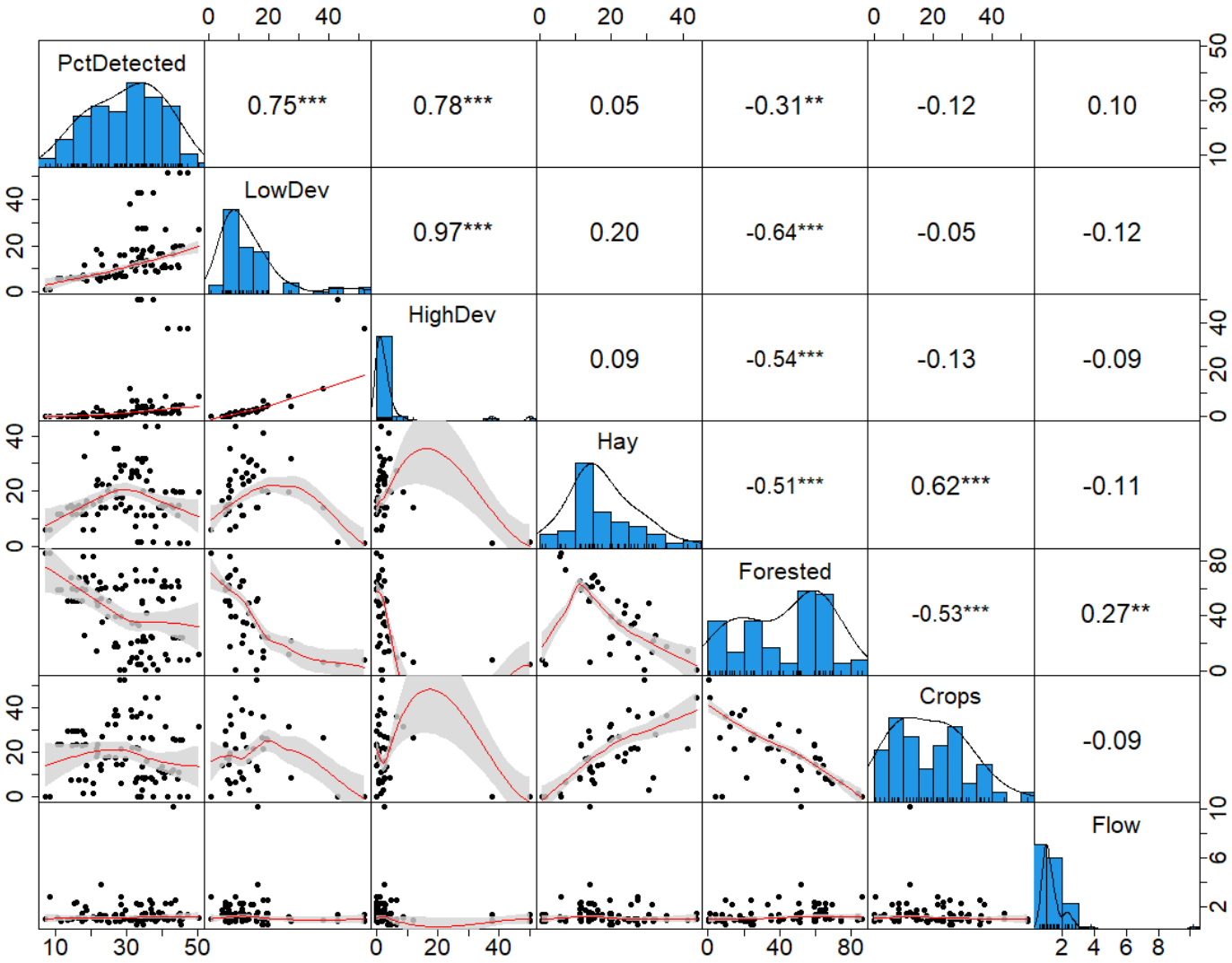


Figure 11. Spearman correlation coefficients, scatterplots, and histograms of percent detected compounds in samples from sites with smaller drainage areas (i.e., < 1000 mi^2) and abiotic explanatory variables per sample. * indicates significance at $p \leq 0.05$, ** indicates significance at $p \leq 0.01$, and *** indicates significance at $p \leq 0.001$. Red lines in scatterplot indicate loess model fit.

Percent detections were then broken down into compound categories. Categories examined were pharmaceuticals, pesticides, hormones, PAHs, PBDEs, and wastewater compounds. There were very few detections in the semi-volatile and PCB categories, so these were not analyzed separately. In addition, total estrogenicity (EEQ) was

categorized independently but was not analyzed here because it was considered the only compound in the category.

In small drainage areas, percent pharmaceutical detections were most significantly correlated with development categories (percent low-intensity developed land use r = 0.63 and percent medium/high-intensity developed land use r = 0.67). Pesticide detections were most significantly correlated with percent low-intensity developed land use (r = 0.65), percent high development (r = 0.64), and percent forested (r = -0.49), but not as strongly with percent hay/pasture (r = 0.29) or percent crops (r = 0.12). Percent hormone detections were not highly correlated with any explanatory variable; the highest correlation was with percent hay/pasture land use (r = 0.33). Percent PAH detections were most positively correlated with percent low-intensity developed land use (r = 0.58) and percent medium/high-intensity developed land use (r = 0.57) and were negatively correlated with percent forested land use (r = -0.39). PBDEs were most strongly correlated with percent forested land use (r = -0.34), then percent low-intensity developed land use (r = 0.33), and then percent medium/high-intensity developed land use (r = 0.28). Wastewater compounds were most strongly correlated with percent medium/high intensity developed land (r = 0.52), then percent low-intensity developed land (r = 0.50).

4.2.3. Total Estrogenicity Concentrations

Total estrogenicity, quantified as the estradiol equivalent factor (EEQ), was not strongly correlated with any land use parameter or flow in small drainage areas (Figure 12, Iwanowicz et al. 2021). A non-parametric Kruskal-Wallis test was conducted on EEQ concentration versus season sampled (winter, spring, or fall), and there was a significant difference among seasons (p = 0.021). Pairwise comparisons using the Wilcoxon rank sum test were conducted to determine which groups were significantly different; only fall and spring were significantly different from one another (p = 0.024) (Figure 13). There was only a small number of winter samples because winter samples were only collected in 2017; this may have contributed to the lack of difference with winter samples.

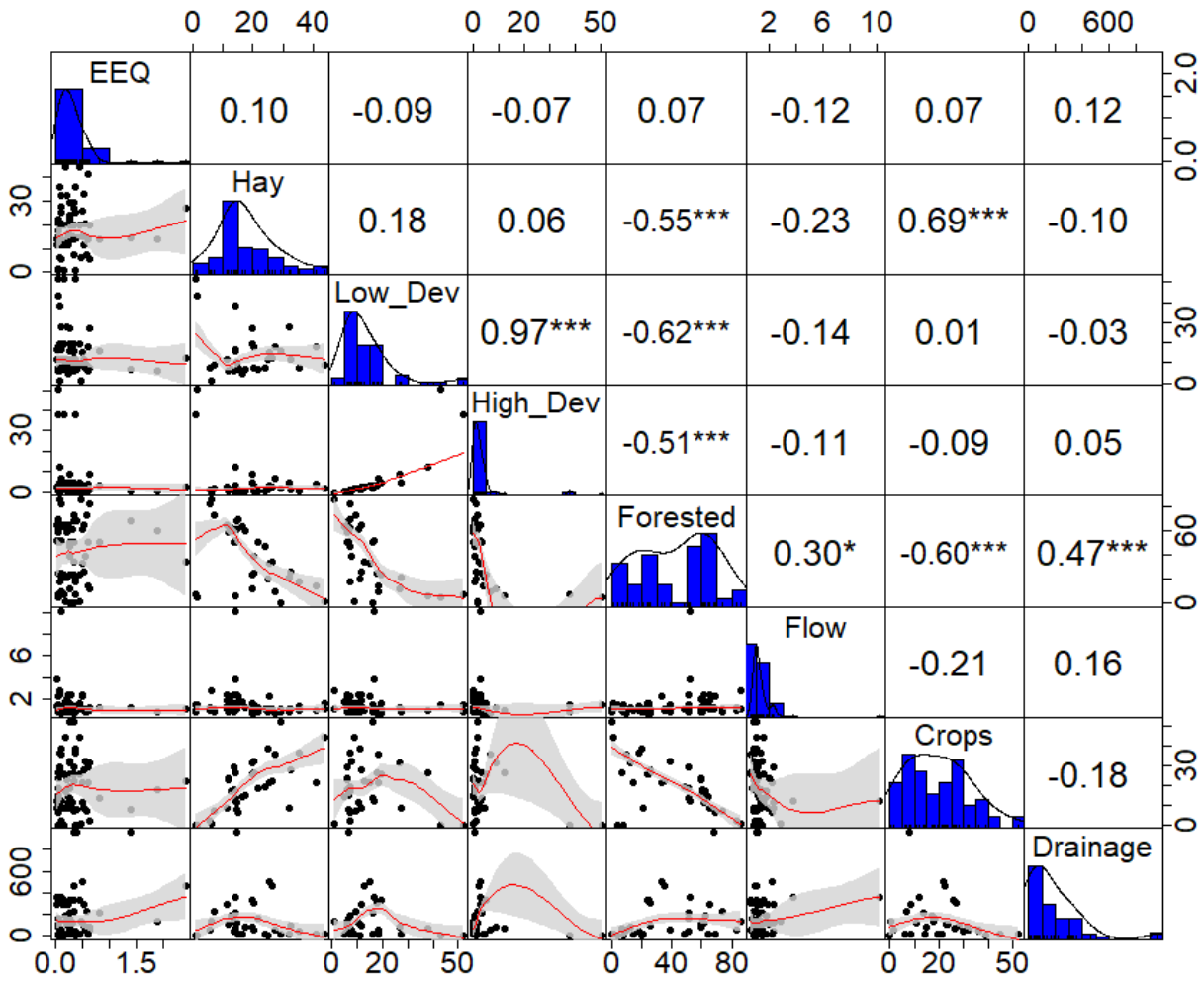


Figure 12. Spearman correlation coefficients, scatterplots, and histograms of total estrogenicity (EEQ) concentration (ng/L) and abiotic explanatory variables per sample from sites with smaller drainage areas (i.e., < 1000 mi^2).
* indicates significance at $p \leq 0.05$, ** indicates significance at $p \leq 0.01$, and *** indicates significance at $p \leq 0.001$. Red lines in scatterplot indicate loess model fit.

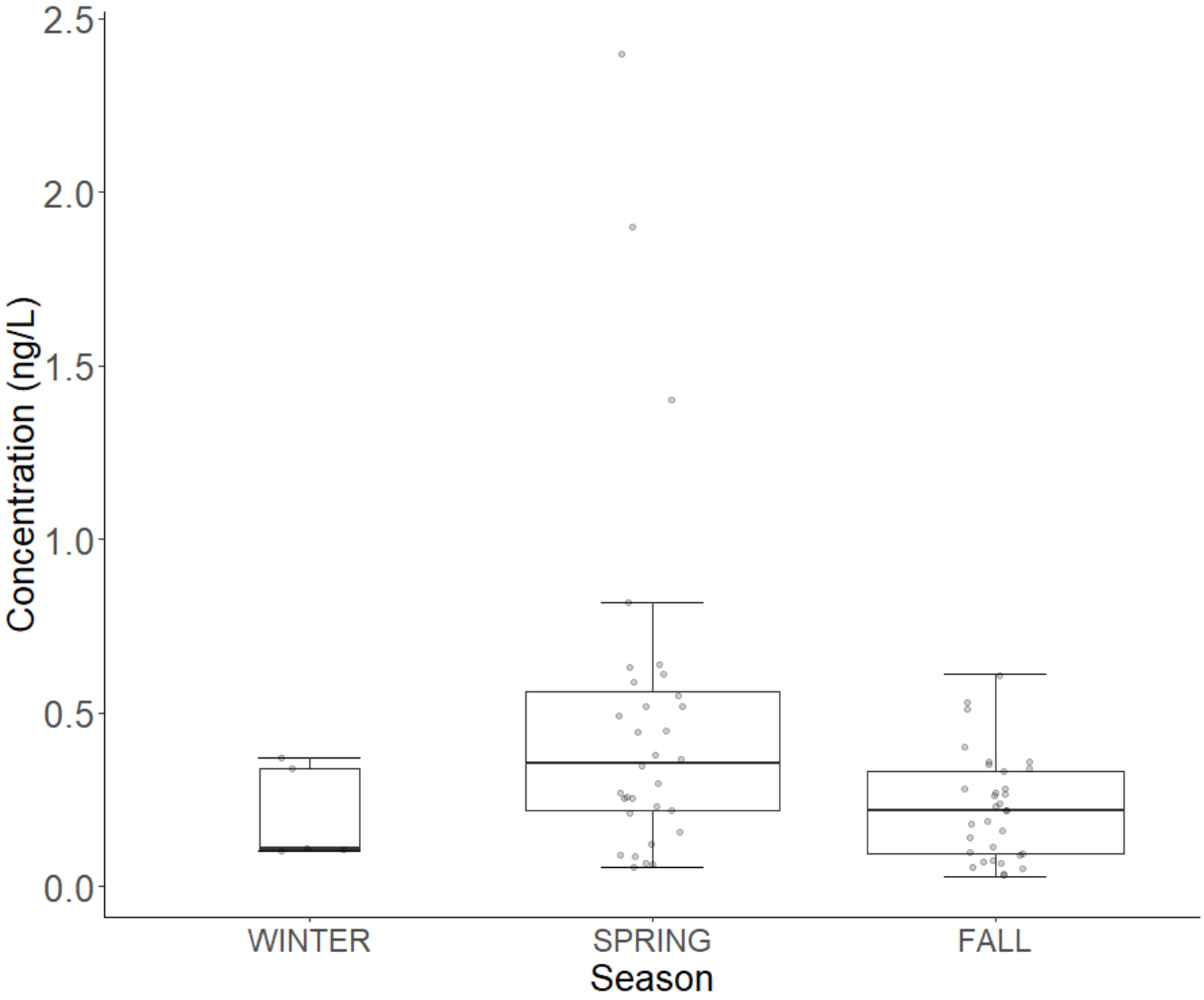


Figure 13. Total estrogenicity concentrations (ng/L) by season sampled. Width of each box is proportional to sample size.

4.3. Local-Scale Pattern Analyses

Smaller subsets of the main dataset were investigated here. The field replicate sites were included in these analyses. For each subset of data, the distribution of percent of all compounds detected are depicted in a boxplot showing each local-scale factor (e.g., upstream versus downstream of an STP), followed by a similar boxplot showing any category of compounds (i.e., pharmaceuticals, hormones, wastewater compounds, pesticides, PBDEs, PAHs, semi-volatile organic compounds, or PCBs) for which there was a statistically significant difference associated with the local-scale factor.

4.3.1. Upstream versus Downstream of Sewage Treatment Plants (STPs)

The effect of point-source STP discharges on the percent of CEC compounds detected was investigated by comparing sample results from sites upstream and downstream of STPs. Samples were collected upstream and downstream of STPs at two sites: Conestoga River at Lancaster Sewage Treatment Plant; and Frankstown Branch Juniata River at Hollidaysburg Borough Sewage Authority. Conestoga data did not appear normally distributed and did have all paired observations, so a Wilcoxon rank sum test was used on the upstream and downstream samples. At a significance level of 0.05, the two groups were not significantly different ($p = 0.1333$; Figure 14a). Normality testing of the Franksdown Branch data was conducted, and the data appeared normally distributed. At a significance level of 0.05, a paired t-test of the Frankstown Branch samples showed the upstream and downstream samples were not significantly different ($p = 0.06172$), although they were close to being significantly different (Figure 14b). Downstream sites tended to have higher percentages of compounds detected than the upstream sites.

