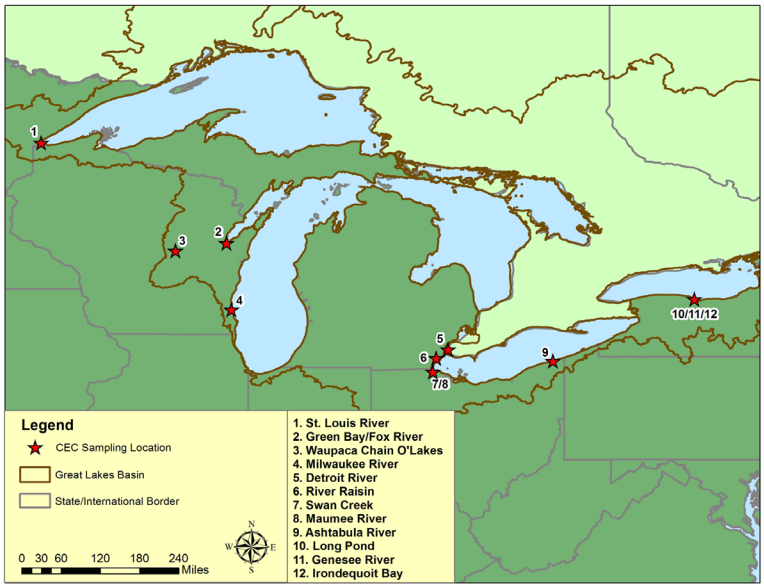
U.S. Fish & Wildlife Service

Contaminants of Emerging Concern in the Great Lakes Basin: A Report on Sediment, Water, and Fish Tissue Chemistry Collected in 2010-2012

Biological Technical Publication

BTP-R3017-2013



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Abstract

Despite being detected at low levels in surface waters and sediments across the United States, contaminants of emerging concern (CECs) in the Great Lakes Basin are not well characterized in terms of spatial and temporal occurrence. Additionally, although the detrimental effects of exposure to CECs on fish and wildlife have been documented for many CECs in laboratory studies, we do not adequately understand the implications of the presence of CECs in the environment. Based on limited studies using current environmentally relevant concentrations of chemicals, however, risks to fish and wildlife are evident. As a result, there is an increasing urgency to address data gaps that are vital to resource management decisions. The U.S. Fish and Wildlife Service, in collaboration with the U.S. Geological Survey, is leading a Great Lakes Basin-wide evaluation of CECs (CEC Project) with the objectives to (a) characterize the spatial and temporal distribution of CECs; (b) evaluate risks to fish and wildlife resources; and (c) develop tools to aid resource managers in detecting, averting, or minimizing the ecological consequences to fish and wildlife that are exposed to CECs. This report addresses objective (a) of the CEC Project, summarizing sediment and water chemistry data collected from 2010 to 2012 and fish liver tissue chemistry data collected in 2012; characterizes the sampling locations with respect to potential sources of CECs in the landscape; and provides an initial interpretation of the variation in CEC concentrations relative to the identified sources.

Data collected during the first three years of our study, which included 12 sampling locations and analysis of 134 chemicals, indicate that contaminants were more frequently detected in sediment compared to water. Chemicals classified as alkyphenols, flavors/fragrances, hormones, PAHs, and sterols had higher average detection frequencies in sediment compared to water, while the opposite was observed for pesticides, pharmaceuticals, and plasticizers/flame retardants. The St. Louis River and Maumee River sampling locations had the most CEC detections in water and sediment, relative to other sites, as well as the largest number of maximum detected concentrations across all sites in the Basin. No consistent temporal CEC occurrence patterns were observed at locations sampled multiple times each day. Most appearances and increases in chemical concentrations in sediments occurred at sites immediately downstream from wastewater treatment plants and at sites with predominantly developed land use. The location with the most observed appearances and increases was the St. Louis River. Perfluorinated compounds were commonly detected in fish liver tissues with detections in 100% of both benthic and pelagic species. The occurrence of these chemicals in liver tissue of benthic and pelagic species was generally similar.

Introduction

Although the environmental concentrations of the majority of contaminants of emerging concern (CECs) have not been fully characterized, previous surveys have shown that some CECs are ubiquitous in the environment, including pharmaceuticals, hormones, personal care products, current-use pesticides, plasticizers, and flame retardants. A national reconnaissance conducted by the U.S. Geological Survey (USGS) indicated the detection of at least one CEC in 80% of sampled streams (n=139) across 30 states (Kolpin et al., 2002). Apical effects of CEC exposure on biota in the environment are also largely unknown, although laboratory studies have shown that CECs can have detrimental effects on aquatic organisms (Weinberger and Klaper, 2013; Painter et al., 2009; Martinovic et al., 2007; Balch et al., 2004). Effects include altered reproduction through endocrine disruption to behavior modification and range from possible population level to organismal impacts (Ankley et al., 2003; Brion et al., 2004; Salierno and Kane, 2009; McGee et al., 2009). As part of the investigation into CEC occurrence in sediments, surface waters, and fish tissues in the Great Lakes Basin (CEC Project) by the U.S. Fish and Wildlife Service (FWS) and USGS, an ecotoxicology database was developed that summarizes the available laboratory research on the effects of CECs. Despite a growing body of knowledge, the majority of CECs have not been fully characterized in terms of their environmental concentrations or effects on fish and wildlife. Many of the known effects are sub-lethal, making impact quantification on individuals and populations difficult. These effects could alone, or when combined with other environmental stressors, significantly impact fish and wildlife health and populations. Threatened and endangered species are particularly vulnerable. Additionally, effects in the environment are often variable and do not necessarily follow patterns that would be expected based on the composition of CECs detected in the environment (Writer et al., 2010). The limited empirical data from laboratory studies do not always account for the cumulative, antagonistic, and synergistic effects of CEC mixtures. Yet, sources of CECs, including point sources such as municipal wastewater treatment plants (WWTPs) and combined sewer outfalls (CSOs), and non-point sources such as agricultural and urban runoff, often produce complex mixtures of both CECs and better recognized pollutants (Reif et al., 2012; Petrie et al., 2014). Given these complexities, considerable uncertainty remains regarding the cumulative consequences of CEC exposure to free-ranging fish and wildlife.

The CEC Project was designed with the objectives to (a) characterize the spatial and temporal distribution of CECs; (b) evaluate the risk to fish and wildlife populations; and (c) develop tools to aid resource managers in predicting, detecting, averting, or minimizing the ecological consequences of exposures to CECs in the Great Lakes Basin. This report addresses objective (a) of the CEC Project. Summarized in this report are the results of chemical data collected during the first three years of the study, including an overview of the presence and distribution of CECs in sediments, surface waters and fish tissues; a general characterization of sampling locations with respect to potential sources of CECs on the landscape; and an initial interpretation of the variation in CEC concentrations in sediment relative to identified sources. The information obtained from this study will be used to inform the remaining objectives of the CEC Project and to gain a better understanding of the sources, routes, and hazards of CEC exposure to fish and wildlife resources in the Great Lakes Basin.

Methods

Site Selection

Sampling locations were identified by targeting tributaries within the Great Lakes Basin that contained sources of CECs, including municipal wastewater treatment plans (WWTPs) and combined sewer outfalls (CSOs), and urban and agricultural inputs. Surface water and sediment (i.e., roughly the top 10 cm of sediment) samples were collected by FWS and USGS personnel in 12 Great Lakes water bodies located in Minnesota, Wisconsin, Michigan, Ohio, and New York between September 2010 and September 2012 (Figure 1; Tables 1 and 2). During 2010-2011, locations within Great Lakes Areas of Concern (AOC) tributaries with high human population densities and associated infrastructure were sampled. To reduce confounding effects from legacy contaminants, site selection was not limited to AOC tributaries and was expanded to capture potential non-point sources in 2012.

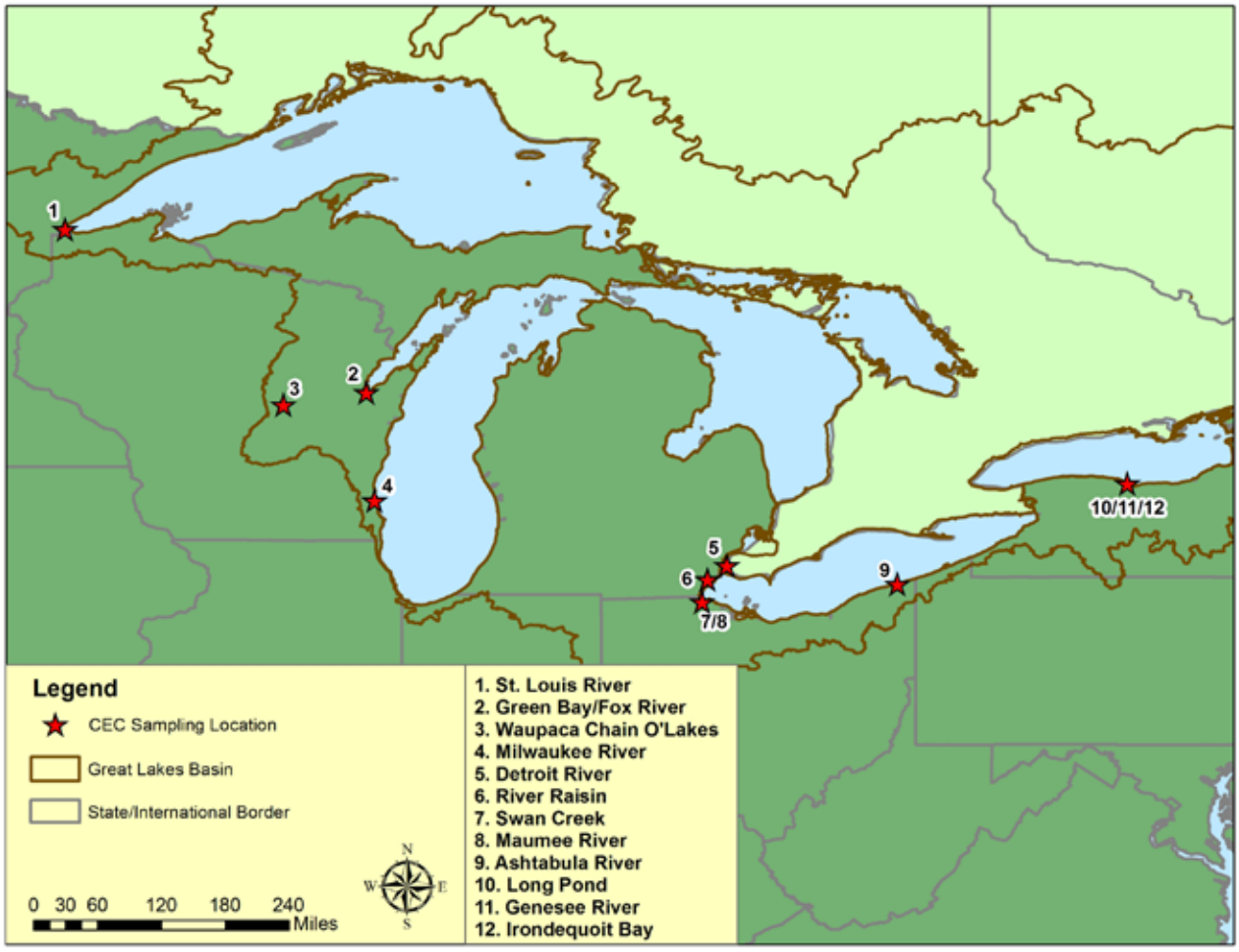

Figure 1. Contaminants of emerging concern sampling locations during 2010-2012.