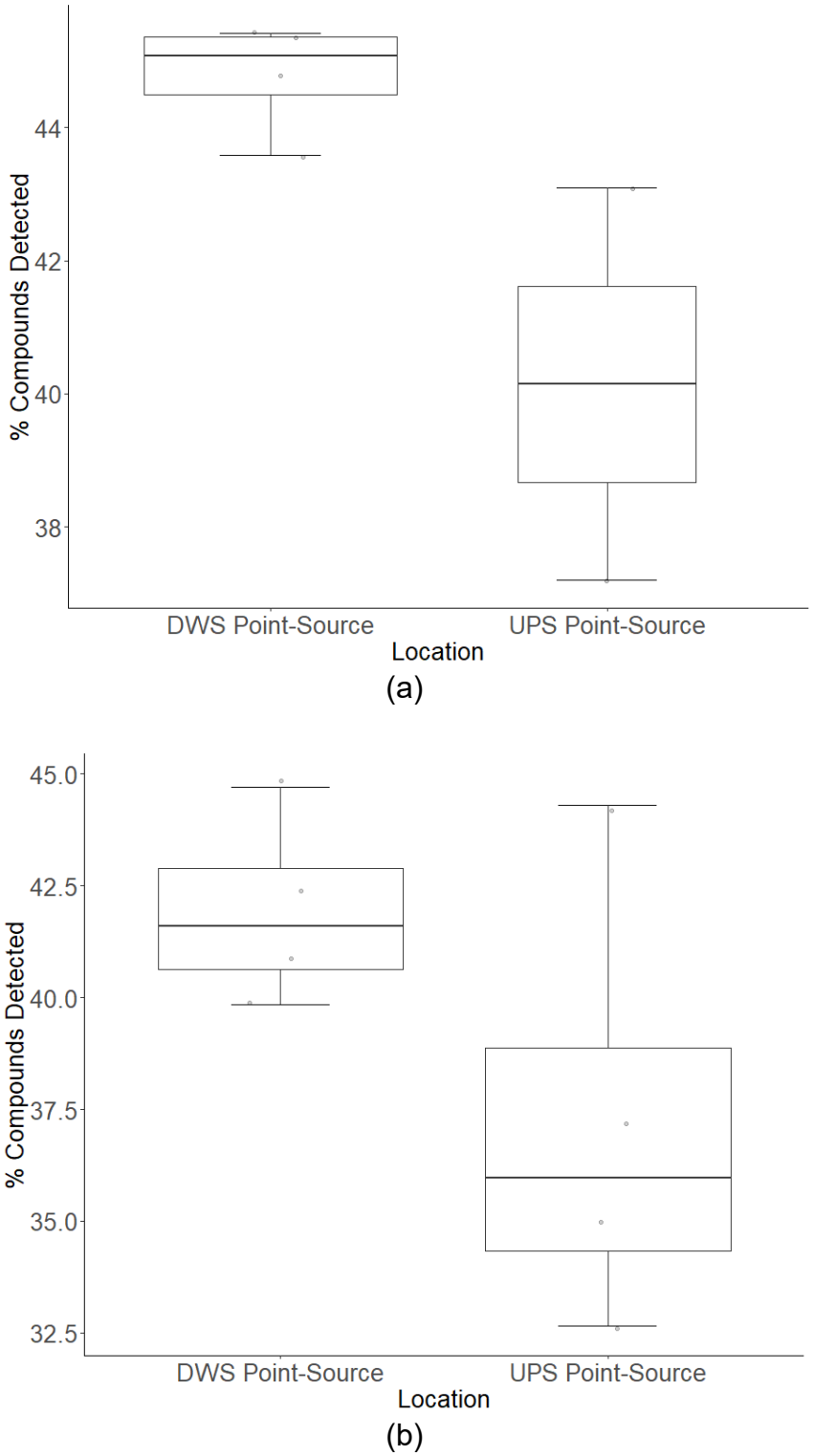
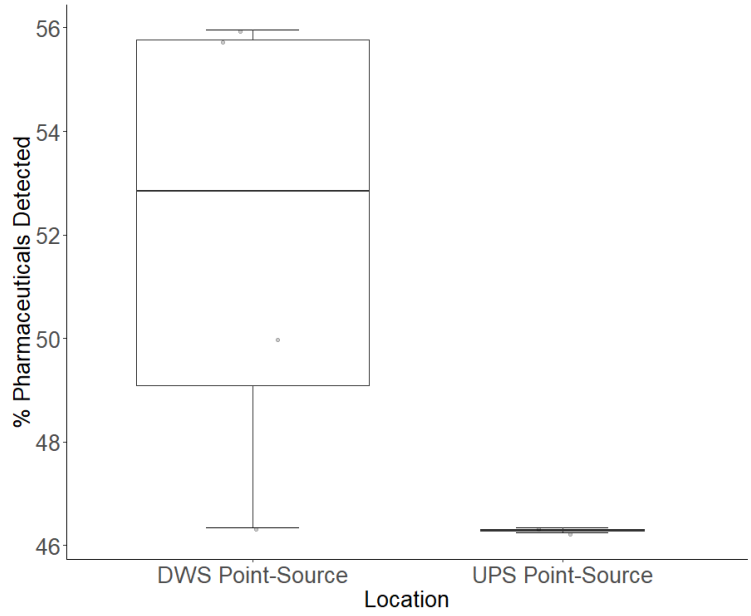
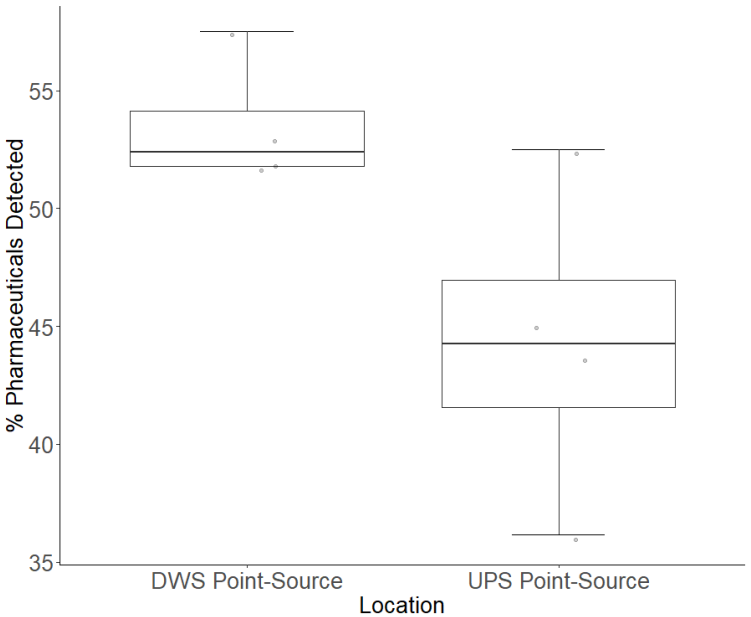


Figure 14. Percent compounds detected upstream (UPS) versus downstream (DWS) of STP discharges: (a) Conestoga River at Lancaster Sewage Treatment Plant and (b) Frankstown Branch Juniata River at Hollidaysburg Borough Sewage Authority. Width of each box is proportional to sample size.

Investigating by compound category showed that there was a significant difference, at a significance level of 0.05, between percent compounds detected for pharmaceuticals upstream and downstream of STPs surveyed (paired samples t-test, p = 0.005) (Figures 15a & 15b) with higher percentages of pharmaceutical compounds detected downstream versus upstream.



(a)



(b)

Figure 15. Percent pharmaceutical compounds detected upstream (UPS) versus downstream (DWS) of STP discharges: (a) Conestoga River at Lancaster Sewage Treatment Plant and (b) Frankstown Branch Juniata River at Hollidaysburg Borough Sewage Authority. Width of each box is proportional to sample size.

4.3.2. Main River Channels versus Near-Shore Locations

Differences between main river channel sites versus near-shore sites were also investigated. Normality testing of data was conducted, and data appeared normally distributed, so an independent samples t-test was performed. At a significance level of 0.05, the two groups were significantly different (p = 0.021). Near-shore sites tended to have higher numbers of compounds detected.

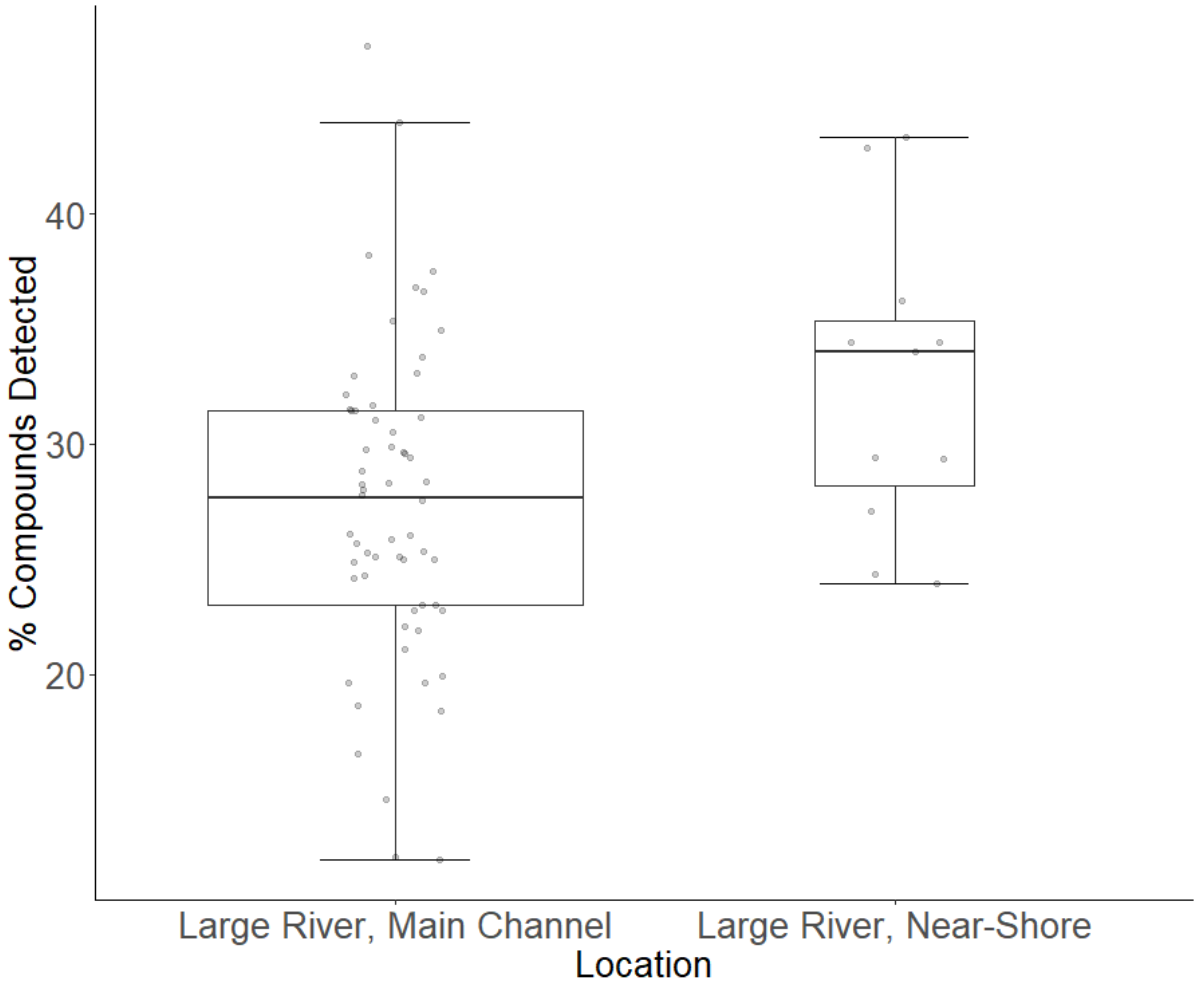


Figure 16. Percent compounds detected in main river channels versus near-shore sites. Width of each box is proportional to sample size.

Investigating by compound group showed that there is a significant difference between percent compounds detected for pesticides (independent samples t-test, p = 0.040) with higher numbers of pesticides detected near-shore versus main channel (Figure 17). There was also a slight significant difference between near-shore and main channel semi-volatile compounds (Wilcoxon rank sum test, p = 0.048).

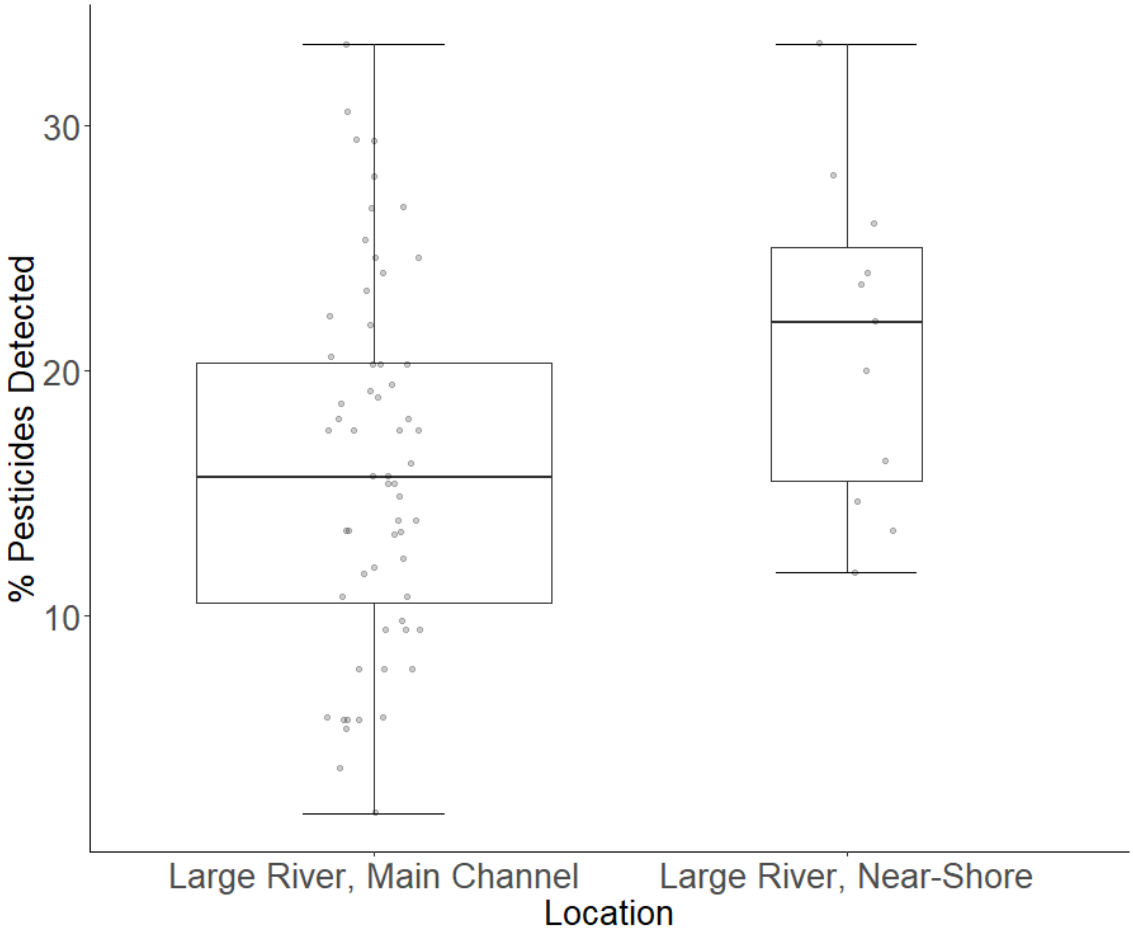


Figure 17. Percent pesticides detected in main river channels versus near-shore sites. Width of each box is proportional to sample size.

4.3.3. Larger Rivers versus Tributaries

Differences between larger river sites versus tributaries for all compounds was investigated (see Appendix A-Site Info). Tributaries were to main rivers as well as smaller tributaries not located directly on major rivers. Data passed normality testing but variances between the two datasets were not homogenous ($p = 0.009$), so a Wilcoxon rank sum test was performed. At a significance level of 0.05, the two groups were not significantly different (Figure 18, $p = 0.308$). These samples did not include the upstream and downstream STP samples so as to not confound the larger river versus tributary comparison. Pesticides were significantly different in larger river versus tributary sites (Figure 19, $p = 0.002$). In addition, PBDEs were also significantly different ($p = 0.013$), as well as wastewater compounds ($p = 0.047$), with tributaries tending to have higher percent detected compounds than larger rivers.

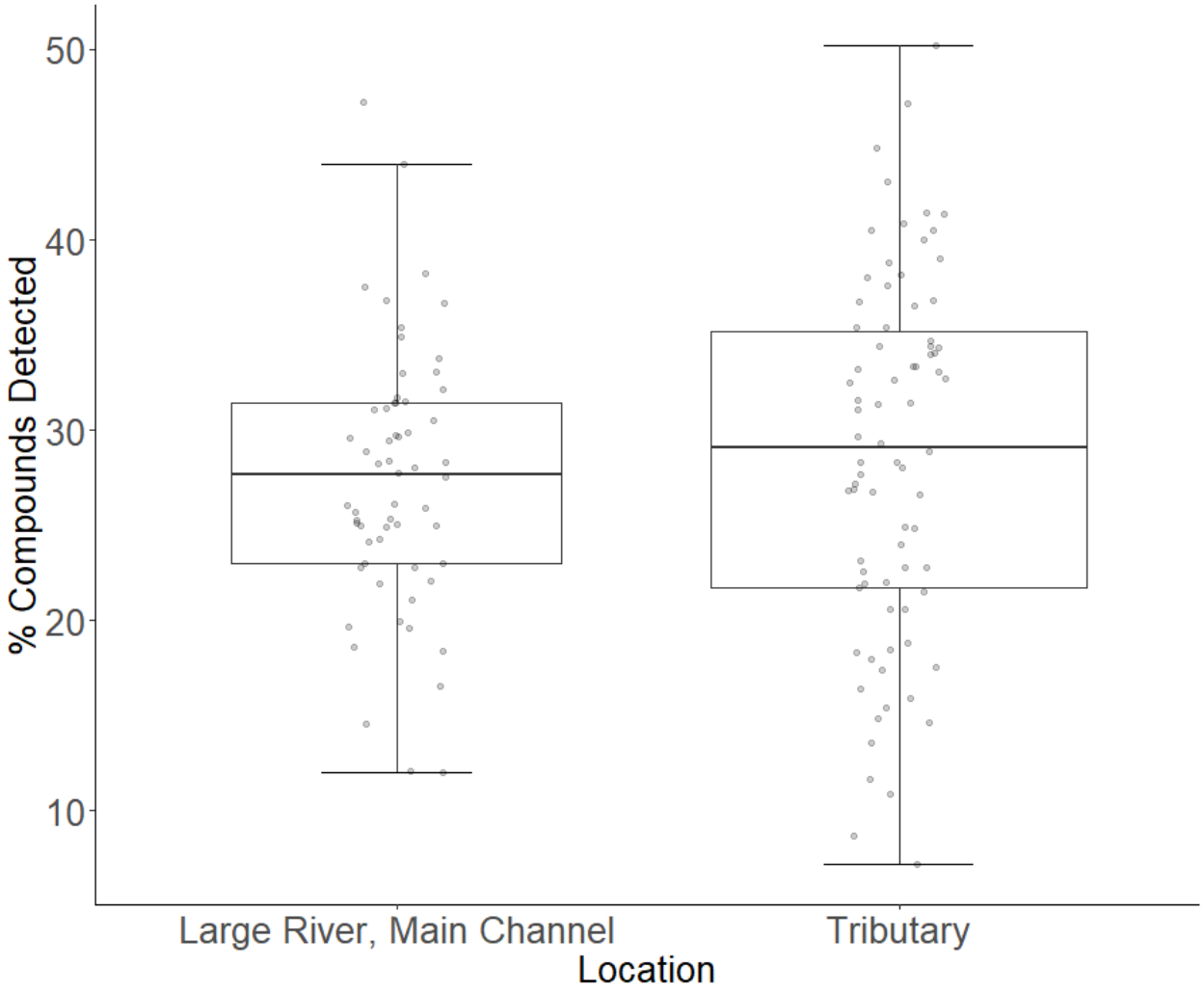


Figure 18. Percent compounds detected in larger rivers versus tributaries. Width of each box is proportional to sample size.

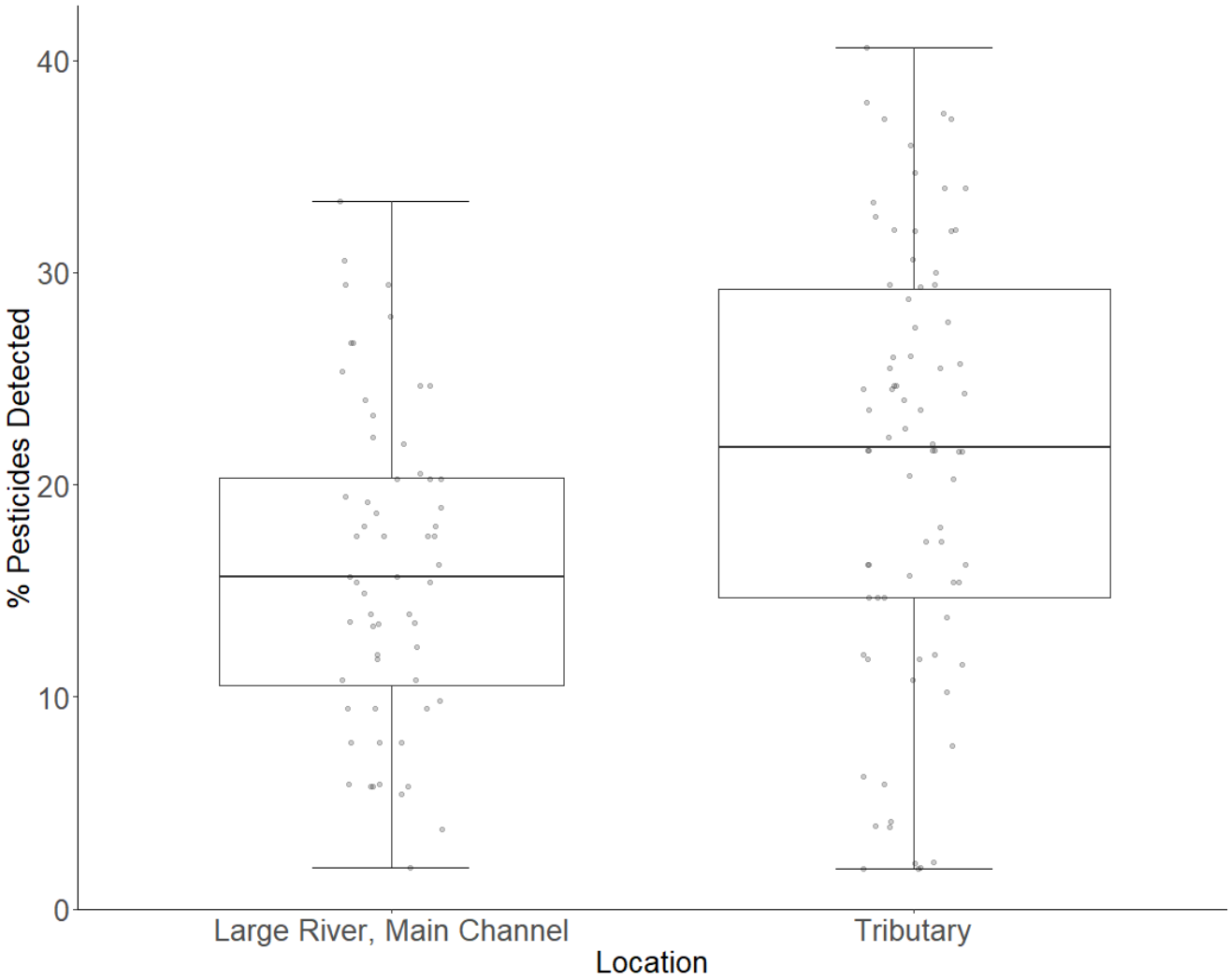


Figure 19. Percent pesticides detected in larger rivers versus tributaries. Width of each box is proportional to sample size.

4.4. Temporal Analyses

Many sites were sampled over multiple years and seasons. At the very least, samples from most sites were collected over two or three seasons in one year. By collecting repeatedly at several “core” sites, patterns over time and seasons can be analyzed.

4.4.1. Season

There was no significant difference observed with percent compounds detected among seasons (ANOVA, p = 0.779) (Figure 20). There was a significant difference between seasons for semi-volatile compounds (Kruskal-Wallis rank sum test, p = 0.000006) with the most, although few, detections occurring in spring; for pesticides (ANOVA, p = 0.023), with spring tending to have more percent detections than winter and fall; and for PAHs (ANOVA, p = 0.0002), with winter tending to have more percent detections than spring and fall.

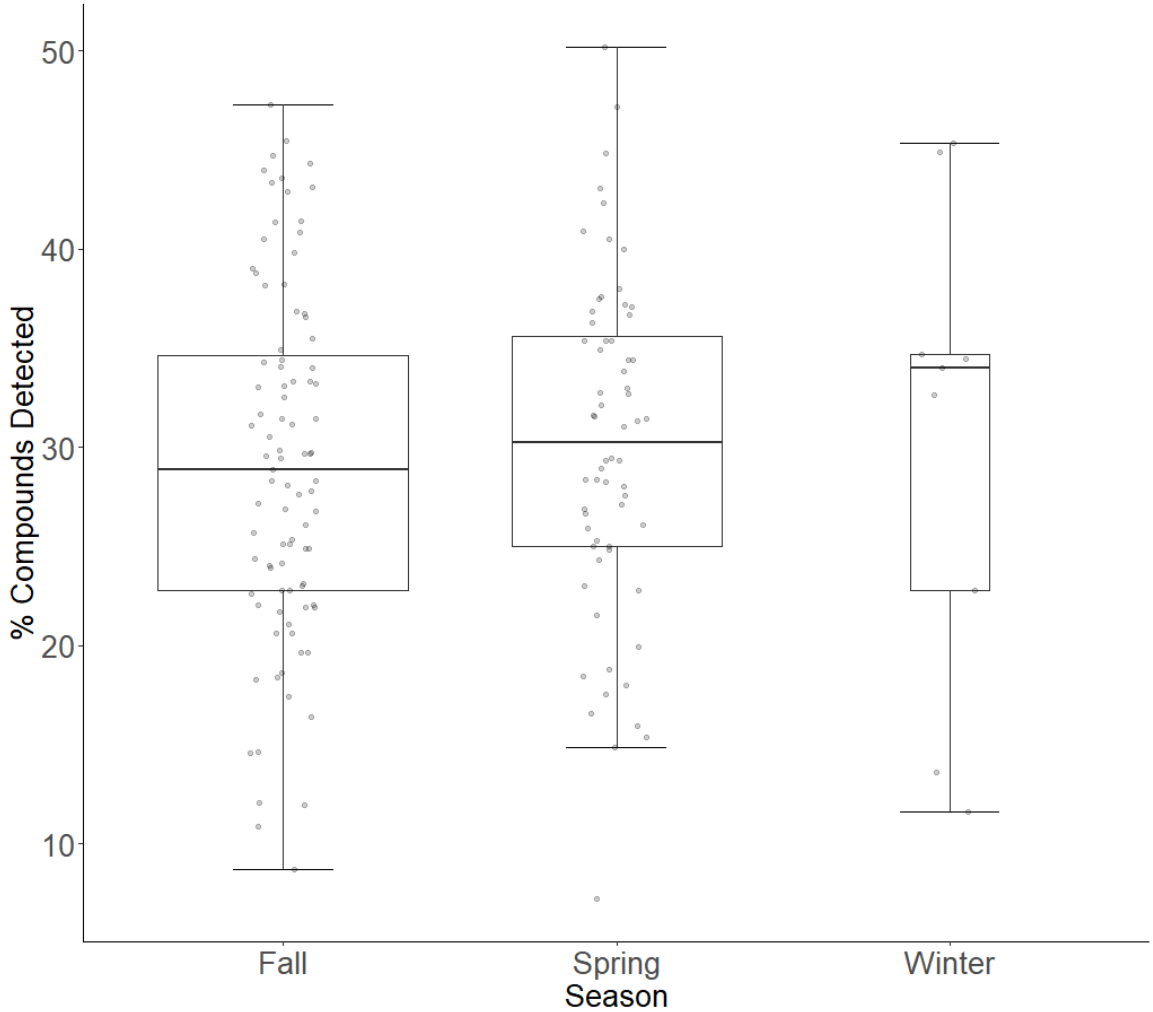


Figure 20. Percent compounds detected by season. Width of each box is proportional to sample size.

4.4.2. Susquehanna River at Rockville

One “core” site was the Susquehanna River at Rockville. Samples were collected from three locations along a transect – west (ROCK2.5), middle (ROCK6.5) and east (ROCK14.5). Samples were collected six times from spring 2015 through fall 2017. DEP has recognized that the Susquehanna River does not exhibit uniform water quality consistently from one bank to the other (Shull & Lookenbill 2017). Upstream tributaries often influence water quality on one bank of the river for many miles downstream. Specifically, the Juniata River enters the Susquehanna River on its western side approximately nine miles upstream of Rockville. Therefore, contaminant concentrations and prevalence could be vastly different from one bank of the river to the other.

While the analysis methods and laboratories for various analyses changed from 2015 to 2017, the wastewater compound analyses used the same method and lab through all years (USGS National Water Quality Laboratory, Lakewood, Colorado); therefore, percent of wastewater compounds detected through time can be compared (Figure 21). The three locations at Rockville did exhibit differences in percent wastewater compounds detected over time; however, there were no pronounced differences in percent wastewater compounds detected among the three locations themselves. The main influence of wastewater compounds detected at the Rockville sites appear to be due to when samples were collected. Spring 2016 noticeably had the lowest percent of wastewater compounds detected, except for ROCK 6.5 (ROCK14.5 was not sampled for wastewater compounds in Spring 2015).

During the 2016 spring sampling period, there was one of the highest average discharge and gage heights during DEP’s passive sampling events at Rockville as documented by the data from USGS Gage #01570500 on the Susquehanna River at Harrisburg (Figure 22, Table 6). Conversely, the Fall 2016 sampling period had the lowest average discharge and gage height of any sampling period at Rockville (Figure 22, Table 6), and the highest percent wastewater compounds detected (Figure 21). These observations suggest an inverse relationship between river flows and percent wastewater compounds detected at Rockville, but this pattern did not hold in other sampling periods. For instance, the highest average discharge and gage height during a sampling period at Rockville was Spring 2017 (Figure 22, Table 6), but the percent wastewater compounds detected in the Spring 2017 sampling period were between those observed in Spring 2016 (another high-flow sampling period) and Fall 2016 (a low-flow sampling period) (Figure 21).