Table 1. Number of sediment sampling events at each Great Lakes sampling location during 2010-2012.

Location				Number of Sampling Events				
State	**City**	**Water Body**	**Area of Concern**	**Fall 2010**	**Spring 2011**	**Spring 2012**	**Fall 2012**	**Total**
Minnesota	Duluth	St. Louis River^	St. Louis River	18	9	0	12	39
Wisconsin	Green Bay	Fox River^	Green Bay and Lower Fox River	6	3	5	0	14
Wisconsin	King	Waupaca Chain O'Lakes*^		0	0	2	0	2
Wisconsin	Milwaukee	Milwaukee River	Milwaukee Estuary	0	3	0	0	3
Michigan	Detroit	Detroit River^	Detroit River	6	3	0	0	9
Michigan	Monroe	River Raisin^	River Raisin	0	0	4	0	4
Ohio	Toledo	Swan Creek^	Maumee River	12	3	0	2	17
Ohio	Toledo	Maumee River^	Maumee River	0	0	7	9	16
Ohio	Ashtabula	Ashtabula River	Ashtabula River	0	3	0	0	3
New York	Rochester	Long Pond**^		0	0	6	0	6
New York	Rochester	Genesee River	Rochester Embayment	6	3	0	0	9
New York	Rochester	Irondequoit Bay**^		0	0	6	0	6
Total				48	27	30	23	128

*Baseline for Green Bay and Lower Fox River AOC; sampled at headwaters of watershed.
**Immediately adjacent and hydrologically connected to the Rochester Embayment AOC and formerly within the AOC boundary.
^2012 fish collection site.

Table 2. Number of surface water sampling events at each Great Lakes sampling location during 2010-2012.

Locations				Number of Sampling Events				
State	**City**	**Water Body**	**Area of Concern**	**Fall 2010**	**Spring 2011**	**Spring 2012**	**Fall 2012**	**Total**
Minnesota	Duluth	St. Louis River^	St. Louis River	21	4#	9	14	48
Wisconsin	Green Bay	Fox River^	Green Bay and Lower Fox River	6	4	6	0	16
Wisconsin	King	Waupaca Chain O'Lakes*^		0	0	2	0	2
Wisconsin	Milwaukee	Milwaukee River	Milwaukee Estuary	0	4	0	0	4
Michigan	Detroit	Detroit River^	Detroit River	6	4	3	0	13
Michigan	Monroe	River Raisin^	River Raisin	0	0	4	0	4
Ohio	Toledo	Swan Creek^	Maumee River	12	4	0	4	20
Ohio	Toledo	Maumee River^	Maumee River	0	2	7	10	19
Ohio	Ashtabula	Ashtabula River	Ashtabula River	0	3	0	0	3
New York	Rochester	Long Pond**^		0	0	6	0	6
New York	Rochester	Genesee River	Rochester Embayment	6	3	0	0	9
New York	Rochester	Irondequoit Bay**^		0	0	6	0	6
Total				51	28	43	28	150

*Baseline for Green Bay and Lower Fox River AOC; sampled at headwaters of watershed.
**Immediately adjacent and hydrologically connected to the Rochester Embayment AOC and formerly within the AOC boundary.
#Collected in August of 2011.
^2012 fish collection site.

Sample Collection

Field and laboratory methods, as well as quality control/quality assurance data, are provided in detail in Lee et al. (2012; 2015). During the 2010-2012 period, a total of 128 sediment and 275[1] surface water samples were collected and analyzed for a broad suite of compounds (103 analytes in sediment samples; 134 analytes in water samples) that are indicators of industrial, domestic, and agricultural influences. Prior to sample collection, water-quality properties (e.g., dissolved oxygen, temperature, pH, and specific conductance) were measured with a calibrated Yellow Springs Instrument (YSI) submersible sonde (YSI Incorporated, Yellow Springs, OH, USA)[2]. Unfiltered surface water samples were collected at mid-depth with a stainless steel weighted bottle sampler using a modified depth-integrated technique. Sediment samples were collected with a stainless steel Ekman grab sampler or other stainless steel coring equipment to obtain the most recently deposited (i.e., roughly the top 10 cm) sediment.

Fish were collected at a subset of the water and sediment sampling sites using a variety of methods including electrofishing and fyke and seine netting. Four littoral-zone fish species were targeted for analyses based on their representation of either a benthic or pelagic community. The benthic species included white suckers (*Catostomus commersonii*) and brown bullheads (*Ameiurus nebulosus*), and the pelagic species included smallmouth bass (*Micropterus dolomieu*) and largemouth bass (*Micropterus salmoides*). Morphometric data were recorded for each fish, and their livers, gills, kidneys, gonads and blood were extracted for histological analysis. The remaining carcasses were packed on wet ice in the field and then placed in long-term frozen storage at the FWS Field Offices. A sub-sample of 150 livers from fish collected in 2012 was submitted for the chemical analysis of 60 CECs.

Chemical Analyses

All sediment and water samples were analyzed at the USGS National Water Quality Laboratory in Denver, Colorado, USA, using the techniques detailed in Lee et al. (2012; 2015). Sediment and water samples were analyzed for a broad suite of wastewater indicators, steroidal hormones, and pharmaceuticals (Appendix A, Table A1). The wastewater schedule includes chemicals that are considered CECs as part of this project (e.g., antimicrobials, fragrances, plastic components, and surfactant metabolites) and chemicals that are not considered CECs (e.g., polycyclic aromatic hydrocarbons [PAHs]). All chemicals were evaluated and are presented. Briefly, wastewater indicators and steroidal hormones were extracted from sediment samples using pressurized liquid extraction (PLE) with an accelerated solvent extraction instrument and then determined using gas chromatography/tandem mass spectrometry (GC/MS/MS) methods. Steroidal hormones were determined using an isotope dilution standard (IDS) quantification procedure similar to that used for water samples. Pharmaceuticals were extracted from sediment samples with an acetonitrile/water (70/30) solvent using PLE. Pharmaceuticals were then determined using high-performance liquid chromatography/tandem mass spectrometry methods. Unfiltered water samples were also analyzed for wastewater indicators, steroidal hormones, and pharmaceuticals (Appendix A, Table A1). Wastewater indicators and pharmaceuticals were extracted from unfiltered water samples with methylene chloride in liquid-liquid extractors and then analyzed using capillary-column gas chromatography/mass spectrometry methods. Steroidal hormones were extracted from unfiltered water samples using solid phase extraction after IDS compounds were added to the samples and determined using GC/MS/MS methods.

A subset of 150 livers from fish collected in 2012 were submitted to ALS Environmental Laboratory in Kelso, Washington, USA, for analyses of a subset (n=60) of CECs (Appendix A, Table A2). This subset of CECs was selected based on CECs analyzed in sediment and water as well as available laboratory schedules. Samples were analyzed for pharmaceuticals, hormones and other known endocrine disrupting compounds (EDCs; modified EPA method 1694 [U.S. Environmental Protection Agency, 2007]) and perfluorinated compounds (PFCs; modified EPA method 537 [U.S. Environmental protection Agency, 2009a]). Additionally, eight samples from the Detroit River were submitted for brominated diphenyl ether (BDE) analysis. Brominated diphenyl ethers were extracted from samples using automated Soxhlet extraction (EPA method 3541; U.S. Environmental Protection Agency, 1994) and then analyzed using SIM-PAH (EPA method 8270D; U.S. Environmental Protection Agency, 2014) selective ion monitoring [SIM]). Insufficient liver mass was available to conduct all analyses in some samples due to a substantial fraction of the liver being used for histological analyses for biological endpoints. In these reduced mass liver samples, priority for analysis was given to pharmaceuticals, personal care products and specific EDCs, with 150 samples (61 benthic species samples and 89 pelagic species samples) analyzed for chemicals in these suites and 114 samples (46 benthic and 68 pelagic species samples) analyzed for PFCs.

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[1] Includes QA/QC samples that were not counted in Table 2.

[2] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

[3] For the temporal variation analyses, time series samples were analyzed separately.

[4] Sampling at these sites was coordinated with other projects evaluating CECs and funded under Focus Area 1 of

Quality Control/ Quality Assurance

To ensure sediment and water data integrity and assess variability and potential sources of contamination, both laboratory and field quality control measures were employed (Lee et al. 2012; 2015). Reagent-water blanks and spikes were included in every laboratory analysis to evaluate possible contamination and method performance over time. Surrogate compounds were also added to samples prior to extraction to monitor procedural performance. Environmental sample concentrations less than ten times a laboratory or field blank sample concentration were not used in analyses or given a value of "0". These environmental samples were excluded or given a value of "0" to reduce the possibility of false positives in the dataset while accepting that actual concentration maybe higher than zero. Laboratory spike and surrogate compound recoveries were generally within acceptable ranges (60-120%). Some compounds typically had lower laboratory spike sample recoveries, and thus their reported environmental concentrations may be biased low (e.g., 3,4-dichlorophenyl isocyanate, cotinine, *d*-limonene, tetrachloroethene, and bisphenol-A). No compounds had spike sample recoveries above the acceptable range. For some chemicals, the environmental concentrations were identified below the laboratory reporting level. Because the USGS National Water Quality Laboratory (NWQL) reports "information rich" data, an estimated value was reported when the chemical met the criteria for a positive identification, which was accepted as a detection and used in the analyses. Environmental concentrations that were detected at levels above the laboratory reporting levels were included in the data analysis, with the assumption that these concentrations may be above the reporting level used in the analysis and, as a result, biased low. Analytes that were detected as present but for which the concentration was low and not verified were not used in the data analysis (i.e., treated as "0"). Additionally, analytes found in blank samples, indicating potential field or laboratory contamination, were not used in the analysis.

For the fish liver samples, several measures were used to ensure the integrity of the chemical data, including method blanks, laboratory control samples, spiked-duplicate samples, and laboratory surrogates. Method blanks and laboratory control samples were used to evaluate sample contamination. Spiked-duplicate samples and laboratory surrogates were used to verify acceptable method recoveries. In accordance with ALS Environmental Laboratory quality assurance/quality control (QA/QC) procedures, environmental sample results less than 20 times the concentration found in the method blank were considered estimated and were included in the analyses. Generally, recovery and relative percent differences of matrix spikes were within acceptable laboratory ranges. Specific details are available in the QA/QC reports generated by ALS Environmental Laboratory and the FWS Analytical Control Facility. These reports are not published, but can be made available upon request to FWS.