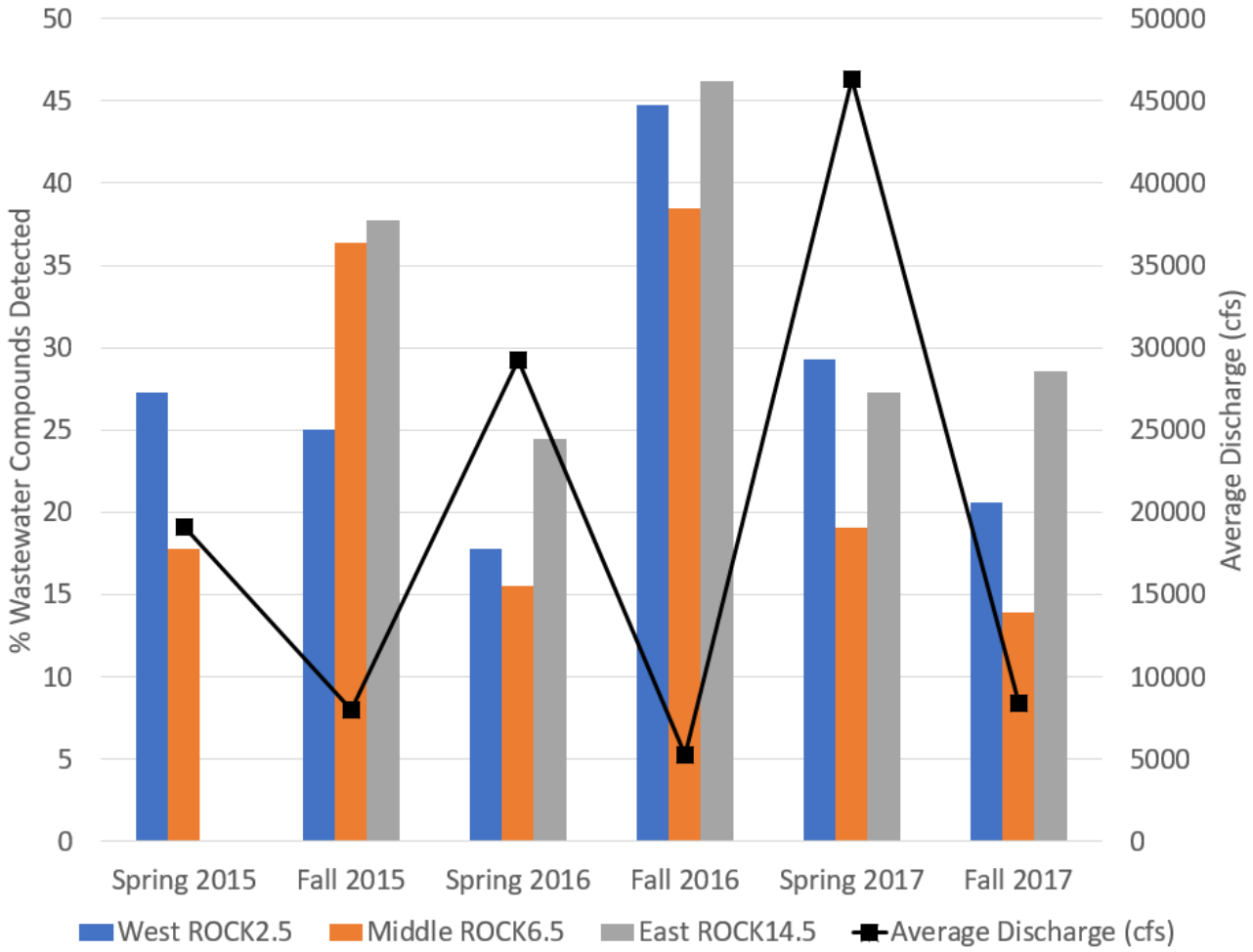


Figure 21. Percent wastewater compounds detected at Susquehanna River at Rockville over three transect locations and six sampling periods.

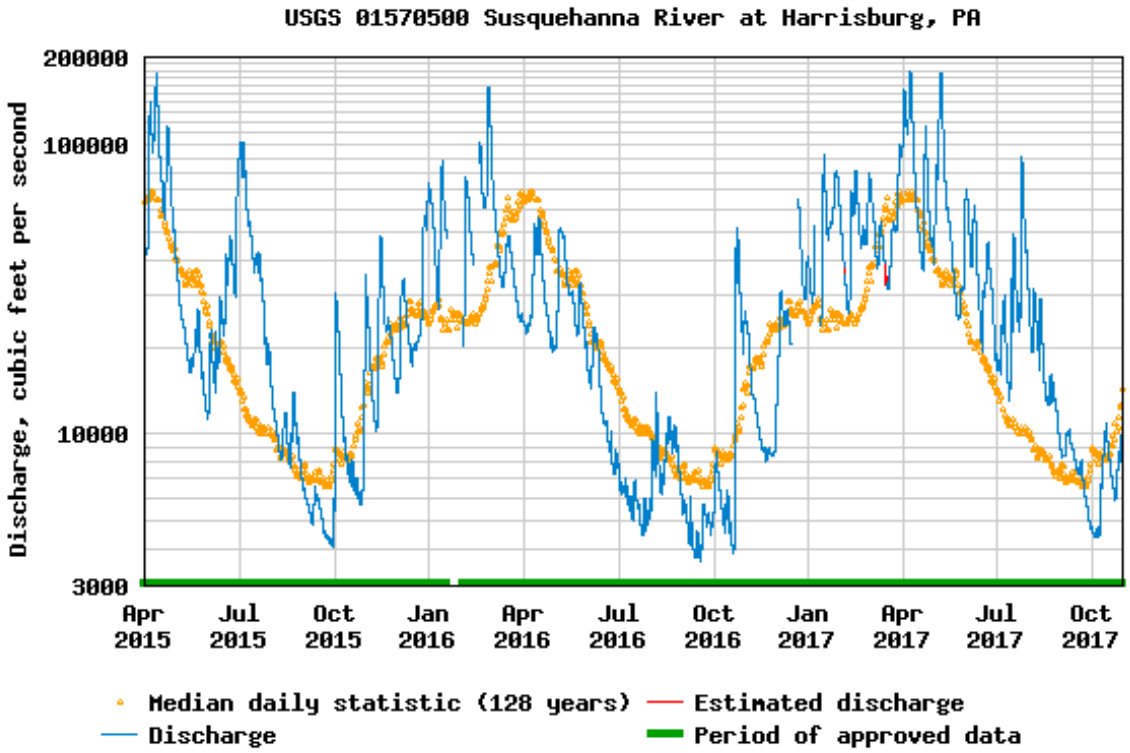


Figure 22. Discharge from April 2015 to October 2017 for Susquehanna River at Harrisburg (USGS Gage 01570500); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

Table 6. Average discharge and gage heights over each sampling time period (Susquehanna River at Harrisburg USGS Gage 01570500).

Sampling Event	Date Range Sampled	Avg. Discharge (cfs)	Avg. Gage Height (ft)
Spring 2015	05/04/2015 - 06/09/2015	19145	4.2
Fall 2015	08/26/2015 - 10/15/2015	8017	3.4
Spring 2016	05/02/2016 - 06/08/2016	29241	4.6
Fall 2016	08/29/2016 - 10/11/2016	5236	3.1
Spring 2017	05/11/2017 - 06/14/2017	46331	5.5
Fall 2017	08/23/2017 - 10/04/2017	8372	3.4

4.4.3. Juniata River at Newport

Another “core” site was the Juniata River at Newport (Figure 23). Samples were collected at this site over six sampling events.

Figure 23 displays each category of compounds and the percent detected during each sampling event at the Juniata River at Newport site. No PCBs were detected at any sampling event at this site. Semi-volatile compounds were only sampled in Spring 2016 and were minimally detected. There may be a seasonal fall versus spring pattern for a few groups of compounds. In general, PBDEs, PAHs, and pesticides were all higher in spring samples than in fall samples.

The Juniata River at Newport site has a USGS gage (#01567000) that measures discharge and gage height over time, but patterns in percent CEC compounds detected with flow were somewhat variable at this site. Viewing each deployment separately (Figure 24 – Figure 29), the Fall 2014 deployment did have a fairly consistent and sustained decrease in flow over the entire sampling period. In contrast, the Spring 2016 deployment had flashier, higher discharge spikes over the course of sampler deployment. Likewise, Spring 2014, which also had comparatively high numbers of compounds detected, had the highest overall average discharge of all deployment periods and had some high, flashy discharge points.

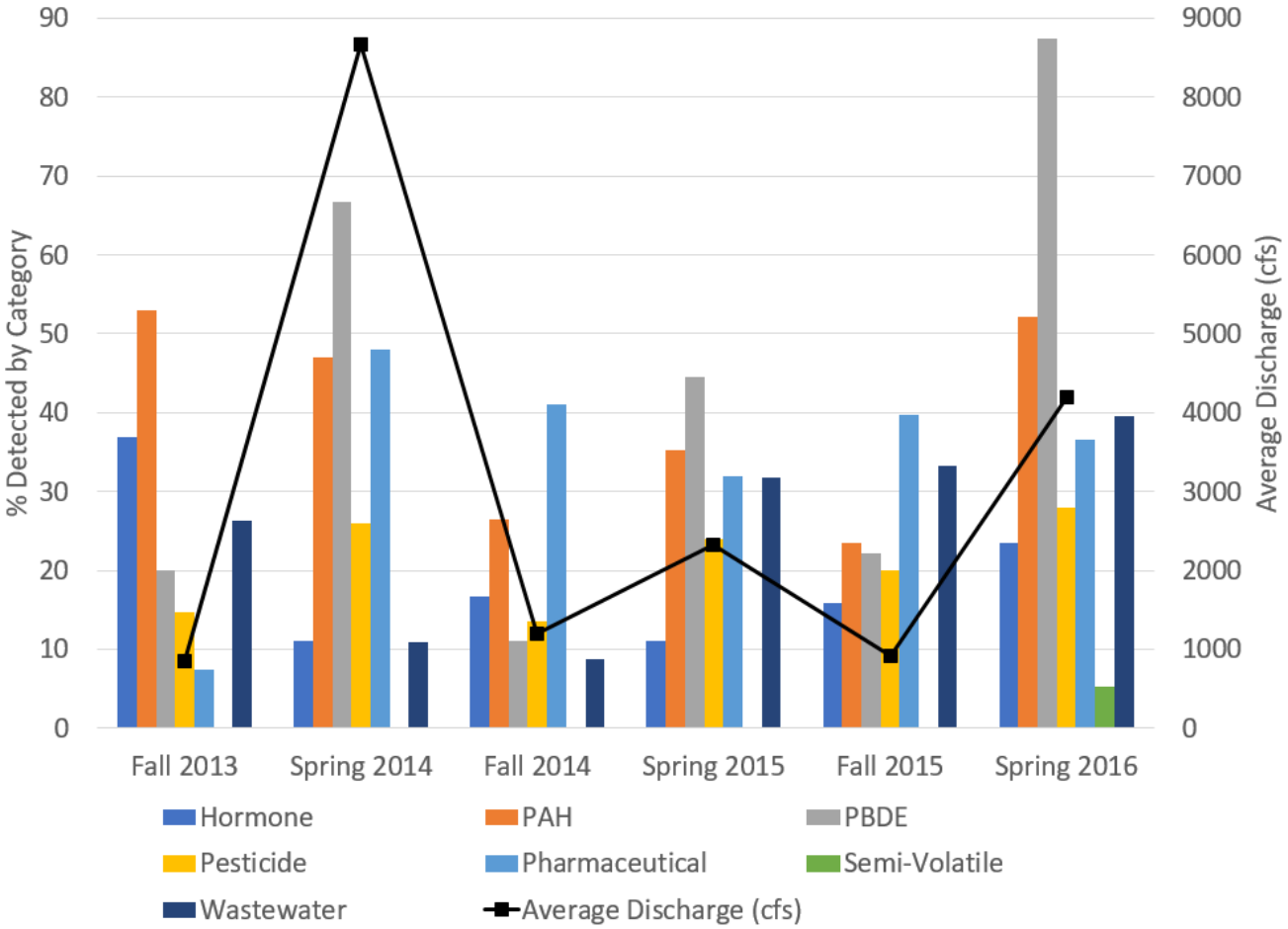


Figure 23. Percent compounds detected at Juniata River at Newport from eight compound categories and six sampling periods.

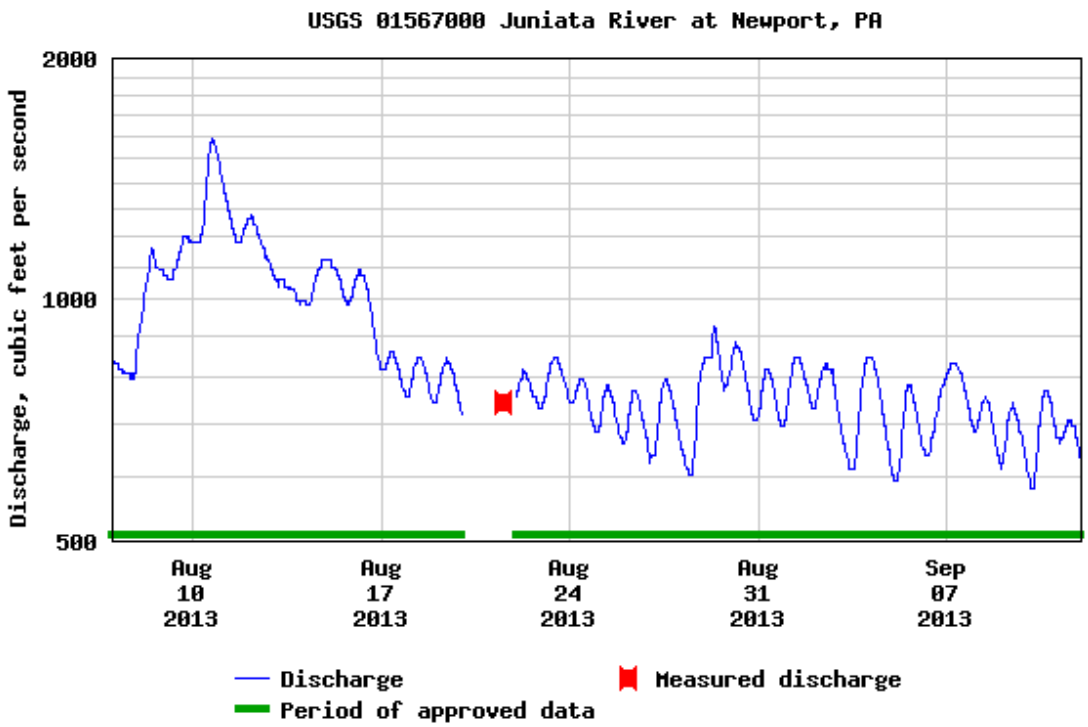


Figure 24. Fall 2013 discharge for Juniata River at Newport (USGS Gage 01567000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

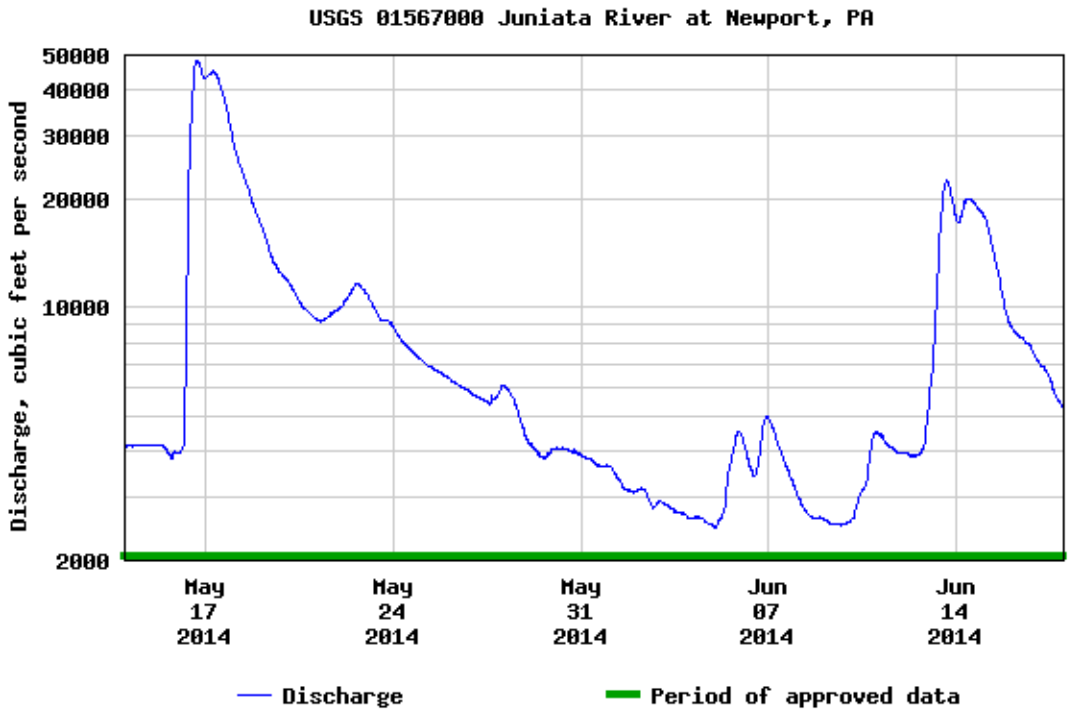


Figure 25. Spring 2014 discharge for Juniata River at Newport (USGS Gage 01567000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

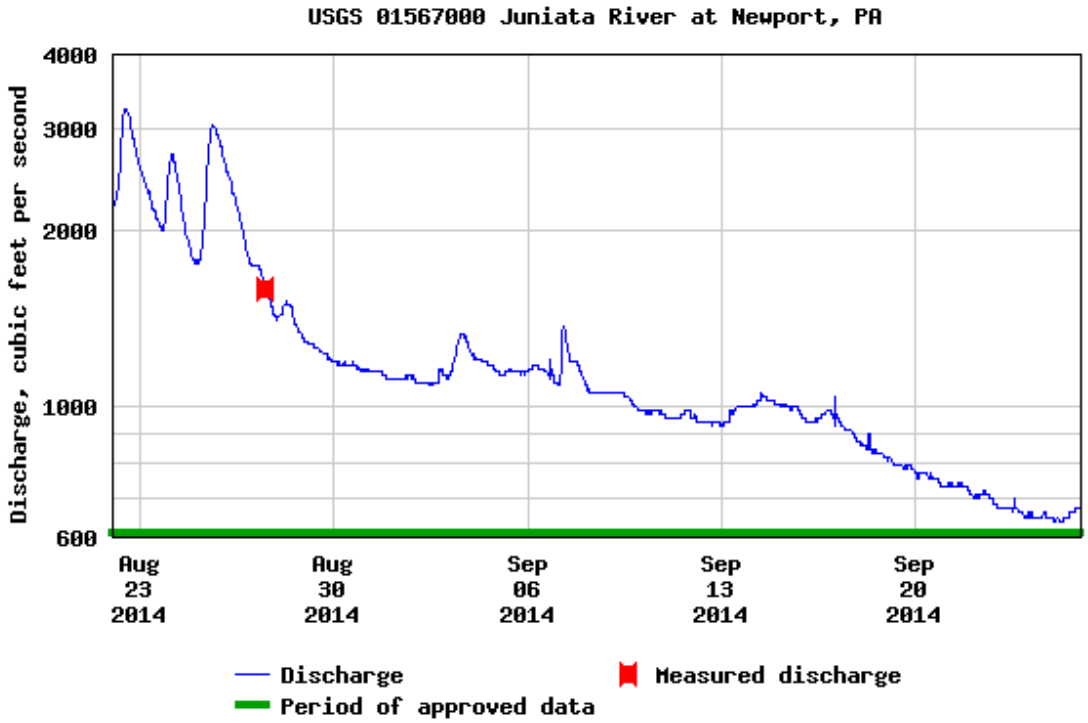


Figure 26. Fall 2014 discharge for Juniata River at Newport (USGS Gage 01567000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

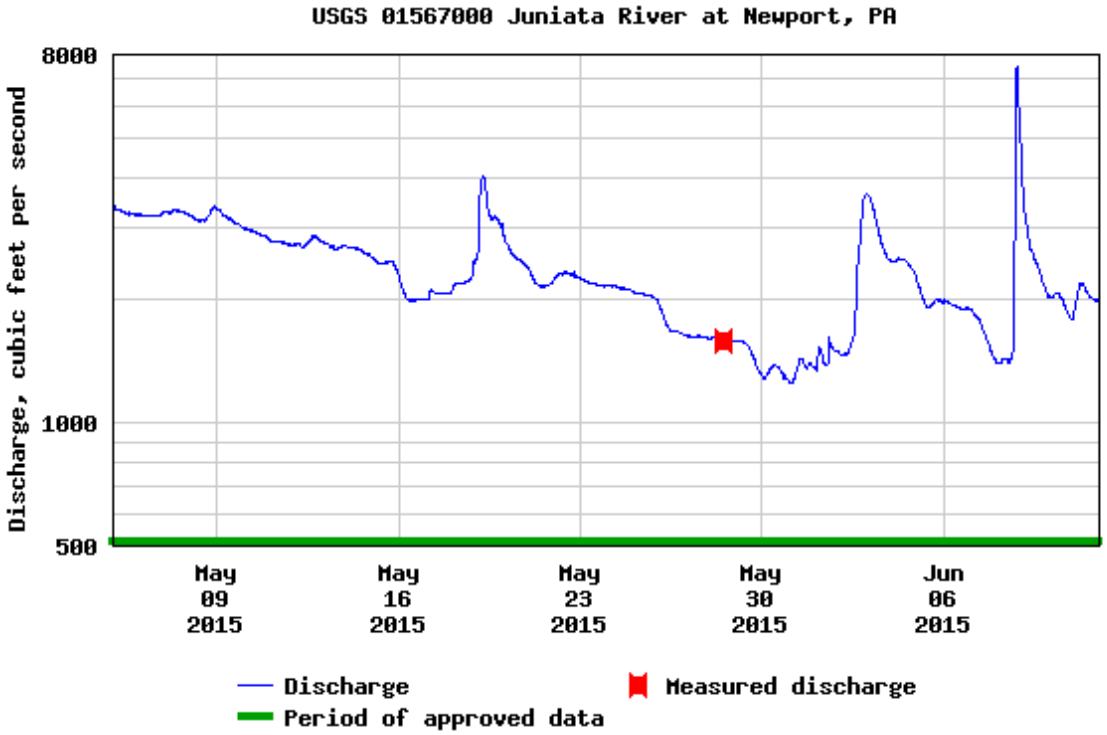


Figure 27. Spring 2015 discharge for Juniata River at Newport (USGS Gage 01567000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

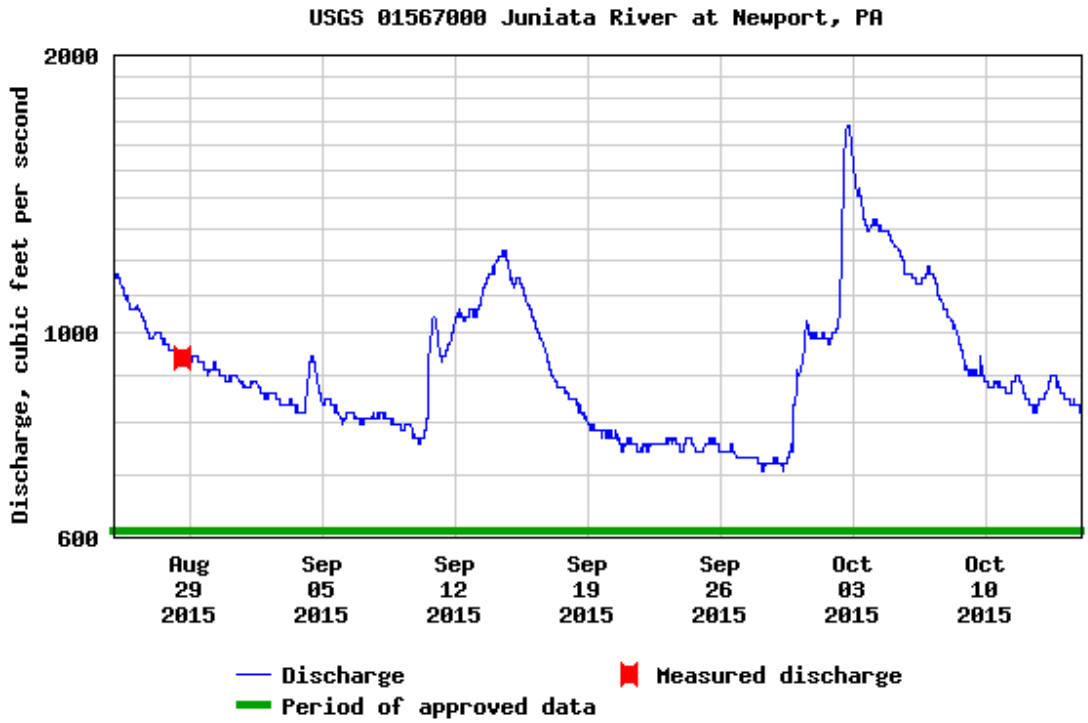


Figure 28. Fall 2015 discharge for Juniata River at Newport (USGS Gage 01567000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

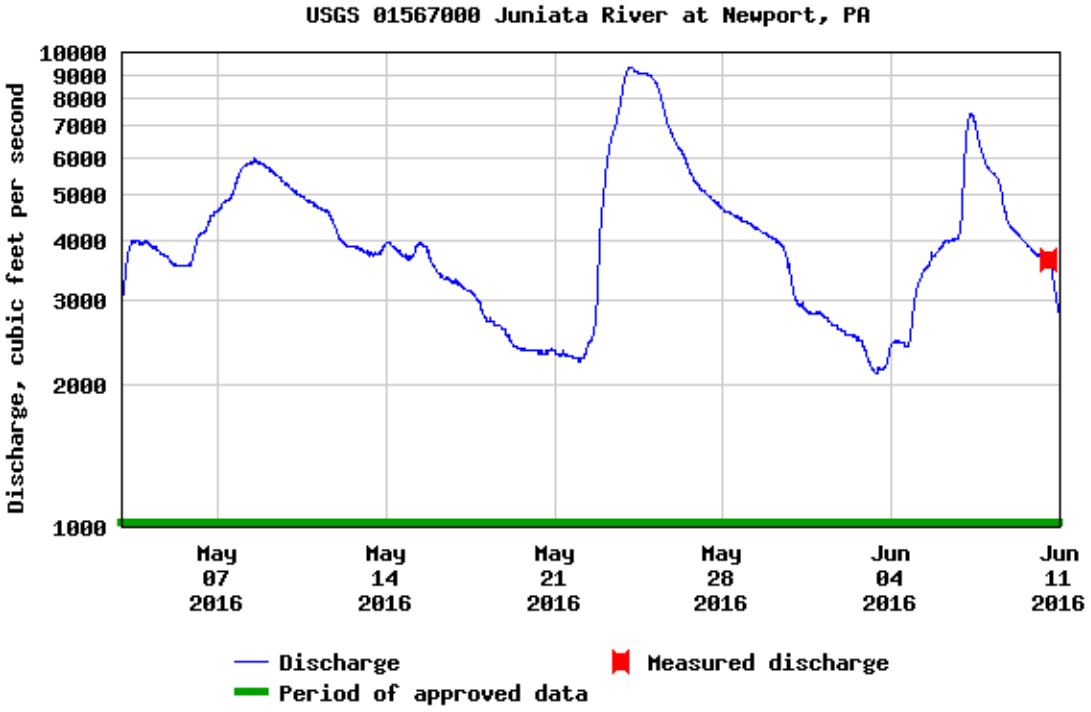


Figure 29. Spring 2016 discharge for Juniata River at Newport (USGS Gage 01567000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

Table 7. Average discharge and gage heights over each sampling time period (Juniata River at Newport USGS Gage 01567000).

Sampling Event	Date Range Sampled	Avg. Discharge (cfs)	Avg. Gage Height (ft)
Fall 2013	08/07/2013 - 09/11/2013	852	3.4
Spring 2014	05/14/2014 - 06/17/2014	8676	6.3
Fall 2014	08/22/2014 - 09/25/2014	1204	3.9
Spring 2015	05/15/2015 - 06/11/2015	2332	4.2
Fall 2015	08/25/2015 - 10/14/2015	924	3.4
Spring 2016	05/03/2016 - 06/10/2016	4188	4.9

4.4.4. Clover Creek

A smaller waterway was Clover Creek in Blair County, a tributary to Frankstown Branch Juniata River. This site has a much smaller drainage area (40.5 mi^2) than the Susquehanna River at Rockville site (23,562 mi^2) and the Juniata River at Newport (3,352 mi^2) site. At the Clover Creek site, percent urban land use in the upstream watershed is relatively small (5.9%), while forest and agriculture make up most of the land use in the watershed (50.6% and 43.4%, respectively). Compared with the 2015 samples collected at this site, the 2017 samples collected at this site had lower percent compounds detected for pesticide and – to a smaller degree – wastewater compounds, but higher percent compounds detected for PAH, PBDE, and – to a smaller degree – pharmaceutical compounds (Figure 30). At this site, only five compounds from the wastewater suite were tested in Spring 2017, with one detected. Otherwise, between 34 to 46 wastewater compounds were tested for at each sampling event. Semi-volatiles were only sampled in 2017 and were not detected. There were no PCB detections.

Flow could be a cause of the percent CEC compounds detected patterns observed at the Clover Creek site; in general, 2017 was wetter than 2015 as recorded by a nearby gage on Frankstown Branch Juniata River (USGS Gage #01556000, Figure 31 – Figure 35, Table 8).

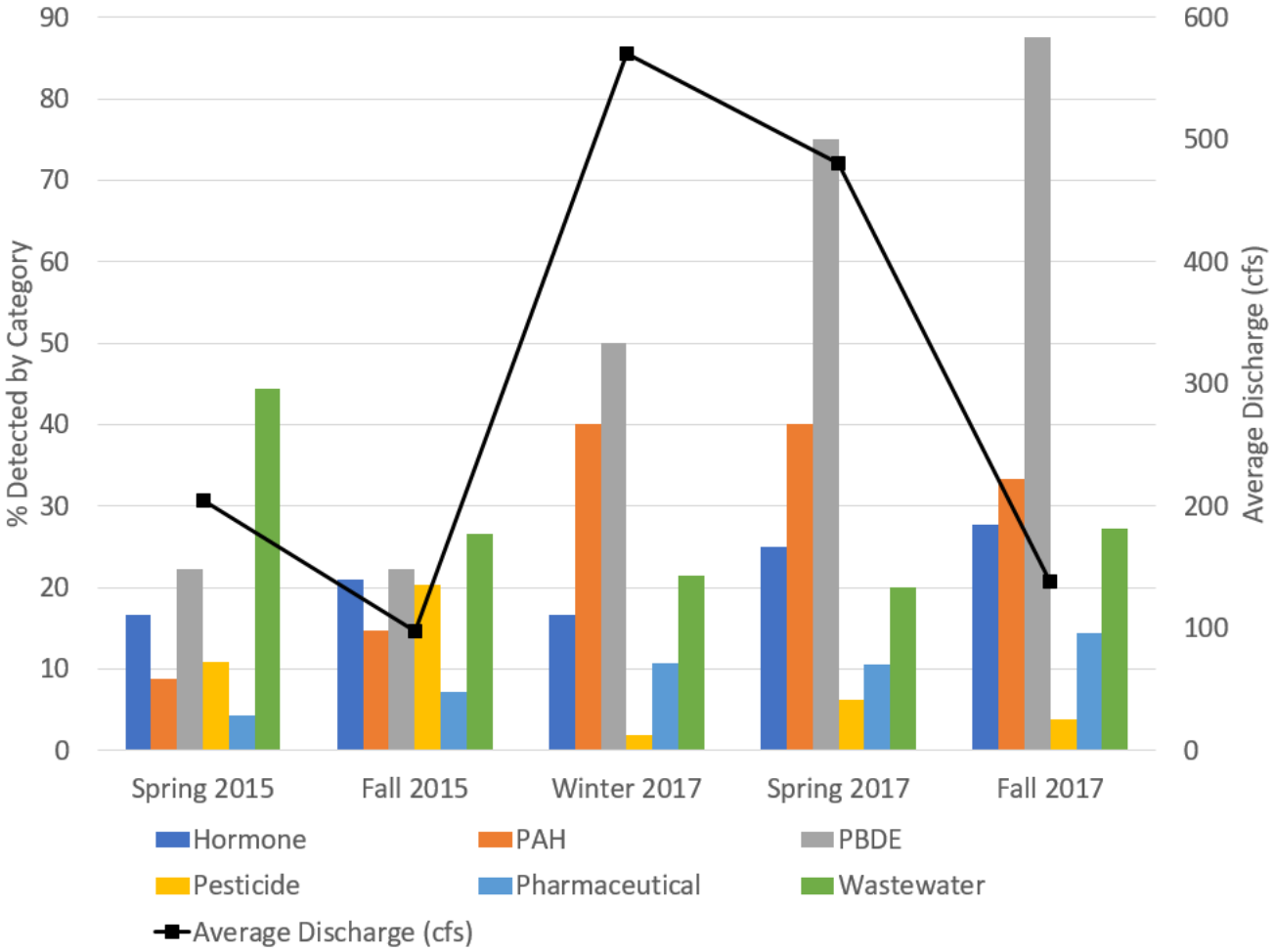


Figure 30. Percent compounds detected at Clover Creek from six compound categories and five sampling periods.