Data Analysis

Further processing of the data presented in Lee et al. (2012; 2015) was completed to facilitate the data analyses included in this report, or summarize the dataset. Duplicate samples and their respective environmental sample as well as time series samples (i.e., samples that were collected at the same sites during the same time period on different days) were arithmetically averaged to create one value for the analyses . In the St. Louis River, multiple sampling sites were established in proximity to one another (due to combined sampling objectives). Chemical concentrations were summarized for all of the 2010 and 2011 samples from the Western Lake Superior Sanitary District (WLSSD), Minnesota Power (MP), and Fond du Lac (FDL) sites (Appendix D, Table D1) using the geometric mean. Descriptive statistics (including the minimum, maximum, geometric mean, and median concentration of all analytes across all sites and years) were calculated to summarize the data for sediment and water samples and can be found in Appendix B, Tables B1 and B2, respectively. Non-detects were assigned a "0" concentration value and thus excluded from the calculation of summary statistics. This was done to be consistent with the other data quality assurance procedures to reduce the possibility of over-reporting the presence and concentrations of some contaminants. As a result, the reported geometric means are biased high and represent the geometric mean of detections as opposed to the geometric mean of the environmental dataset. Analytes were also assigned to classes (Appendix A, Table A1) based on common chemical and/or use characteristics to better elucidate patterns in the presence and distribution of CECs and to provide an organized and consistent method of comparing the results (Table 3).

Table 3. Number of analytes analyzed in sediment and water samples.

	Number of CECs Analyzed in Sediment	Number of CECs Analyzed in Water
Alkylphenols	9	9
Flavors/Fragrances	8	8
Hormones	17	17
PAHs	9	9
Pesticides[1]	8	11
Pharmaceuticals	29	51
Plasticizers/Flame Retardants	9	9
Sterols	4	4
"Other" CECs[2]	10	16
Total	103	134

Frequency Evaluation

The detection frequency of chemical classes and individual CECs was calculated by dividing the number of detections by the total number of samples. For chemical classes, detections of one chemical or all chemicals within a class were counted as the same. Detects were defined as chemical concentrations measured in total samples above "0" per the QA/QC definitions described above

Locations and Sites with the Highest Concentrations

Preliminary analysis to determine patterns in the maximum concentrations of CECs in the Great Lakes focused on analytes with at least a 20% detection rate. The 20% threshold was used to better elucidate any patterns in the dataset and to remain consistent with the cluster analyses (see next section). In other words, the patterns in maximum concentrations may be easier to identify in CECs with high detection frequencies as opposed to CECs with relatively elevated concentrations at only a few sites. Additionally, elevated concentrations do not necessarily equate to effect potential.

Co-Occurring Chemicals

Patterns of chemical occurrence were assessed using cluster analyses. Dendrograms, showing clusters of the CECs and sites, were generated using hierarchical clustering of Euclidian distance matrices on rank-transformed data. The observed clusters indicate which chemicals were often detected together as well as sites at which co-occurring chemicals were detected. The rank-transformed CEC concentrations were used to remove skewness and are based on ranks of the maximum concentrations of each CEC at each sampling site. Given the small sample size and high prevalence of non-detect values, the maximum concentrations were used because of their ability to capture CEC occurrence; the arithmetic means were inappropriate due to the highly skewed distribution of the data, and the geometric means could not have been used due to the large amounts of non-detects. The data were further filtered to include only the CECs detected in at least 20% of the samples to facilitate the identification of CEC and site clusters. Cluster dendrograms, combined with a heatmap graphic, were generated using the *heatmap.2* routine of the *gplots* package (Warnes et al., 2015) for the statistical program *R* (R Core Team, 2015).

Temporal Variation

Water chemistry was analyzed for temporal relationships through visual inspection of time series graphs. The time at which time series samples were collected was plotted on an x-axis and concentration was plotted on a y-axis to help identify patterns such as specific times of day when chemical concentrations or number of chemicals detected were highest (Appendix C, Figures C9 through C15). In 2012, water samples were taken at different times of the day and on different days during both the spring and fall in the St. Louis River and during the fall in the Maumee River.

Location and Site Characterization

Spatial patterns in the presence and distribution of CECs relative to potential point and non-point sources were evaluated at each location. Possible point sources were identified utilizing the U.S. Environmental Protection Agency's (EPA's) Facility Registry Services database to identify National Pollutant Discharge Elimination System (NPDES) permittees (U.S. Environmental Protection Agency, 2016). The NPDES permit program is responsible for the regulation of point-source dischargers of regulated pollutants (not CECs) into surface waters and includes WWTPs. Other datasets used to evaluate potential point sources of CECs included locations of concentrated animal feeding operations (CAFOs) and CSOs and were obtained by request from state and federal agencies.

To evaluate potential non-point sources of CECs, percentages of land use types within target watersheds were calculated using the 2006 version of the USGS National Land Cover Database (NLCD; Fry et al., 2011). For the Canadian portion of the Detroit River watershed, the Ontario Ministry of Natural Resources' Provincial Land Cover 2000 dataset was used to identify land cover (Smyth, 1999). The land cover classifications defined in the Provincial Land Cover dataset were combined to best match the classifications used for the NLCD. The "Extract by Mask" tool in *ArcMap* 10.2.2 was used to delineate land use data within the relevant watersheds (Environmental System Research Institute, 2014). The number of pixels corresponding to each land use type was then divided by the total number of pixels in the watershed raster dataset to obtain the percentage by land use type for each watershed included in our study. The pixels in the NLCD dataset measure 30m x 30m. The watershed level used for the mask was determined by the analysis. For example, in order to describe a sampling location as a whole, the smallest hydrologic unit code (HUC) that encompassed all sites within the sampling location was used; the USGS 8-digit HUC (U.S. Geological Survey, 1999) was used for most sites. If a specific sampling site was being characterized compared to other sites within the same location, smaller hydrologic units (e.g., 12-digit HUC, or HUC-12) in which the sampling site was located were used. A description of the land use classes can be found in Table 4 and Appendix D, Table D2, and a color code for land use in site maps can be found in Figure 2. For simplicity, the "Planted/Cultivated" land use class is referred to as "agricultural" in this report.

Potential sources of CECs at each location were further investigated by comparing sample site data upstream and downstream from potential sources. The data were analyzed for the occurrence of increases and/or appearances in sediment CEC concentrations. An "increase" at a sampling site was defined as a 2-fold or greater increase relative to the sampling site immediately upstream. A CEC concentration "appearance" was defined as an occurrence in which a chemical was reported as a non-detect (see Quality

Control/Quality Assurance section) but was then detected at the next sampling site downstream. An upstream point source was considered "near" or "in the vicinity" of a sampling site if it was within 1km of the site. Although the initial, spatially coarse analysis included in this report represents a step toward identifying potential significant sources of CECs in the study area, it should be noted that the analysis is based on grab samples that represent a "snapshot" of the CEC concentrations in space and time rather than a more integrated index. A detailed source analysis is beyond the scope of this report; an additional, more in-depth evaluation of contaminant source is ongoing. Summarized watershed information, including the drainage area and average streamflow during sampling periods, number of WWTPs, number of CSOs, and dominant land use, is provided in Table 5.

[3] For the temporal variation analyses, time series samples were analyzed separately.

[4] Sampling at these sites was coordinated with other projects evaluating CECs and funded under Focus Area 1 of the Great Lakes Restoration Initiative.

[5] For the purposes of this report, all insecticides, herbicides and pesticides were categorized as pesticides.

[6] The "Other" category included CECs that did not fit well within any of the other defined classes of CECs.

Table 4. Land cover classifications used for sites sampled during 2010-2012 for the presence of CECs. Classifications and descriptions are based on the USGS 2006 National Land Cover Dataset (see Appendix D, Table D2, for full descriptions).

Land Use Classification	Classification Description
Water	Areas of open water, with generally less than 25% cover by vegetation or soil.
Developed	Areas with a mixture of constructed materials, vegetation (in the form of lawn grasses), and impervious surfaces. Includes green spaces, parks, golf courses, single-family housing units, apartment complexes, and commercial and industrial developments.
Barren	Areas of bedrock, scarps, talus, glacial debris, sand dunes, strip mines, gravel pits, and other accumulations of earthen material; vegetation generally accounts for less than 15% of the total cover.
Forest	Areas dominated by trees greater than 5 meters tall and greater than 20% of the total vegetation.
Shrubland	Areas dominated by shrubs less than 5 meters tall with a shrub canopy that is typically greater than 20%.
Herbaceous	Areas dominated by herbaceous vegetation, generally greater than 80% of the total vegetation.
Planted/Cultivated (Agriculture)	Areas of grasses, legumes, or grass-legume mixtures planted for livestock grazing or the production of seed or hay crops, and/or areas used for the production of annual crops; crop vegetation accounts for greater than 20% of the total vegetation.
Wetland	Areas where forest and shrubland or herbaceous vegetation account for greater than 20% or 80% of the vegetative cover, respectively, and the soil or substrate is periodically saturated with or covered with water.

Table 5. General background information for focal watersheds. The smallest watershed unit (i.e., U.S. Geological Survey HUC) that encompassed all sites at each location was used for the general site description; descriptions of smaller watersheds within a larger unit that contained individual sites or sub-sets of individual sites are provided where necessary in the text. Sampling periods for streamflow statistics determined by sampling dates at each site; all available years of data were used to calculate average streamflow (USGS, 2016).

Sampling Location	Watershed Name	Hydrologic Unit Code	Drainage Area (km^2)	Average Streamflow Spring Sampling Periods (m^3/s)	Average Streamflow Fall Sampling Periods (m^3/s)	Number of Wastewater Treatment Plants in Watershed	Number of Combined Sewer Outfalls in Watershed	Dominant Land Use in Watershed
Saint Louis River	St. Louis and Cloquet	8	9665.56	162	24.4	4	0	Wetland
Fox River	Lower Fox	8	1678.62	160	161	6	0	Agriculture
Waupaca Chain O'Lakes	Waupaca River	10	745.98	--	--	1	0	Agriculture
Milwaukee River	Milwaukee	8	2276.51	22.3	--	6	113	Developed
Detroit River	Detroit	8	2298.10	5530	5050	6	123	Developed (U.S.); Agriculture (Canada)
River Raisin	Raisin	8	2753.30	14.2	--	4	1	Agriculture
Swan Creek	Upper and Lower Swan Creek	10	529.93	6.90*	1.10*	0	19	Agriculture
Maumee River	Lower Maumee	8	2791.62	41.7	15.62	6	93	Agriculture
Ashtabula River	Ashtabula-Chagrin	10	353.97	6.91**	--	1	0	Forest
Long Pond	Black-Creek-Frontal Lake Ontario	10	182.75	--	--	1	0	Developed
Genesee River	Lower Genesee	8	2763.59	101*	29.5*	6	4	Agriculture
Irondequoit Bay	Irondequoit Creek-Frontal Lake Ontario	10	513.36	--	--	1	2	Developed

*Averaged historical data; recent data unavailable.
**Averaged historical and incomplete data; recent complete data unavailable.