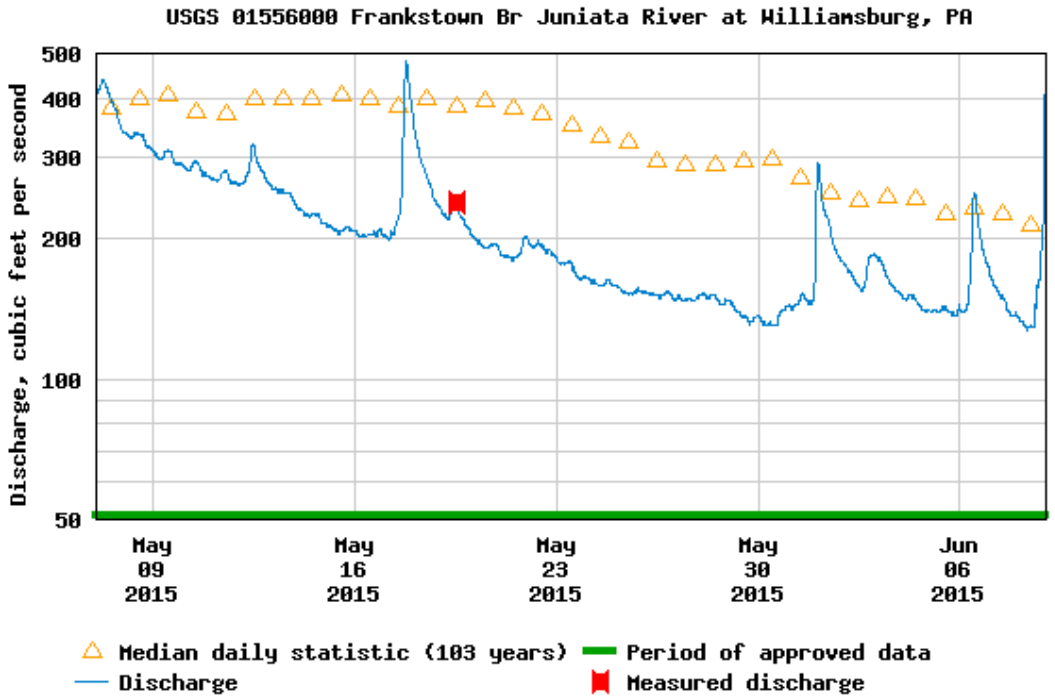


Figure 31. Spring 2015 discharge for Frankstown Branch Juniata River (USGS Gage 01556000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

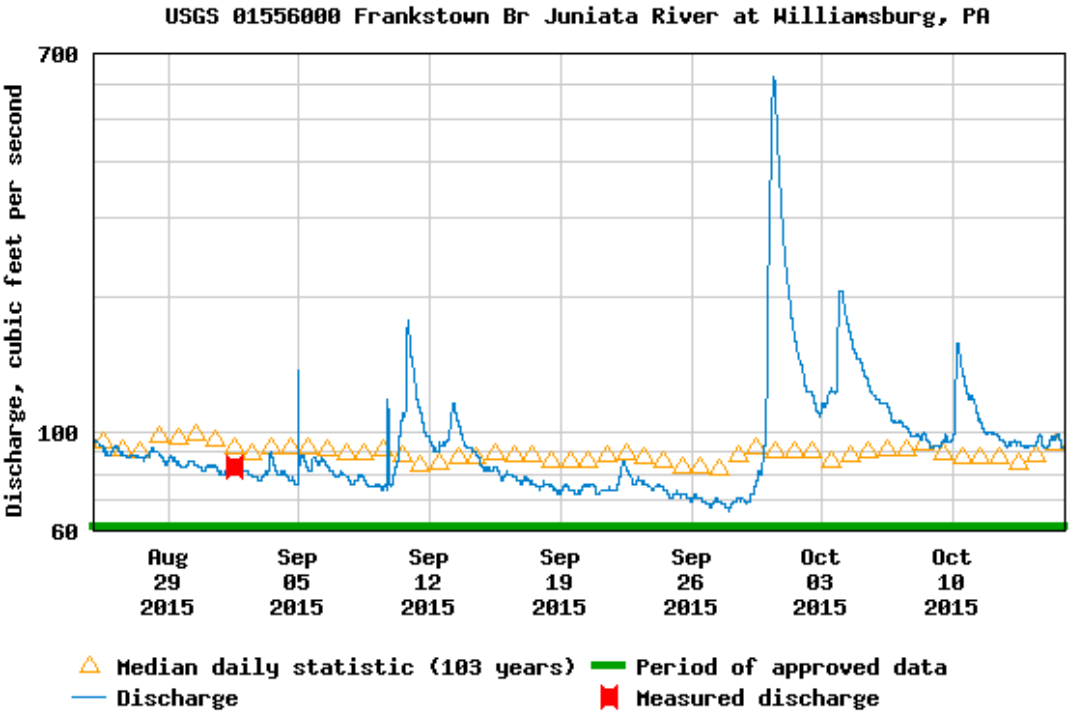


Figure 32. Fall 2015 discharge for Frankstown Branch Juniata River (USGS Gage 01556000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

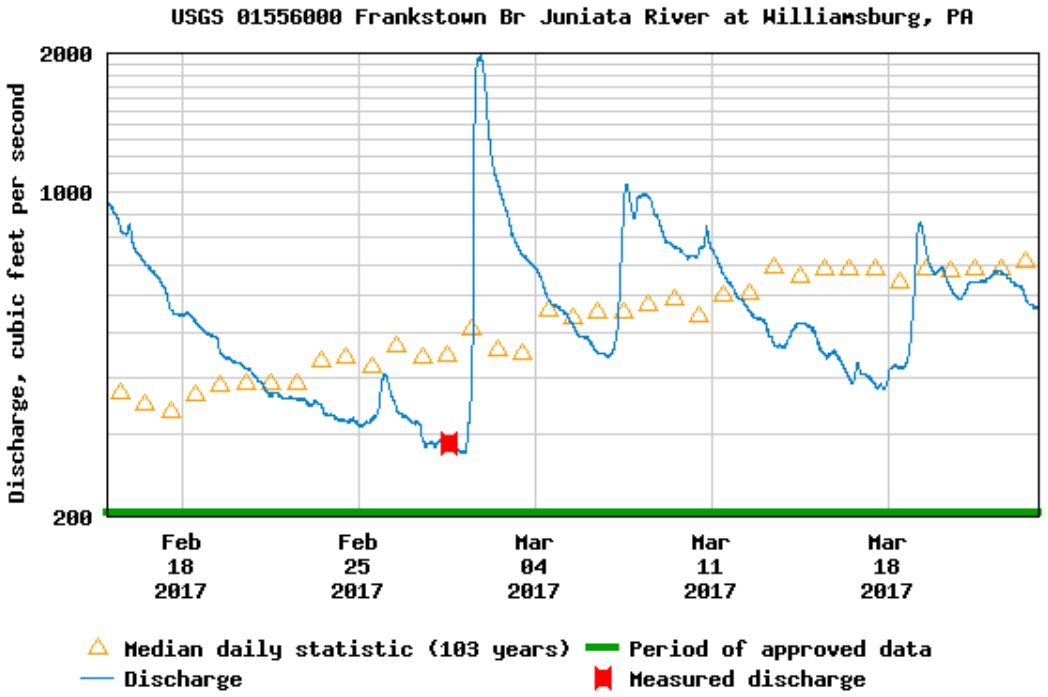


Figure 33. Winter 2017 discharge for Frankstown Branch Juniata River (USGS Gage 01556000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

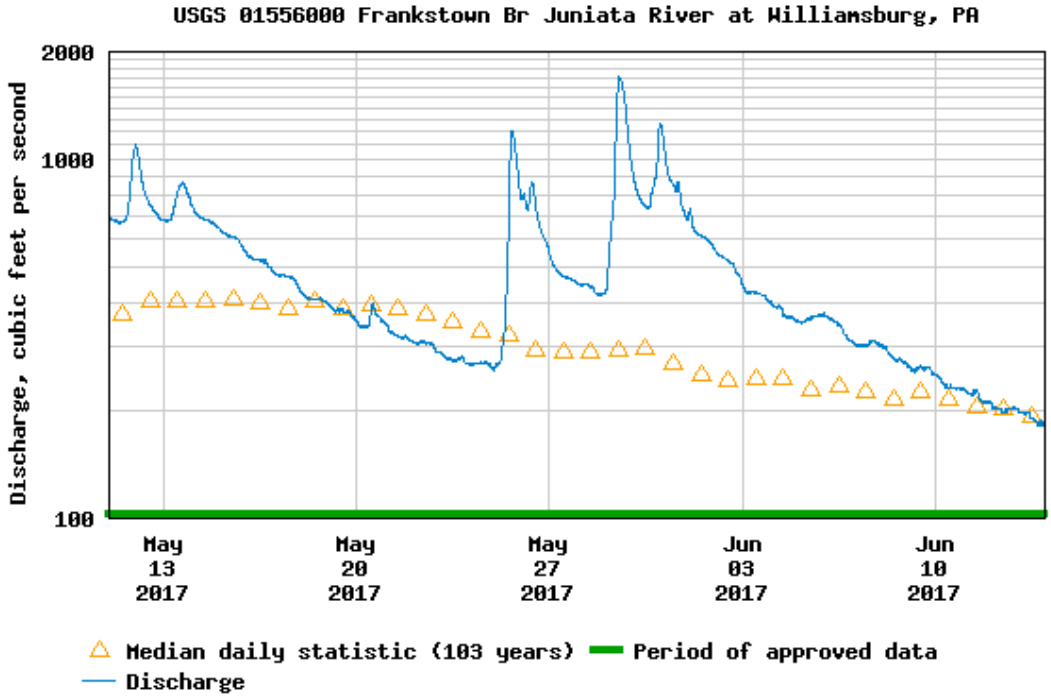


Figure 34. Spring 2017 discharge for Frankstown Branch Juniata River (USGS Gage 01556000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

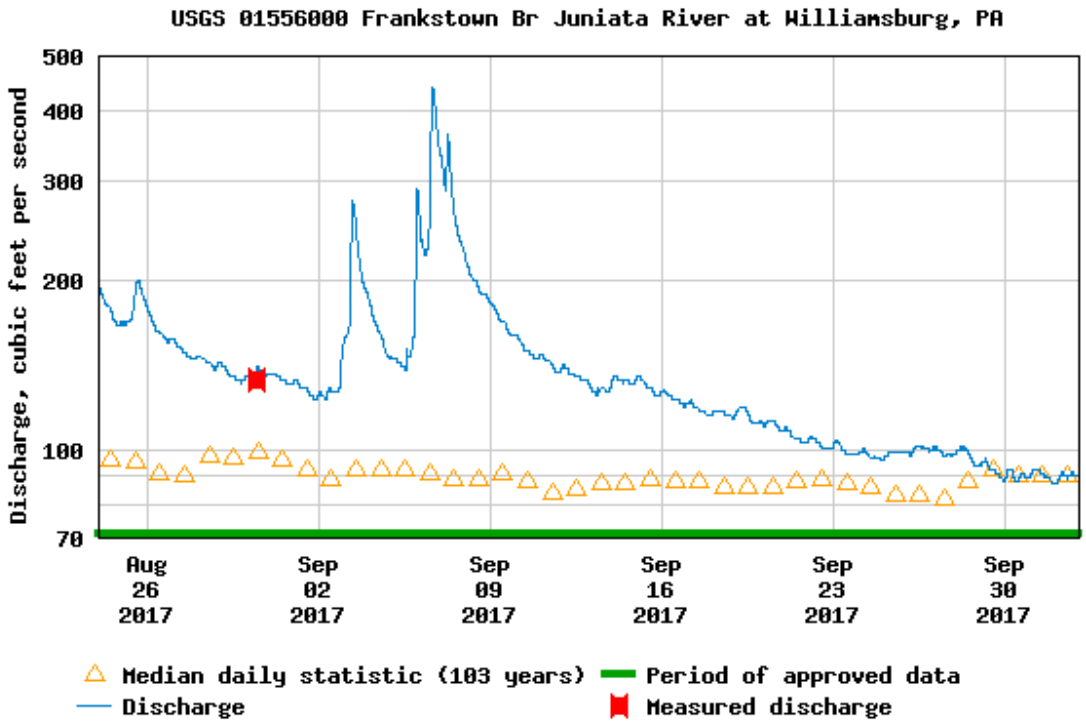


Figure 35. Fall 2017 discharge for Frankstown Branch Juniata River (USGS Gage 01556000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

Table 8. Average discharge and gage heights over each sampling time period (Frankstown Branch Juniata River USGS Gage 01556000).

Sampling Event	Date Range Sampled	Avg. Discharge (cfs)	Avg. Gage Height (ft)
Spring 2015	05/07/2015 - 06/08/2015	204	3.1
Fall 2015	08/25/2015 - 10/15/2015	98	2.5
Winter 2017	02/15/2017 - 03/23/2017	570	4.2
Spring 2017	05/11/2017 - 06/13/2017	480	3.9
Fall 2017	08/24/2017 - 10/02/2017	138	2.8

4.4.5. Spruce Creek

Another small site is Spruce Creek in Huntingdon County, a tributary to Little Juniata River. The drainage area at the Spruce Creek site (109 mi^2) was larger than the Clover Creek site but much smaller than the Susquehanna River and Juniata River “core” sites. Relatively high percent detections of PBDEs and PAHs were evident at this site, particularly in the Spring 2016, Fall 2016, and Winter 2017 samples; low percent detections of other compounds were also observed (Figure 36). The land use in this watershed is mainly forested (59.1%) with moderate agricultural (35%) and relatively little developed (5.8%) land use. While low percent detections of PBDEs and PAHs may

be expected from the relatively small extent of developed land use in this watershed, the opposite was observed, indicating that some sources of PAHs and PBDEs may be entering the watershed upstream, perhaps from runoff or discharges. Studies have shown these compounds to be in waste or fertilizers. Gaylor et al. 2014 detected PBDEs in waste sludge-applied soils and invertebrates, but not in reference, unapplied sites. Krzebietke et al. 2020 demonstrated higher PAHs in soils fertilized with farmyard manure than soil where only mineral fertilizers were applied. The actual TWA concentrations of the chemicals in Spruce Creek were low, with the highest PBDE concentration detected in Fall 2016 (PBDE-47 = 0.018 ng/L) and highest PAH concentration detected in Winter 2017 (fluoranthene = 1.7013 ng/L).

As recorded by nearby USGS Gage #01558000 on Little Juniata River, the two springtime sample periods at the Spruce Creek site did have relatively high flows, which could have contributed to runoff entering the stream (Figure 37 – Figure 41, Table 9).

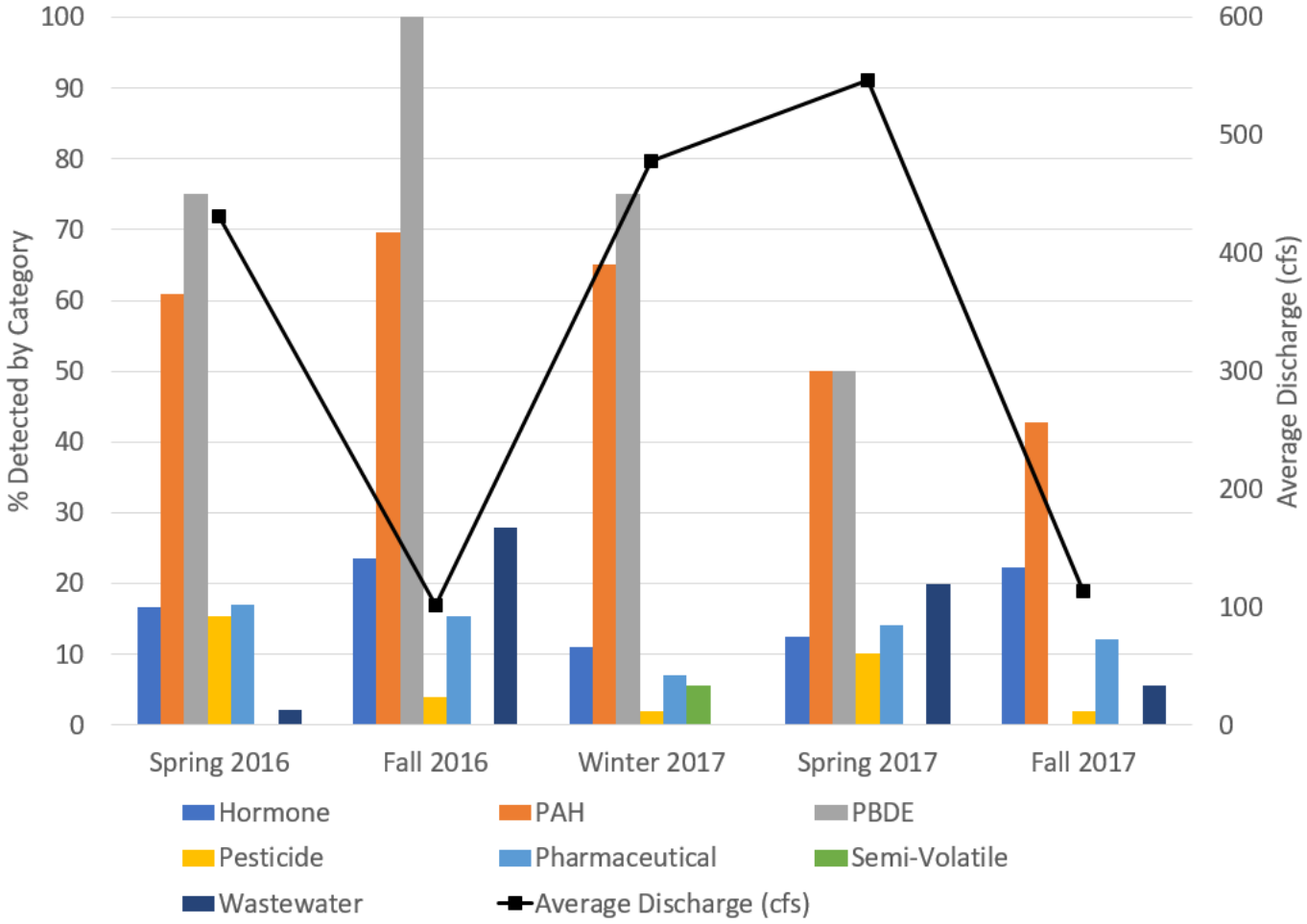


Figure 36. Percent compounds detected at Spruce Creek from eight compound groups and five sampling periods.

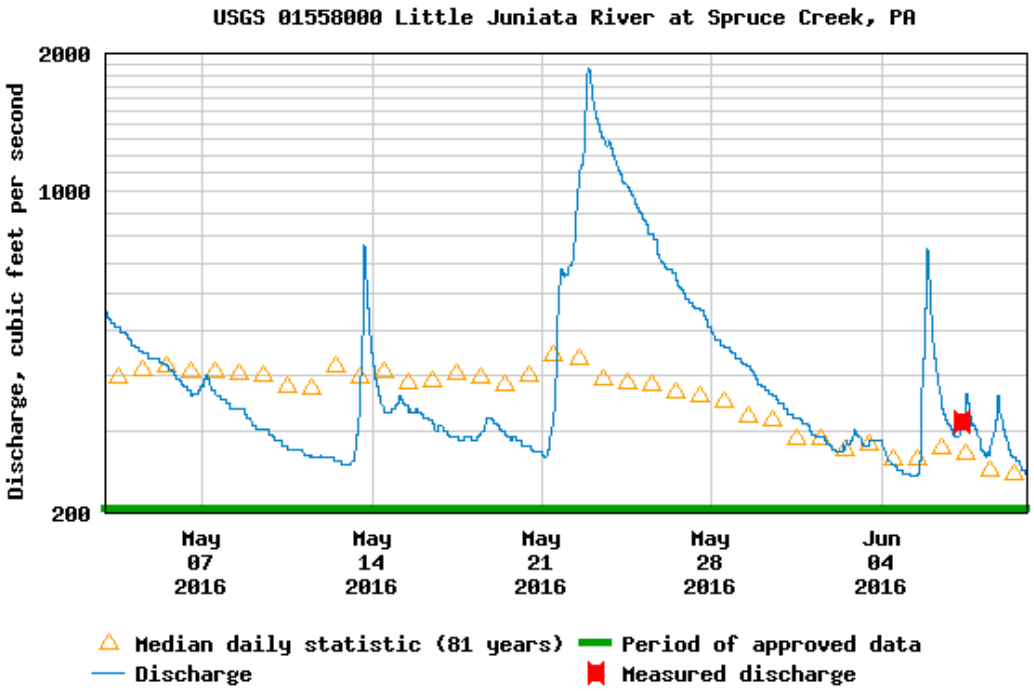


Figure 37. Spring 2016 discharge for Little Juniata River (USGS Gage 01558000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

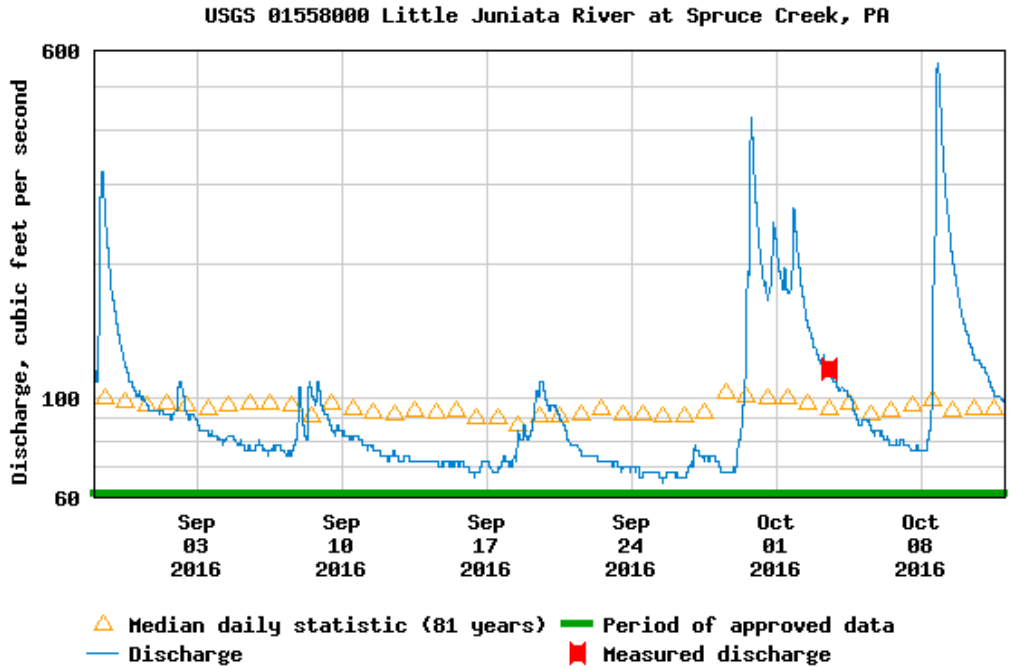


Figure 38. Fall 2016 discharge for Little Juniata River (USGS Gage 01558000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

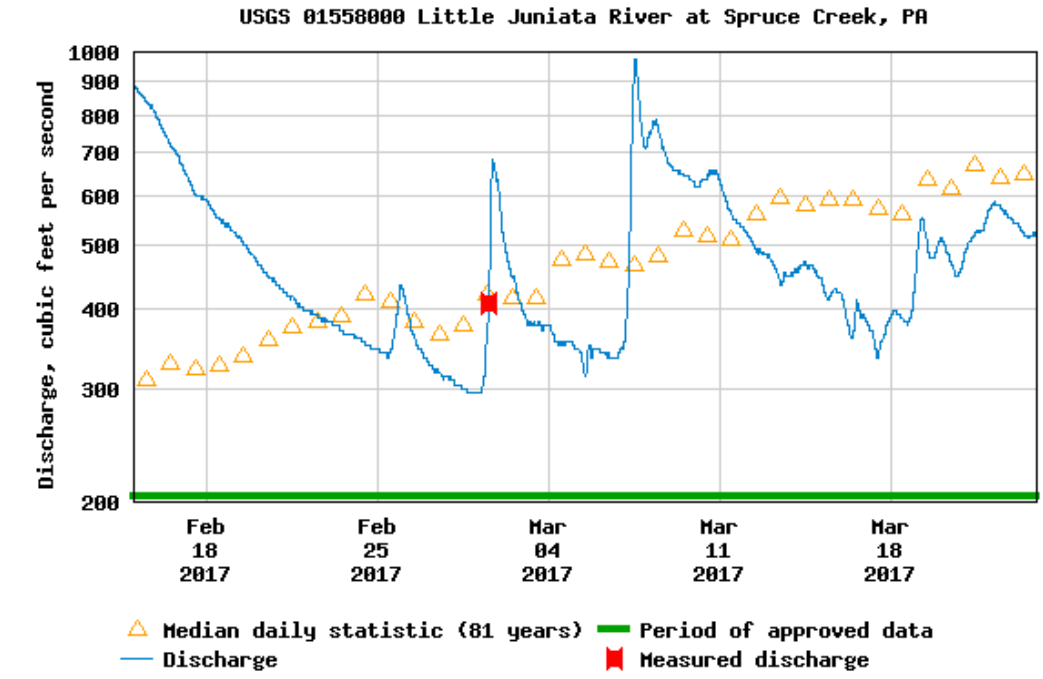


Figure 39. Winter 2017 discharge for Little Juniata River (USGS Gage 01558000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

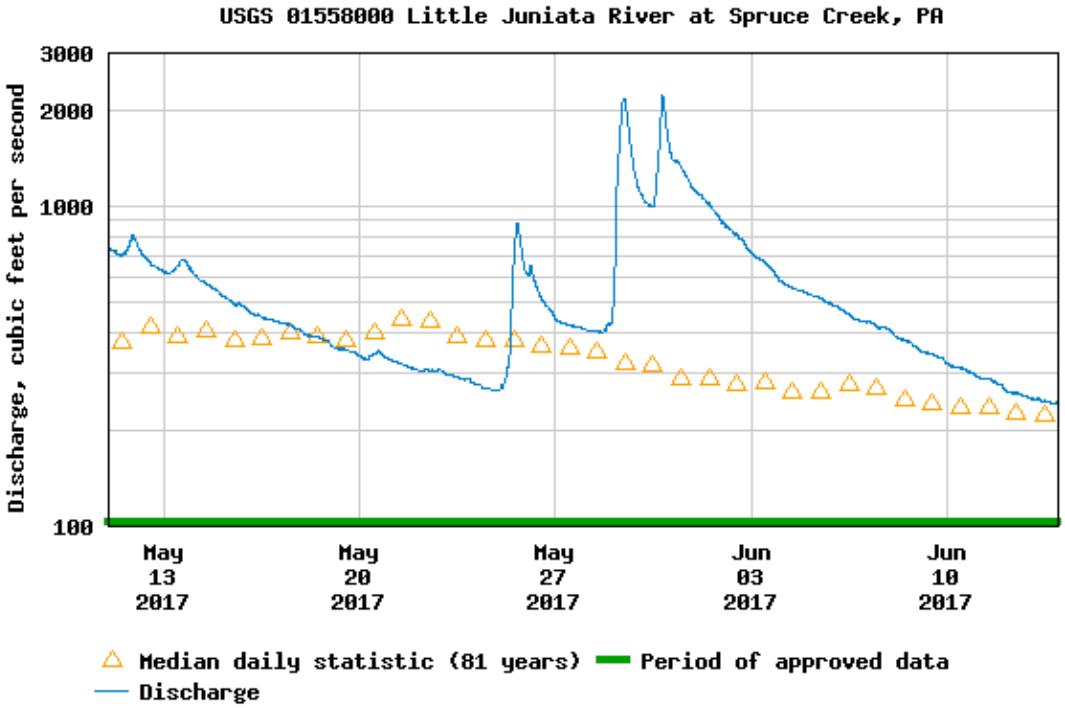


Figure 40. Spring 2017 discharge for Little Juniata River (USGS Gage 01558000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

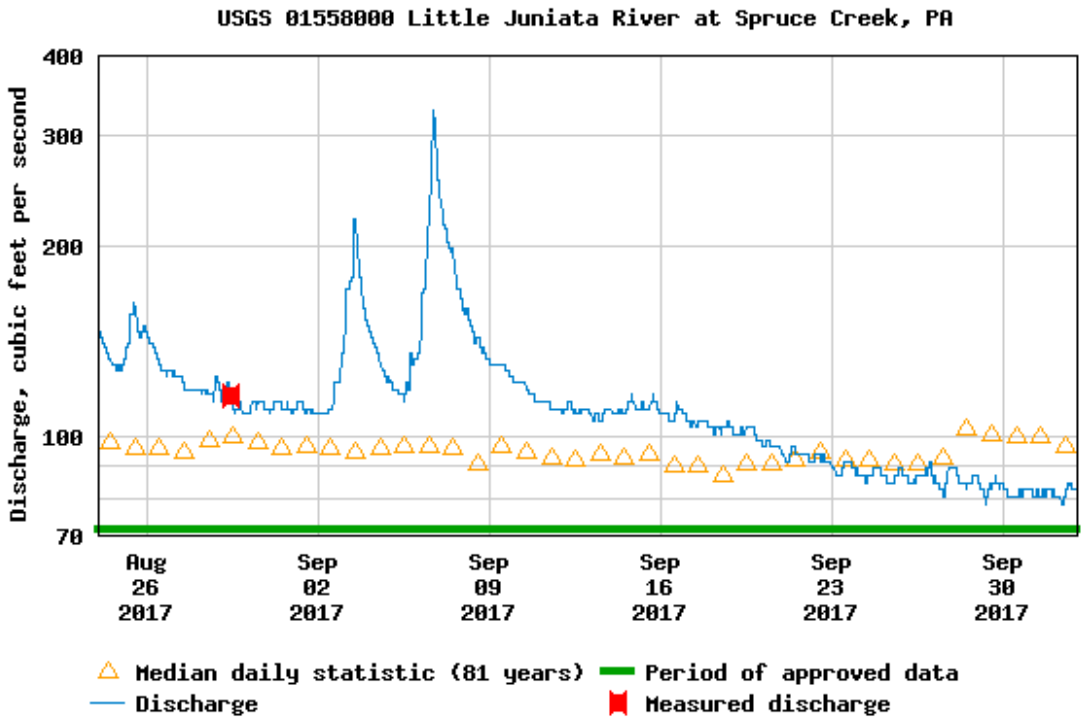


Figure 41. Fall 2017 discharge for Little Juniata River (USGS Gage 01558000); USGS Current Conditions for the Nation (https://nwis.waterdata.usgs.gov/nwis/uv?).

Table 9. Average discharge and gage heights over each sampling time period (Little Juniata River USGS Gage 01558000).

Sampling Event	Date Range Sampled	Avg. Discharge (cfs)	Avg. Gage Height (ft)
Spring 2016	05/03/2016 - 06/09/2016	431	2.7
Fall 2016	08/29/2016 - 10/11/2016	101	1.9
Winter 2017	02/15/2017 - 03/23/2017	478	2.8
Spring 2017	05/11/2017 - 06/13/2017	547	2.9
Fall 2017	08/24/2017 - 10/02/2017	114	1.9

4.5. Differences Between Laboratories

Analyses were completed of differences between percent detected compounds at different laboratories because labs changed from the 2013 – 2015 time period to the 2016 – 2017 time period. Percent compounds detected per sample were compared between USGS (2013 – 2015), DEP (2016 – 2017), and SGS AXYS (2016 – 2017). Data was not normal, so a non-parametric Kruskal-Wallus test was used to compare the three groups. The three labs were significantly different ($p = 5.597e-07$) with pairwise comparisons using the Wilcoxon rank sum test indicating SGS AXYS & USGS and DEP & USGS labs were significantly different, while DEP & SGS AXYS were not significantly different (Figure 42).