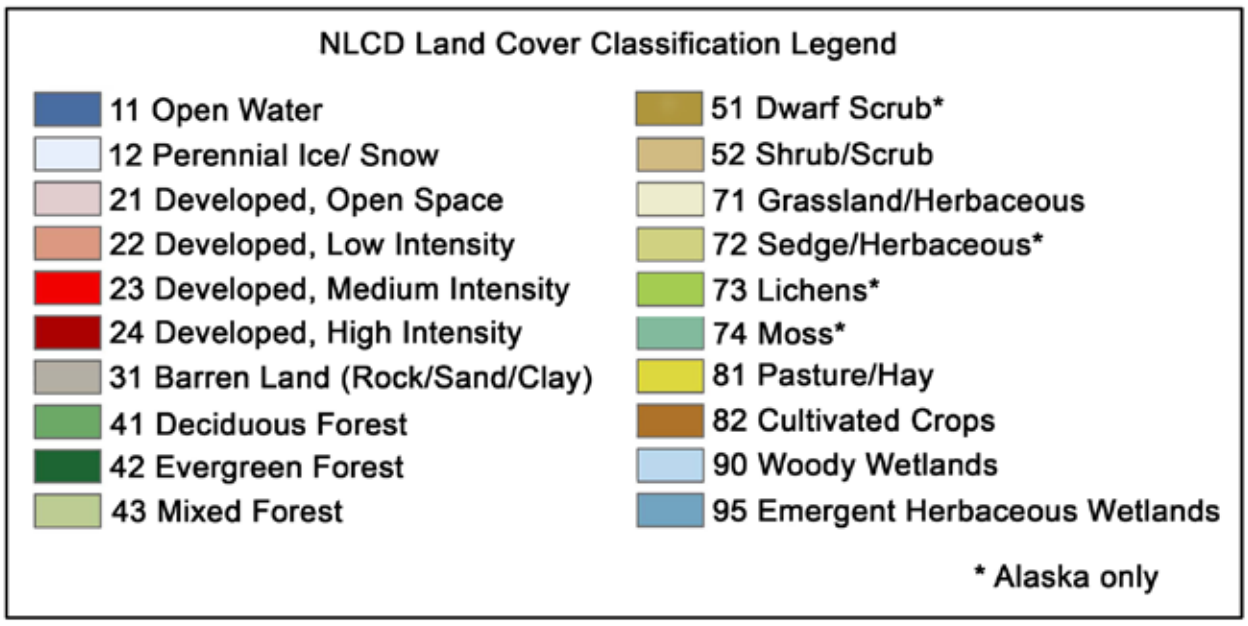

Figure 2. Color codes of land cover classifications (Fry et al., 2011).

St Louis River

The St. Louis River watershed is dominated by wetlands (46%) and forests (35%), with developed land composing only 4% of the drainage. Two WWTPs and a power plant are the primary point sources that were identified in the sampling reach of the lower St. Louis River (Table 5; Figure 3; Appendix D, Figures D1 through D6). Four groups of sampling sites were sampled in 2010 and 2011 within the lowest part of the watershed, encompassing approximately 70 river kilometers: Fond du Lac (FDL), Minnesota Power (MP), Duluth WWTP (WLSSD), and Superior WWTP (SMTP). Site names and identifiers are as presented in Lee et al. (2012; 2015) and were selected using nearby land markers or businesses and do not necessarily indicate CEC influence. The MP, WLSSD, and SMTP sites are in a sub-watershed that is characterized by a much higher percentage of developed land use than the watershed as a whole (42%), and the WLSSD and SMTP sites are also located near WWTP outfalls. In 2012, 15 sampling sites were added to increase the spatial coverage of the CEC sampling to more fully characterize the distribution and presence of CECs throughout the Lower St. Louis River. These additional sites were mostly located upstream from the WLSSD site in areas of the watershed that include some urban influence but are more generally representative of the watershed as a whole.

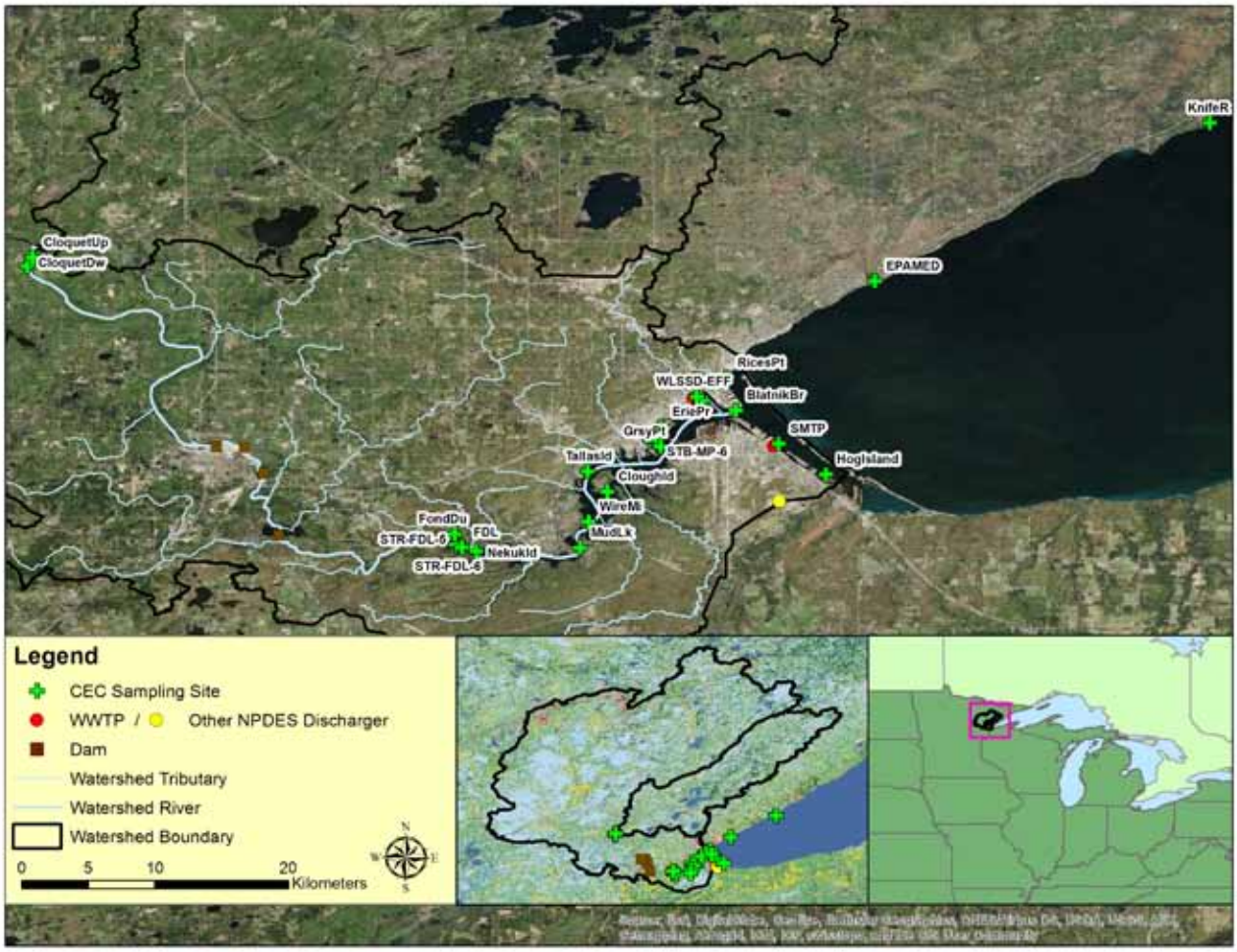

Figure 3. Overview map of the St. Louis River sampling location.

Green Bay and Lower Fox River

The Lower Fox River watershed is dominated by agriculture (55%); however, the samples collected in 2010 and 2011 were concentrated in the downstream reach of the Fox River, where urban developed land use is more prevalent. In 2012, sites were added to the middle stretch of the Fox River to capture the potential agricultural influences that are more representative of the watershed as a whole. Six known WWTPs discharge into the Fox River, although three are at least 10km upstream from the sampling reach, which extends approximately 30 river kilometers from the river mouth (Table 5; Figure 4; Appendix D, Figures D7 and D8). Samples were also collected in the Waupaca Chain O'Lakes to compare surface water and sediment chemistry between the headwaters of the watershed and the sample reach (Table 5; Appendix D, Figure D9). The Waupaca Chain O'Lakes is located within the Waupaca River sub-watershed and is dominated by agricultural land use (51%). Developed land in this sub-watershed occupies only 7% of the land area, compared with 30% in the Lower Fox River. No WWTPs are located upstream from the Waupaca Chain O'Lakes sampling location, although septic systems are likely common.

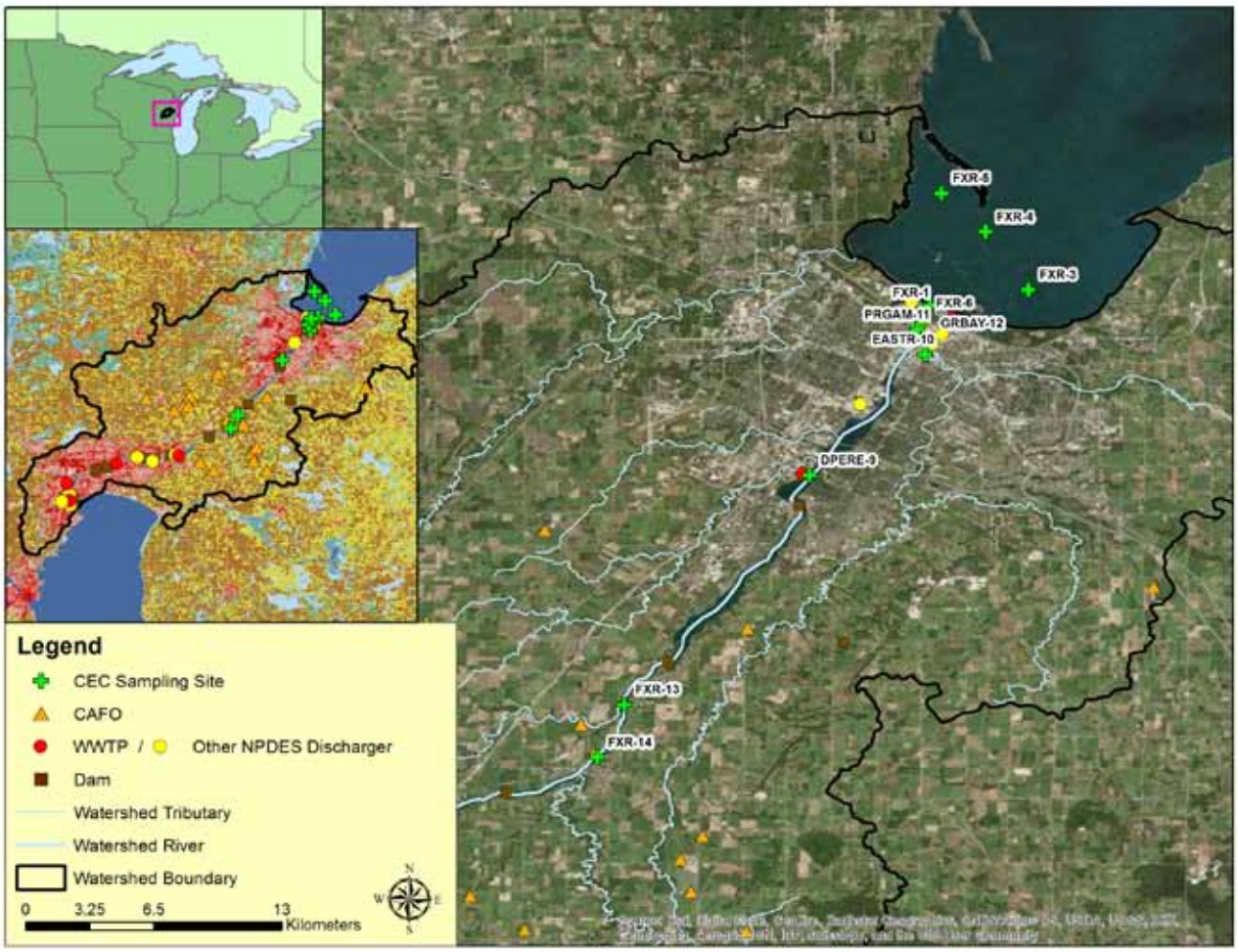

Figure 4. Overview map of the Green Bay and Lower Fox River sampling location.

Milwaukee River

The Milwaukee River watershed contains three major branches: the Milwaukee River, Kinnickinnic River, and Menomonee River. When analyzed as one unit, the watershed is dominated by agricultural land use (43%), followed by developed land use (30%). Sampling sites were located near the lower part of the watershed, where developed land use is concentrated. Point sources in the sampling reach (which includes all three major tributaries) include many CSOs and a WWTP. Five additional WWTPs are located in the upper parts of the watershed (i.e., more than 30km upstream from the closest sampling site), which extends approximately three river kilometers up the Kinnickinnic and Menomonee Rivers and five river kilometers up the Milwaukee River (Table 5; Figure 5; Appendix D, Figure D10).

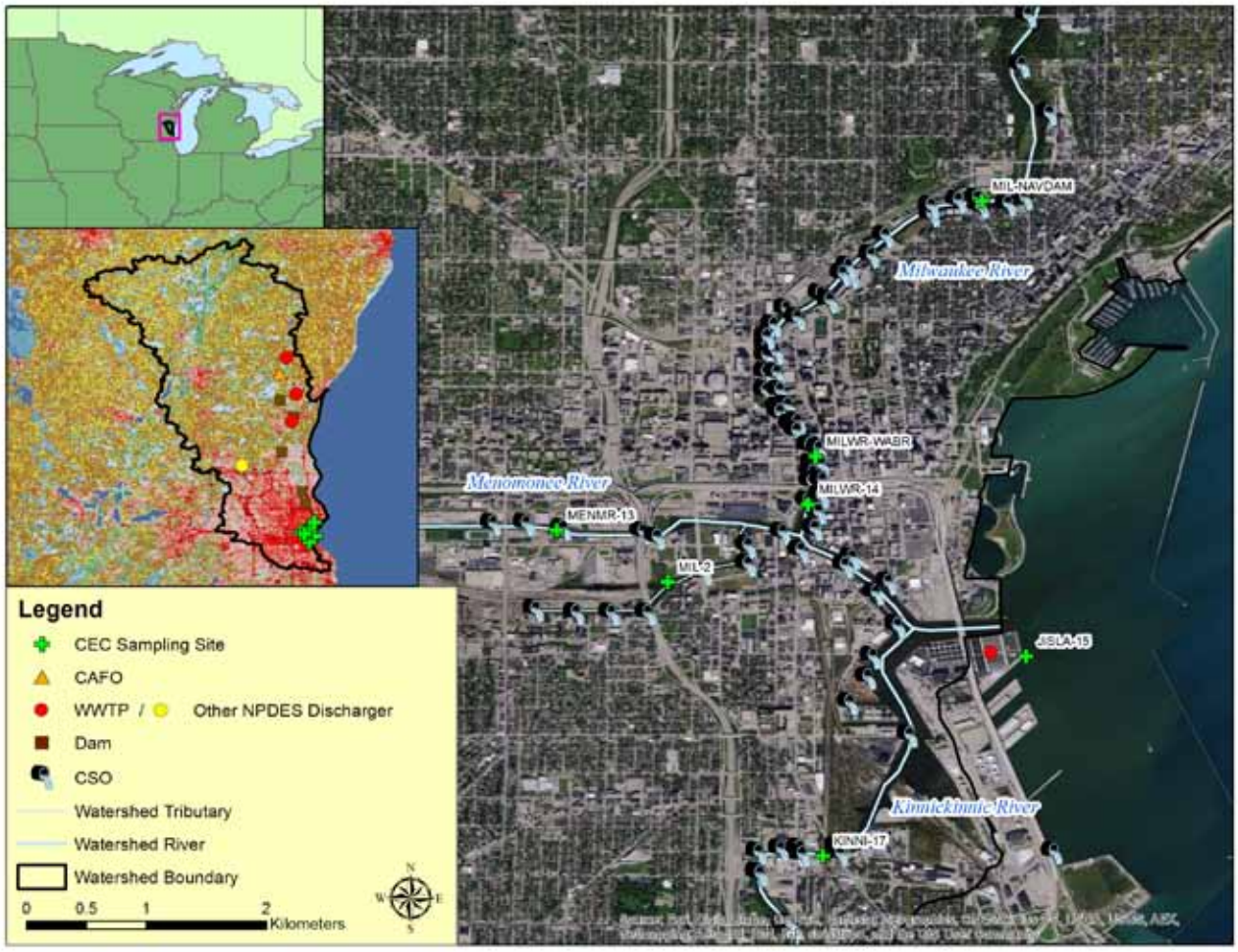

Figure 5. Overview map of the Milwaukee River sampling location.

Detroit River

The Detroit River watershed is heavily influenced by developed land use on the U.S. shoreline (85%) and agricultural land use on the Canadian shoreline (98%). Potential point sources of CECs include CSOs located on the main stem of the Detroit River and along the River Rouge, a tributary of the Detroit River. Additionally, four WWTPs and 10 other NPDES dischargers are located on the U.S. side within the sampling area, which encompasses approximately 26 river kilometers; two other WWTPs and many CSOs are located in the upper part of the watershed (Table 5; Figure 6; Appendix D, Figures D11 and D12).

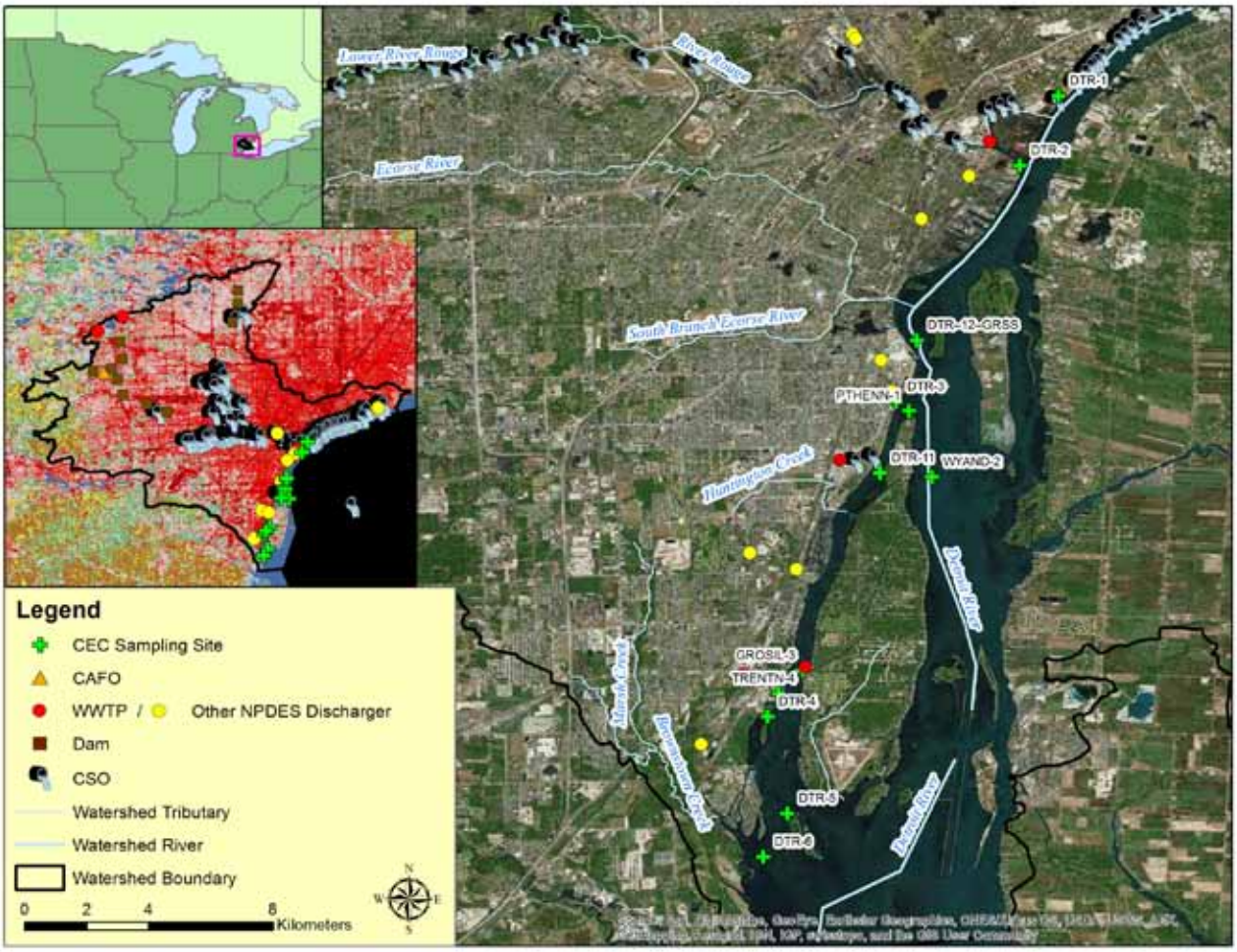

Figure 6. Overview map of the Detroit River sampling location.

River Raisin

The River Raisin watershed is similar to many other locations with respect to the high proportion of agricultural land use (67%). Sampling locations (for 2012 only) were located near the mouth of the River Raisin at its confluence with Lake Erie, where a relatively small proportion of developed land (11%) is concentrated. One WWTP is located within the sampling reach, which occupies just over seven river kilometers of the River Raisin; 3 other WWTPs are located in the upper part of the watershed (Table 5; Figure 7; Appendix D, Figure D13).