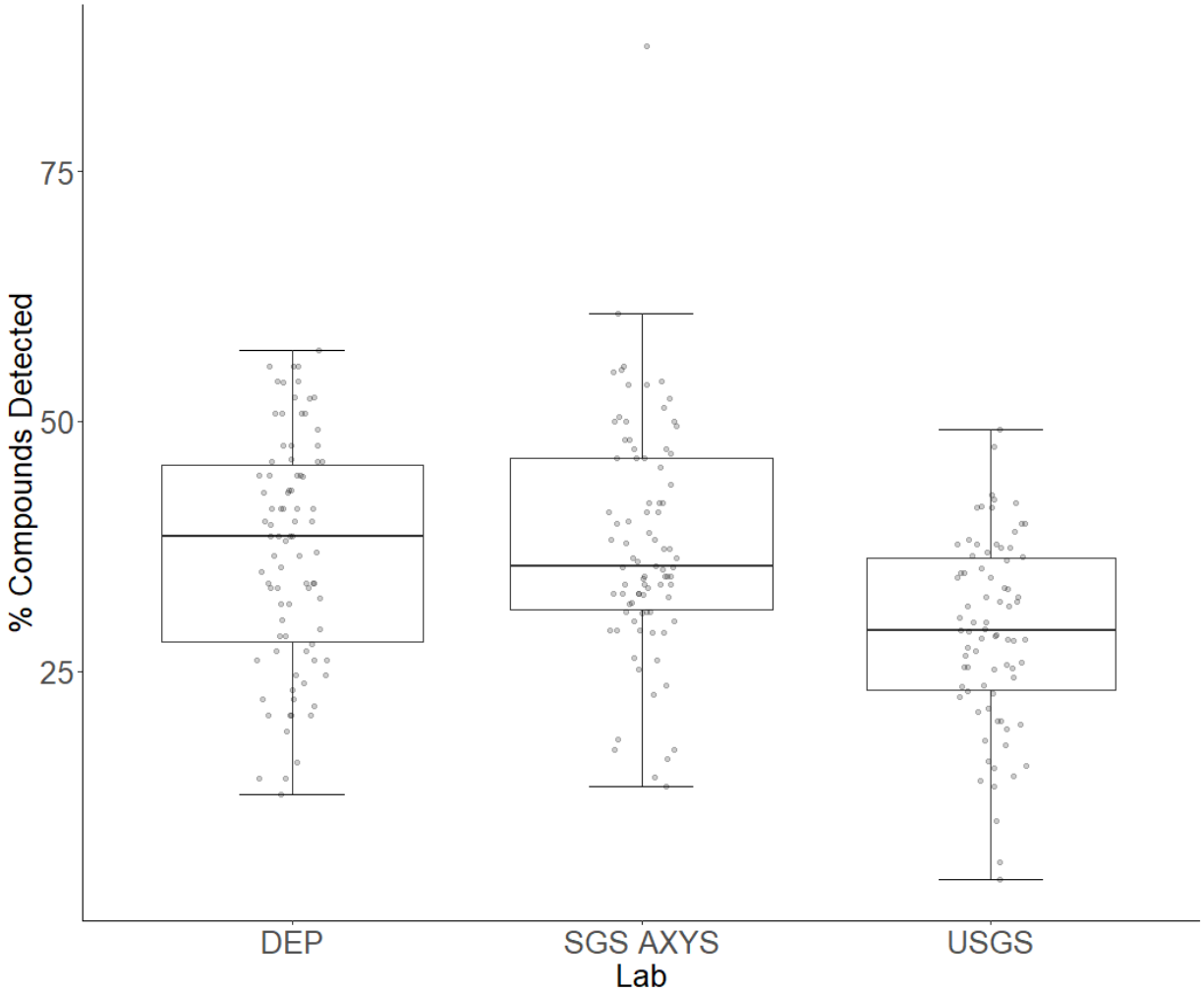


Figure 42. Percent compounds detected using DEP (2016 – 2017), SGS AXYS (2016 – 2017), and USGS (2013 – 2015) laboratories. Width of each box is proportional to sample size.

Subsetting the data into categories of compounds detected (pesticides, PBDEs, PAHs, hormones, and pharmaceuticals) also demonstrated significant differences between labs, as indicated by p-values less than or equal to 0.05 using Wilcoxon rank sum tests (Table 10).

Table 10. Differences of percent compounds detected between laboratories by CEC compound category

Category	Lab 2013-2015	Lab 2016-2017	p-value
Pesticides	USGS	DEP	**0.007**
PBDEs	USGS	SGS AXYS	**<2.2E-16**
Hormones	USGS	SGS AXYS	**4.70E-12**
Pharmaceuticals	USGS	SGS AXYS	0.41
PAHs	USGS	DEP	**<2.2E-16**

p-values ≤ 0.05 are bolded

4.6. Comparison to Sediment Samples

Where available, streambed sediment samples were matched with passive samples based off time and location. A linear regression was performed that found little correlation between percent CEC compounds detected in sediment and percent CEC compounds detected in passive samples (Figure 43). Weak correlations were also seen between percent compounds detected in passive samplers and streambed sediment samples when results were broken down by compound category.

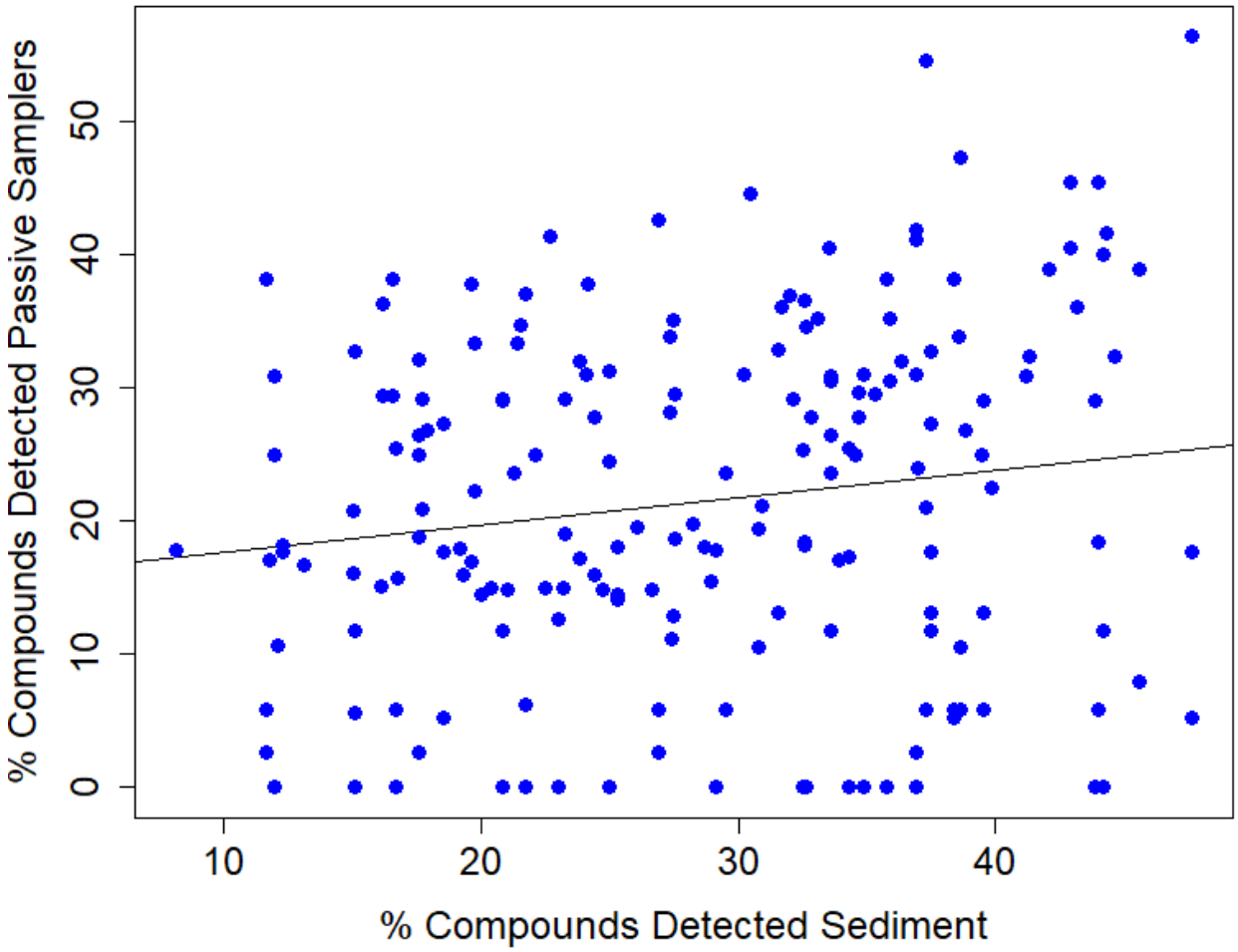


Figure 43. Percent compounds detected in streambed sediment samples versus percent compounds detected in passive samples, 2013 – 2017.

5. DISCUSSION

The monitoring and reporting of CECs come with a large set of challenges, mainly that there is limited knowledge on individual and combined effects of the compounds and little to no water quality benchmarks for many of the compounds. In addition, comparing instream water quality criteria with passive sampler TWA concentrations is challenging. However, the passive sampler studies implemented by DEP show the extent and patterns associated with CECs in flowing surface waters of Pennsylvania. In particular, this study detected roughly 72% of the CEC compounds tested. The most commonly detected compounds were PAHs, which are often found in road runoff, plasticizers, wastewater (Witter et al. 2014), and fertilizers. Atrazine, the most commonly detected pesticide in this study, is applied to a variety of crops for weed control, although over 90% of the atrazine used in the United States is applied to corn (Farruggia et al. 2016). In this study, pesticides as a group were detected less frequently than most other categories of CECs. This follows the idea that newer pesticides likely break down faster. DDT and its metabolites were still detected in this study, decades after DDT use was discontinued. PCBs, a group of chemicals of concern for their ability to bioaccumulate and persist in the environment, were rarely found and, when they were, the concentrations were very low. PCBs are hydrophobic and generally accumulate in sediment (Desmet et al. 2012). DEP's CEC sediment study also included PCBs and they were infrequently detected and at low concentrations in sediment as well (Williams 2021, In Review). These PCB results are encouraging and demonstrate minimal presence and impact in the environment nearly 40 years after PCB production and sale was banned. Estrone had some of the highest occurrences in the hormone category in the study and, given its commonality in humans and other animals, this is not surprising, although it is a weaker estrogen (Tulane University 2021). Antidepressants, present in some of the passive samples in this study, have been detected in freshwater by other studies (Reif et al. 2012, Schultz et al. 2009) and have been shown to affect the behavior of fish at environmentally relevant concentrations (Painter et al. 2009). Although not directly comparable to passive sampler TWA concentrations, it is encouraging that results with known CEC thresholds were largely below specific water quality criteria in 25 Pa. Code § 93.7 (Table 3), water quality criteria for toxic substances in § 93.8c (Table 5), and USEPA recommended criteria/benchmarks.

Developed land, or urban area, appears to be a variable influencing the occurrence of many compounds in smaller streams, with developed urban areas having higher percent compounds detected. Percent forested land use in smaller streams generally had an inverse relationship with percent compounds detected (i.e., smaller streams with highly forested watersheds had fewer CEC detections). These results are logical considering most CEC compounds measured are anthropogenic and would be expected to increase with increased human population density.

In this study, the percent CEC compounds detected were higher downstream of STPs surveyed than upstream; this was particularly true for pharmaceuticals. Although results are somewhat limited in scope, this suggests that traditional wastewater treatment does not remove all pharmaceutical compounds prior to discharge. Nearshore locations also tended to have more compounds detected than main channel locations, suggesting that

compounds may accumulate along banks or may be higher in those locations due to runoff being a more predominant nearshore influence. Nearshore locations, as opposed to mid-channel locations, may be optimal places to put passive samplers if the goal is to capture the highest possible observations on a larger river. Detections in smaller tributaries were comparable to larger river deployments; however, pesticides, PBDEs, and wastewater compounds were significantly higher in tributaries than larger river areas. Overall, there was not a significant difference in percent compounds detected between seasons (winter, spring, and fall). However, there was a significant difference detected in total estrogenicity concentrations between spring and fall samples which may indicate the presence of more potent estrogenic compounds in the springtime versus fall, but not a difference in non-estrogenic compounds.

While streamflow appeared to be an influence on detections across years and sampling events, it was not strongly correlated with percent compounds detected overall. Interestingly, in reference to the temporal analyses, when samples were collected appeared to influence the wastewater compounds found at the three Susquehanna at Rockville sampling locations, which were placed across the river in three different known zones of influence: a location in the eastern part of the river, which is strongly influenced by the North Branch Susquehanna River; a location near the middle of the river, which is strongly influenced by the West Branch Susquehanna River; and a location in the western part of the river, which is strongly influenced by the Juniata River. The passive sampler CEC results in these three zones of influence tended to be similar across any single sampling event, but different among events and influenced by flow conditions during specific sampling events. Therefore, on average, lower streamflow may contribute to higher percent of wastewater compound detections at the Rockville sites. The compounds detected at other sites that were repeatedly sampled appeared to be at least marginally influenced by flow during time of sampling. However, the reasons for patterns in percent CEC compounds detected at other sites sampled over time were more difficult to discern. The Clover Creek site, for example, had lower percent compounds detected in 2015 compared with 2017. For all sites and samples, hormones, PAHs, PBDEs, PCBs, pesticides, and pharmaceuticals were analyzed by USGS in 2013 through 2015 and by DEP and SGS AXYS in 2016, so the change in labs used could be one explanation. With the change in labs, some analyte lists and detection limits changed. This is particularly evident with PAHs and PBDEs, where many more were detected in 2017 than 2015. The detection limits for PBDEs in 2017 (SGS AXYS) were more sensitive than for PBDEs in 2015 (USGS). Therefore, there were more detections in 2017. However, although the analyte list changed slightly for PAHs through the years, the detection limits remained similar and many compounds overlapped between laboratories. Even with these facts, there were far more PAH detections at the Clover Creek site in 2017 than 2015. Another explanation for these differences could be the flow as 2017 was a wetter year at the Clover Creek site than 2015.

Several complications unique to passive sampler deployments were noted during this study. Field blank detections tended to be more frequent than in surface water discrete/grab sampling conducted by DEP. These detections pose problems for data accuracy and analysis. In addition, numerous detections in laboratory blanks occurred,

further complicating the analyses. These interferences are not surprising. SPMDs, in particular, are effective air samplers and therefore exposing them as field blanks during deployments and retrievals can easily detect compounds in the air. Passive samplers have the ability to detect extremely low, trace concentrations, which can also be detrimental to data quality since even very low trace amounts of contamination in lab or field blanks can be measured. It can also be difficult to completely clean field equipment. Numerous studies have reported field or lab blank contamination using passive water samplers (Ahrens et al. 2016, Caton 2012, Van Metre et al. 2017), although some have also had relatively few or no detections (McCarthy et al. 2009, Alvarez et al. 2008).

In addition, the literature and sampling rates of passive samplers are constantly being updated, which results in changes in concentration calculation methods over time that can render comparisons across time difficult or require a recalculation of old data based on new sampling rates. Even with these challenges, passive samplers are very effective at detecting trace and sporadic contamination, which potentially could have many uses in both monitoring and compliance (Booij et al. 2016, Lohmann et al. 2011, Miège et al. 2012).

Ongoing DEP passive sampling data collection efforts will continue to document the presence of CECs throughout Pennsylvania surface waters. Data collection at core sites that have been monitored for several years, over different seasons, and throughout variable environmental conditions will provide the opportunity to document CEC prevalence and concentrations over time and will provide the basis for more powerful analyses of explanatory variables. In addition, targeted monitoring, like sampling upstream and downstream of known point and nonpoint source discharges and impacts, has demonstrated utility in documenting the source of CECs and has helped define how potential sources could contribute to concentrations in surface waters.

Passive samplers have been used to measure impacts to determine compliance (Booij et al. 2016, Lohmann et al. 2011, Miège et al. 2012). DEP has historically used passive samplers to document impacts caused by PCBs. A study conducted in 2000 showed PCBs in effluent at a Pennsylvania Fish and Boat Commission (PFBC) fish hatchery that corresponded to PCB contamination in the fish (PADEP internal document, 2000). Depending on the pollutant, passive samplers will continue to be an opportunity for regulating permitted activities.

While passive samplers have, to date, not been used for the assessment of protected uses in Pennsylvania, the increasing amount of data collected indicates that the development of assessment methods using passive sampler data is very likely, especially for contaminants that are harmful to human health or aquatic life at very low concentrations. Passive samplers also create the opportunity to measure contamination over longer periods of time that could capture acute pollution events that discrete data collection efforts cannot always robustly or accurately characterize. Additional efforts to correlate the relationship of passive sampler results with discrete water column sample concentrations may be necessary, or more defined relationships between passive sampler results and protected water use impairment thresholds would need defined.

Ongoing passive sampling efforts should be paired with discrete data collection efforts. Also, the evaluation of passive sampling data should be included as part of ongoing water quality criteria development efforts. Given their sensitivity, passive samplers are valuable tools for detecting low-level emerging contaminants in Pennsylvania's streams and rivers.

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