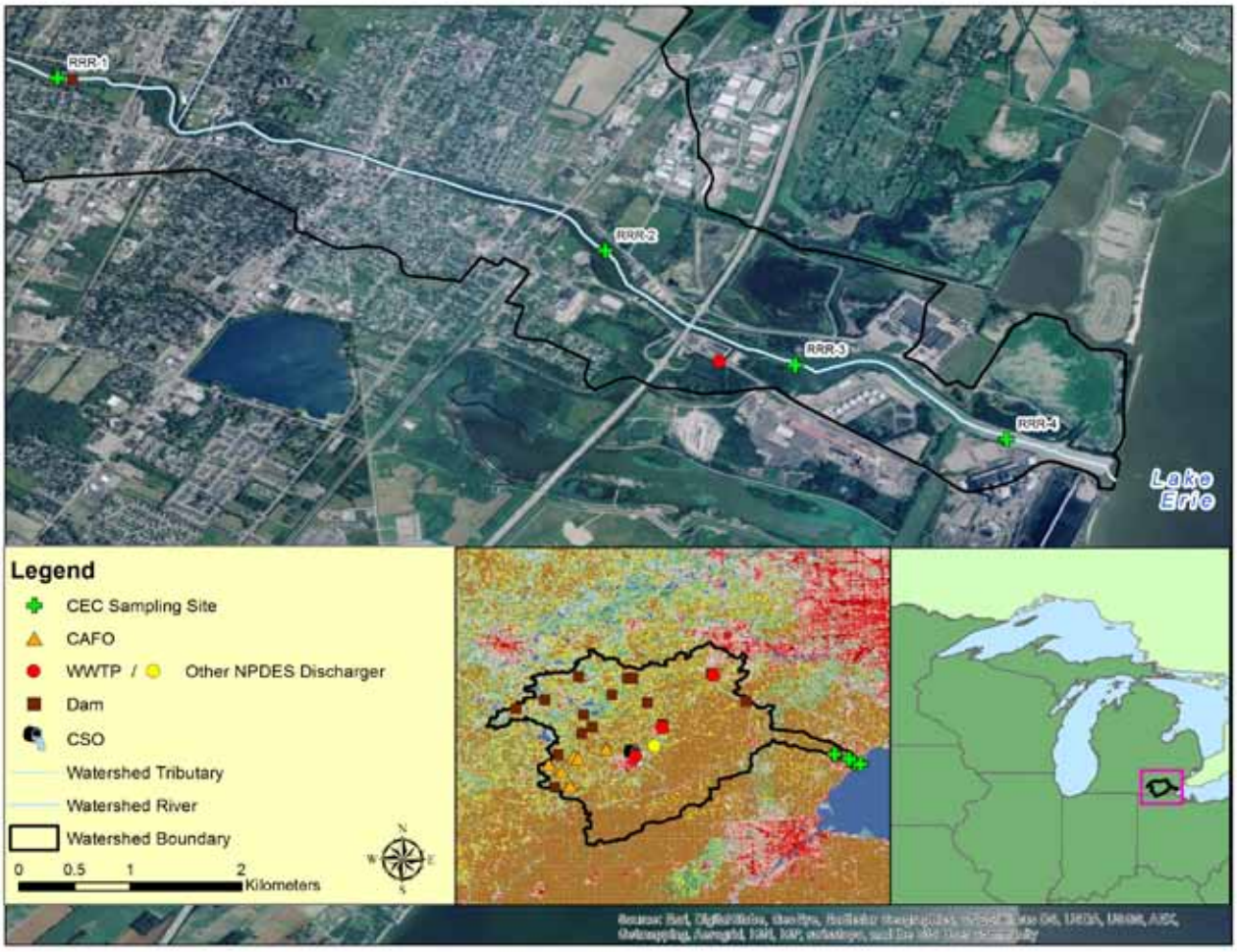

Figure 7. Overview map of the River Raisin sampling location.

Maumee River and Swan Creek

The Lower Maumee River watershed is characterized by agricultural land use (76%), primarily in the upstream reaches. The Swan Creek sub-watershed is located in the lower reaches of the Lower Maumee River watershed. Although the primary land use is also agricultural within the Upper and Lower Swan Creek sub-watersheds (55%), developed land occupies a greater percent area (23%) than in the larger Lower Maumee River watershed as a whole (14%). All but three of the sampling sites are located in the lower reaches of the Lower Maumee River watershed, where three WWTPs and many CSOs are located. The sampled reach of the Maumee River measures approximately 50 river kilometers. Sites sampled in 2011 extended furthest upstream in the sampling reach in order to capture agricultural influence, whereas the sites in 2012 focused on CSO and WWTP influences in the downstream reaches of the river (Table 5; Figure 8; Appendix D, Figures D15 through D17).

Swan Creek offered a unique opportunity to sample a small tributary that is heavily influenced by CSOs. The Heilman Ditch-Swan Creek sub-watershed is composed of 54% developed land with seven CSOs that empty directly into the sampling area, which extends approximately five river kilometers up Swan Creek from its confluence with the Maumee River (Table 5; Figure 8; Appendix D, Figure D14).

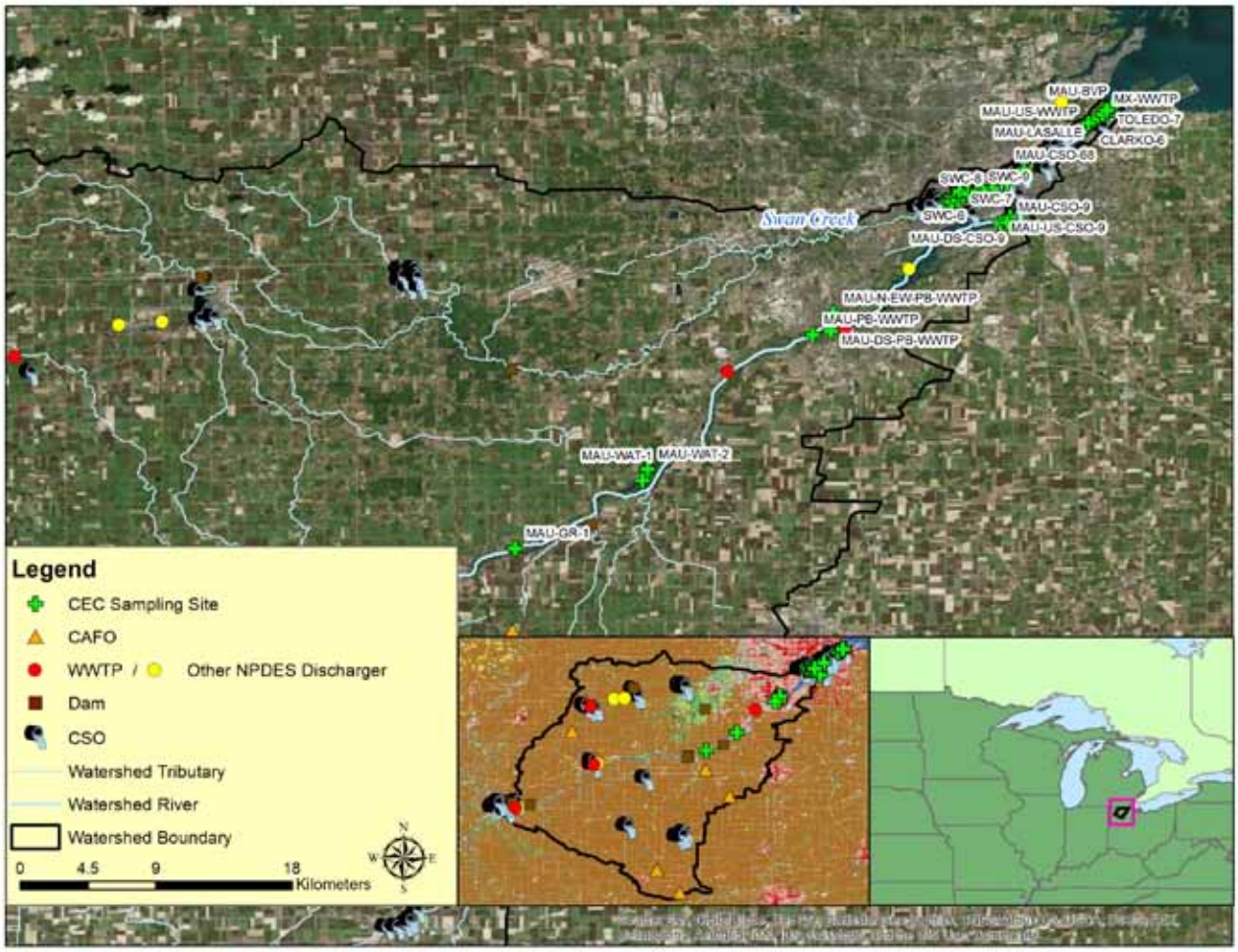

Figure 8. Overview map of the Muamee River and Swan Creek sampling location.

Ashtabula River

The Ashtabula-Chagrin watershed is dominated by forest (42%), followed by agriculture (35%). However, as with most other locations, the sampling sites at this location are located in the downstream segment of the river where a small area of developed land (12%) is concentrated. A WWTP is located in the sub-watershed, although it is unclear where the discharge is located. The sampling reach is relatively small, encompassing just over two river kilometers of the Ashtabula River (Table 5; Figure 9; Appendix D, Figure D18).

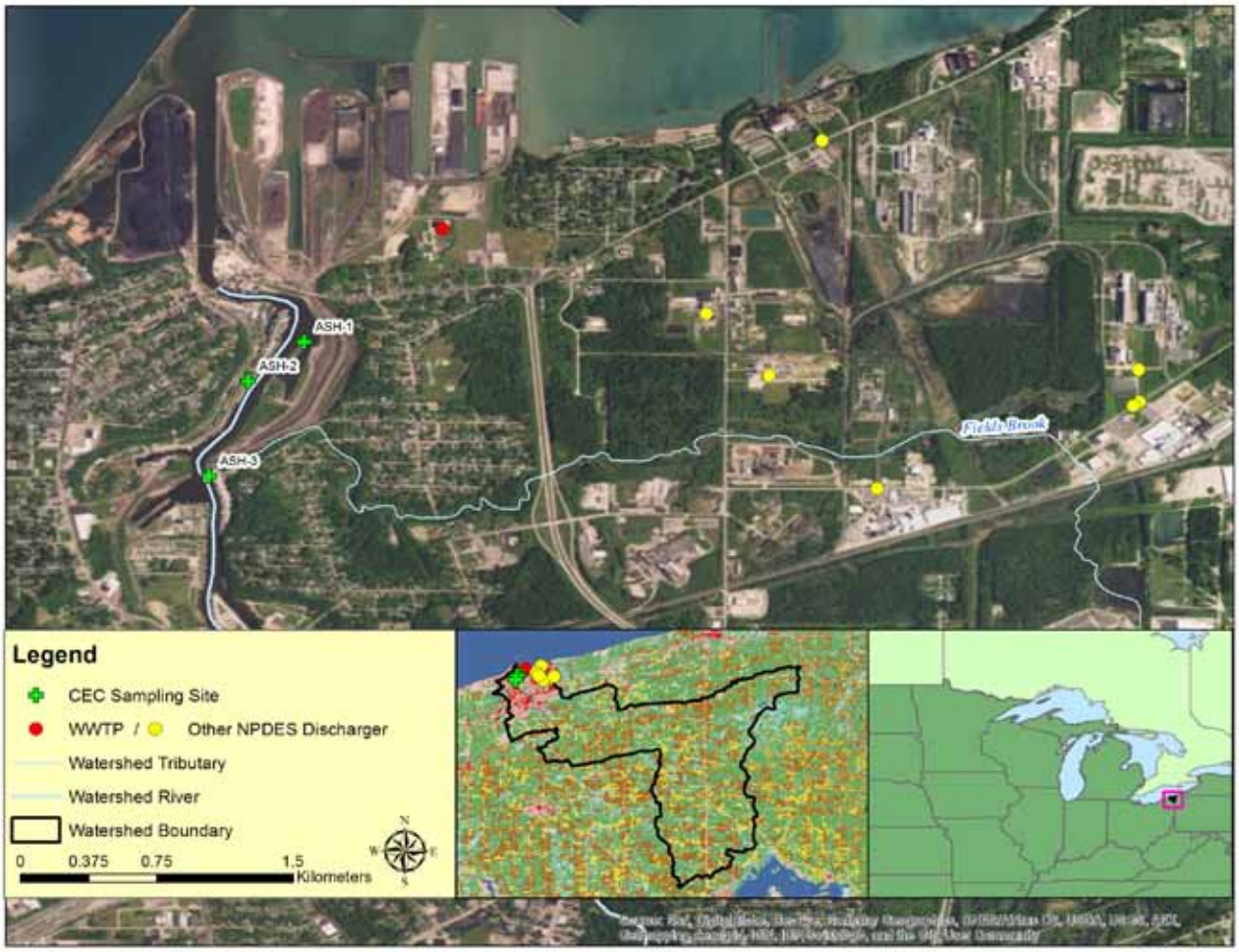

Figure 9. Overview map of the Ashtabula River sampling location.

Long Pond, Genesee River and Irondequoit Bay

Although the Long Pond, Genesee River, and Irondequoit Bay sampling locations are in three different watersheds, all three are associated with the Rochester Embayment AOC. The lower Genesee River is within the current AOC boundary. Long Pond and Irondequoit Bay are immediately adjacent and hydrologically connected to the Rochester Embayment AOC and were formerly within the AOC boundary. Each location is characterized by distinct patterns of land use. The Lower Genesee River watershed consists mostly of agricultural land use (55%), but the sampling sites are located near the mouth of the river, where developed land use is concentrated. As a whole, developed land use makes up only 11% of the total watershed. The Irondequoit Bay and Long Pond sampling sites are located in the Irondequoit Creek-Frontal Lake Ontario and Black Creek-Frontal Lake Ontario watersheds, respectively. The Black Creek-Frontal Lake Ontario watershed is dominated by developed land use (46%), but the sampling sites are located in an area that is surrounded by forest. The Irondequoit Creek-Frontal Lake Ontario watershed is also dominated by developed land use (45%), but the sampling sites are located where agriculture is also a major influence. A WWTP and CSOs are present in the sampling reach of the Genesee River, which includes nearly eight river kilometers; the remaining WWTPs and CSOs are in the upper part of the Genesee River watershed. Although WWTPs also exist in the Irondequoit Creek-Frontal Lake Ontario and Black Creek-Frontal Lake Ontario watersheds, none are within any of the sampling reaches. However, both Long Pond and Irondequoit Bay have been heavily impacted by upstream WWTP discharge (Sherwood, 2004). The sampling reaches of Long Pond and Irondequoit Bay are each approximately three kilometers (Table 5; Figure 10; Appendix D, Figures D19 through D21).

Similar to sediment and water chemistry, summary statistics (i.e., minimum, maximum, geometric mean, and median) were generated for the fish liver tissue chemistry to summarize the dataset. The results were grouped by community (i.e., benthic or pelagic) to account for the different exposure pathways that may result in differing effects (Appendix B, Tables B3 and B4).

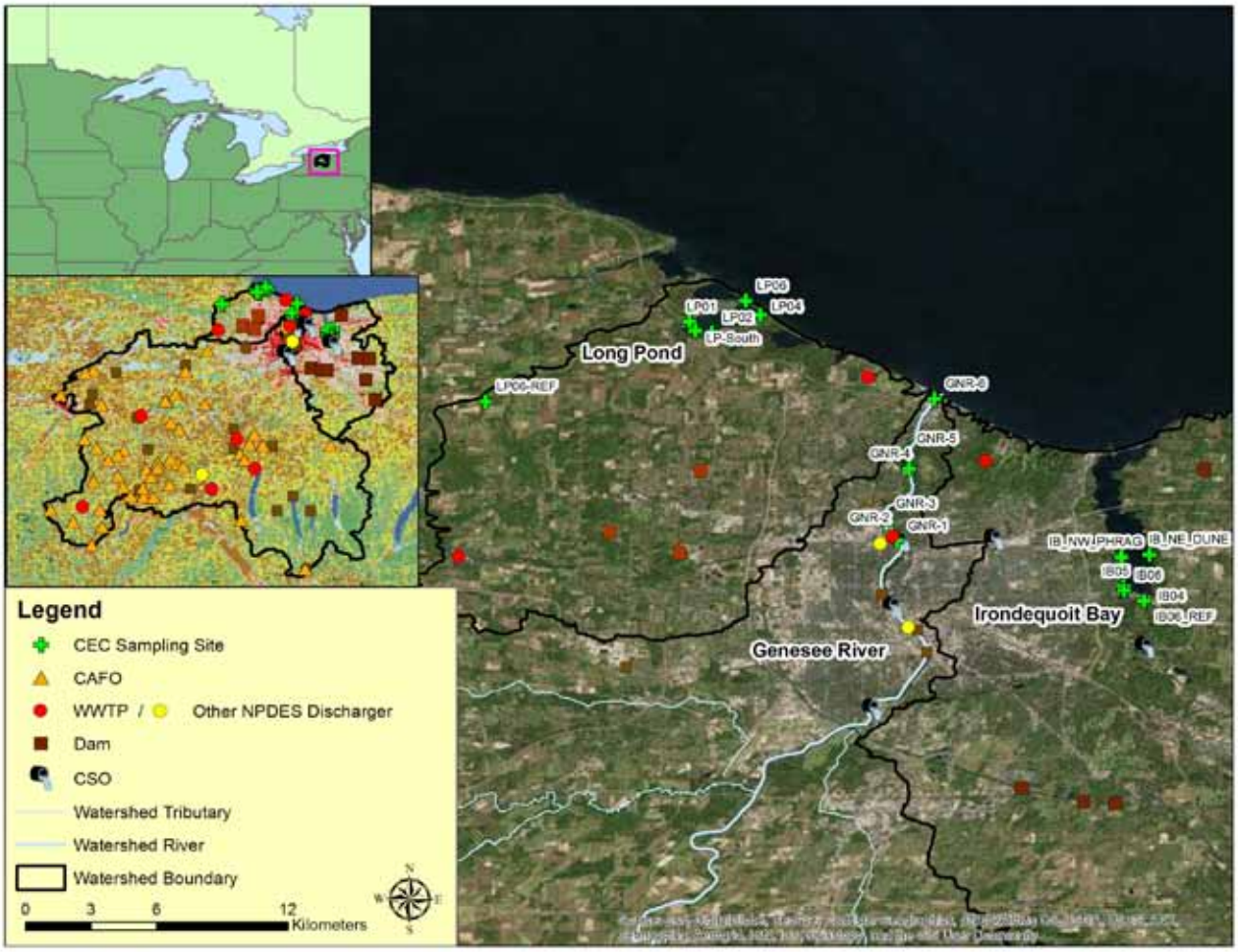

Figure 10. Overview map of the Long Pond, Genesee River and Irondequoit Bay sampling location.

Results and Discussion

Frequency Evaluation

In general, individual CECs were more frequently detected in sediment than in water samples across all sites during 2010-2012. On average, 22% of CECs were detected in sediment samples (n=107), while 11% of CECs were detected in water (n=127 samples). Indole, a flavor/fragrance, was the most commonly detected CEC in sediment (99% of samples). The second most frequently detected chemical in sediment was cholesterol, a sterol, which was detected in 98% of the samples. At least one chemical in the PAH, alkylphenol, pesticide, hormone, and "other" CEC classes was detected in more than 50% of the sediment samples. The CECs that were generally more frequently detected in sediment compared to water were alkylphenols, flavors/fragrances, hormones, PAHs, and sterols (Figures 11-12; Appendix B, Tables B1 and B2).

In contrast to the sediment samples in which 22 chemicals representing all chemical classes were detected in more than 50% of samples, only four chemicals representing two classes were detected in greater than 50% of the water samples. The sterol cholesterol, the most commonly detected chemical in water samples, was detected in 98% of the surface water samples. The pesticides metolachlor, N,N-diethyl-meta-toluamide (DEET), and atrazine were detected in 66%, 65% and 60% of water samples, respectively. Pesticides, pharmaceuticals, and plasticizers/flame retardants were generally more frequently detected in water compared to sediment (Figures 11-12; Appendix B, Tables B1 and B2). The octanol-water partition coefficient (log K_{ow}), which can be used as one indicator of a chemical's tendency to partition into organic soils, did not appear to account for the observed frequency of detection in the sampling media (U.S. Environmental Protection Agency, 2009b; Table 6; Appendix A, Table A1). The chemical properties of CECs will be further analyzed as a part of meeting CEC Project objectives (b) and (c) to determine whether there is a relationship between the K_{oc} (measure of chemical partitioning to organic carbon) and partitioning in sampling media. Notably, many pharmaceuticals have an acid dissociation constant (pK_a) near common environmental pH ranges, and these particular organic chemicals can exhibit a different chemical charge between sampling locations, potentially affecting their partitioning characteristics between water and sediment (Rendal et al., 2011).

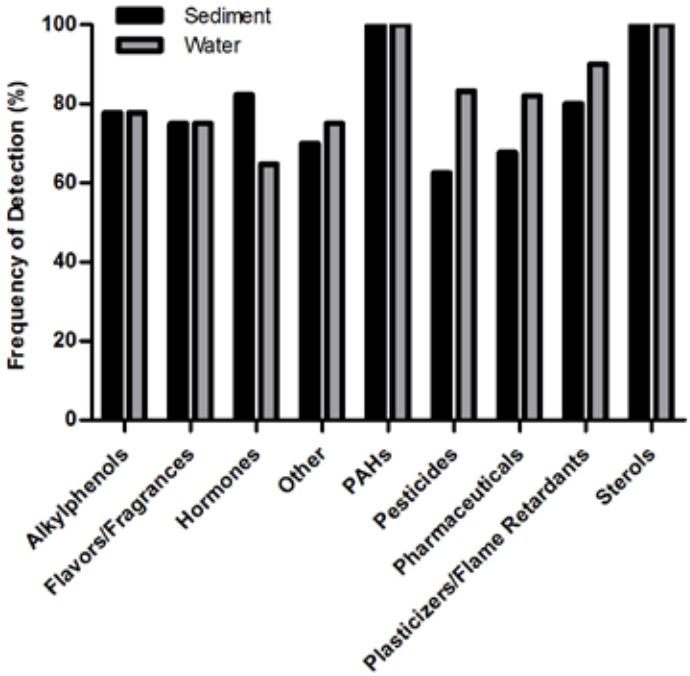

Figure 11. Frequency of Detection (%) of chemical classes in sediment and water across all sites and years (2010-2012).

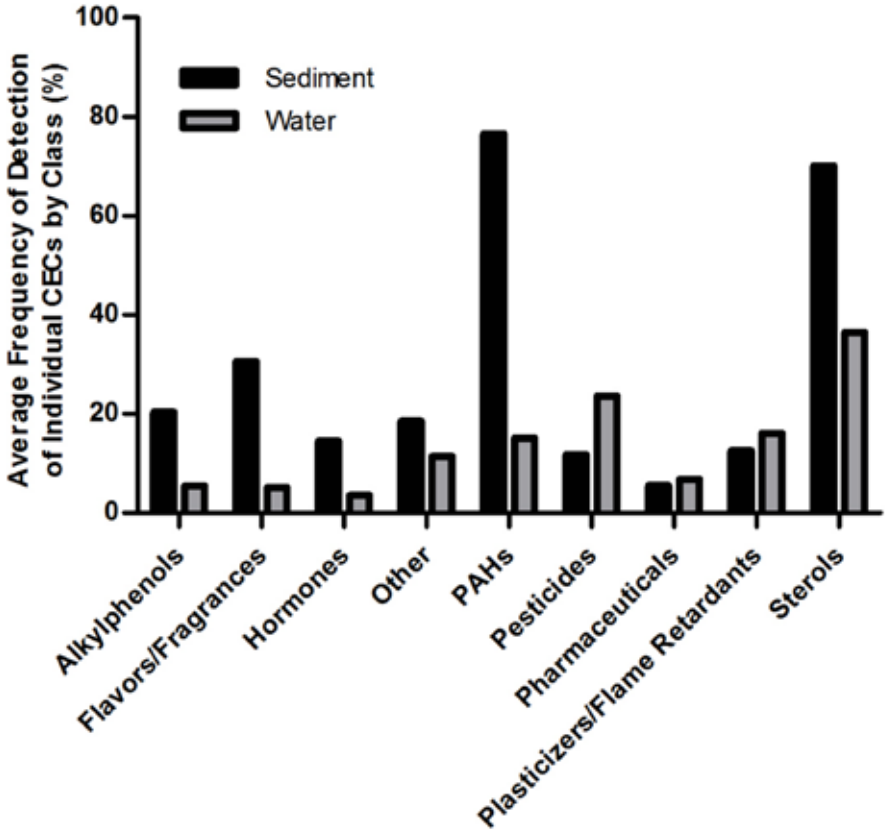

Figure 12. Average frequency of detection of individual CECs grouped by chemical class in sediment and water across all sites and years (2010-2012).

Table 6. Average log K_{ow} of CEC chemical classes.

Class	Average log K_{ow}
Alkylphenols	4.96
Flavors/Fragrances	3.66
Hormones	3.55
"Other" CECs	2.79
PAHs	3.01
Pesticides	2.44
Pharmaceuticals	4.24
Plasticizers/Flame Retardants	4.49
Sterols	9.58

Locations and Sites with the Highest Concentrations of Individual CECs

The highest concentrations of individual CECs with at least a 20% detection rate in sediment and surface water samples were most often recorded in the St. Louis and Maumee River/Swan Creek systems (Figures 13 and 14). These locations were the most extensively evaluated of the 12 locations between fall 2010 and fall 2012. Relative to all other sampling locations, the St. Louis River sites had the highest concentrations of hormones, "other" CECs, PAHs, and pharmaceuticals in sediments. The Maumee River/Swan Creek sites had the highest concentrations of alkylphenols, PAHs, and sterols in sediments and the highest concentrations of flavors/fragrances, "other" CECs, pharmaceuticals, and plasticizers/flame retardants in surface waters relative to all other locations.

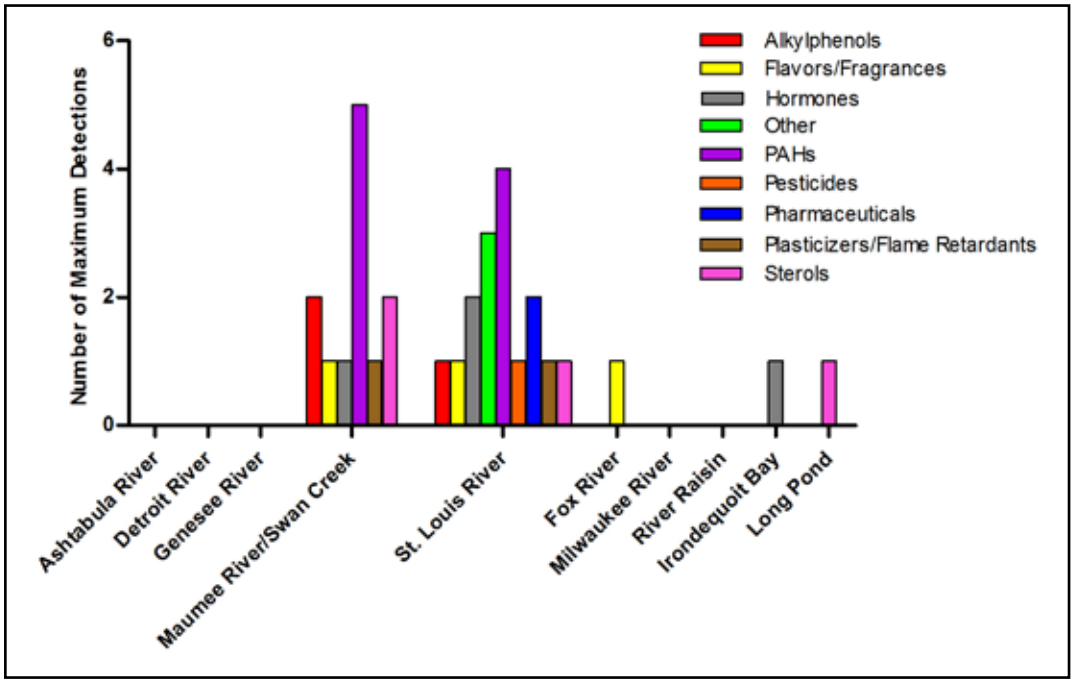

Figure 13. Number of detections of the highest sediment concentrations of individual CECs by class relative to all sites across all years for CECs with at least a 20% detection rate.

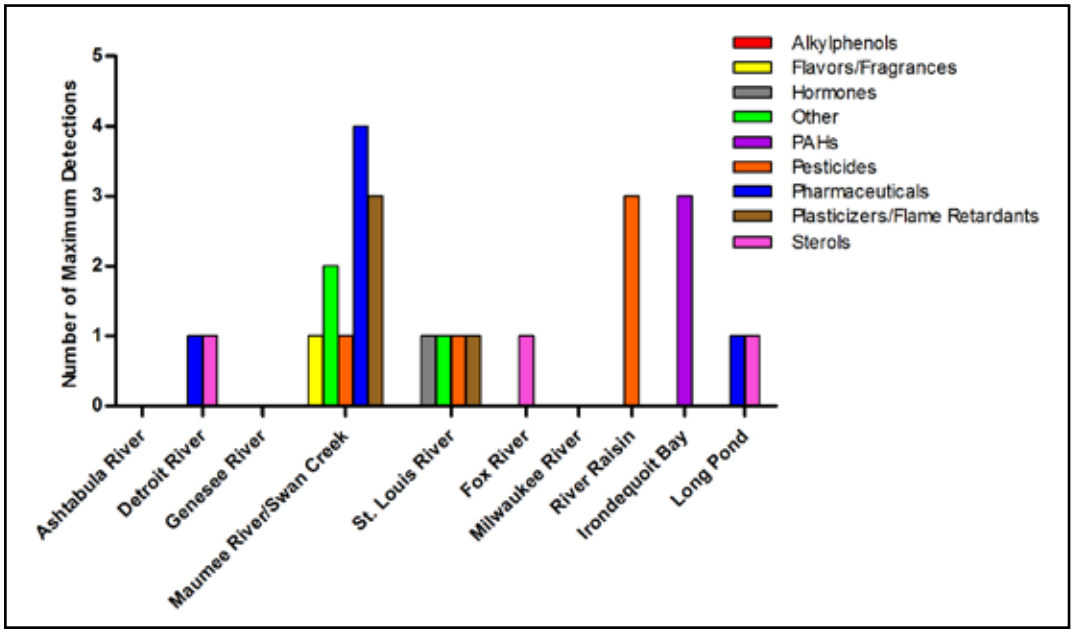

Figure 14. Number of detections of the highest water concentrations of individual CECs by class relative to all sites across all years for CECs with at least a 20% detection rate.

Co-Occurring Chemicals

Polycyclic aromatic hydrocarbons are components of coal tar and fuel oil and have multiple sources to the environment, including incomplete combustion of fossil fuels and other organic matter (Agency for Toxic Substances and Disease Registry, 1995; Agency for Toxic Substances and Disease Registry, 2009). In sediments, cluster analysis using rank transformed data indicates that the PAHs phenanthrene, pyrene, benzo-a-pyrene, anthracene, and fluoranthene were often detected together (Figure 15). These PAHs have higher molecular weights than the napthalenes (discussed below). The chemicals 9,10-anthraquinone and carbazole, both of which have industrial uses in the synthesis of dyes, were also often detected together with the aforementioned PAHs (Windolz et al., 1983). As with PAHs, carbazole is also a component of coal tar, and 9,10-anthraquinone is prepared industrially from PAH components of coal tar (Agency for Toxic Substances and Disease Registry, 2009; International Agency for Research on Cancer, 2013). The lower-molecular weight PAHs naphthalene, 1-methylnapthalene, and 2-methylnapthalene also clustered closely together, indicating that these compounds had a similar pattern of occurrence. These groups of CECs were associated with sites that have large proportions of developed land use as well as sites with WWTP and CSO influences. Additionally, several pairs of compounds were often detected together: the alkylphenols 4-nonylphenol and 4-tert-octylphenol were often detected together, as were the hormones estrone and 4-androstene-3,17-dione and the sterols beta-sitosterol and beta-stigmastanol. These pairs were often associated with sites that have a mix of developed and agricultural land uses (Figure 15).

In water, the pharmaceuticals venlafaxine, lidocaine, phenytoin, and tramadol were commonly detected together and were associated with sites with large proportions of developed land use and WWTP and CSO influences. The plasticizers bisphenol A and tributyl phosphate (TBPE) were often detected together and were associated with sites that have a mix of agricultural and developed land use as well as sites dominated by agriculture or developed land use. The pesticides atrazine and metolachlor (both herbicides) were detected together at sites with land uses that are dominated by agricultural practices (Figure 16).

Many of these observations follow expected patterns (Karpuzcu et al., 2014; Fairbairn et al., 2016a). For example, PAHs are produced as a result of the burning of fossil fuels, and it follows that they would commonly be detected together and at locations with large proportions of developed land use (Van Metre et al., 2000). The herbicides atrazine and metolachlor are herbicides used on row crops, and it follows that these herbicides would be detected together at locations with large proportions of agricultural land use. The cluster analysis indicates other pairs or groupings for which the relationships may not be as clear. For example, triclosan and hexahydrohexamethyl cyclopentabenzopyran (HHCB) were often detected together in sediment. Although these chemicals represented different classes as defined in the methodology, they are all ingredients in personal care products (Centers for Disease Control, 2013; Chemical Book, 2016). Additionally, more in-depth analyses are planned to further explain these relationships. Mixture information obtained through the above analyses was used to determine the common CEC mixtures that are currently being used to address objectives (b) and (c) of the CEC Project, which includes laboratory exposures. Laboratory exposures will provide better understanding of the interaction effects of these complex environmental chemical mixtures.

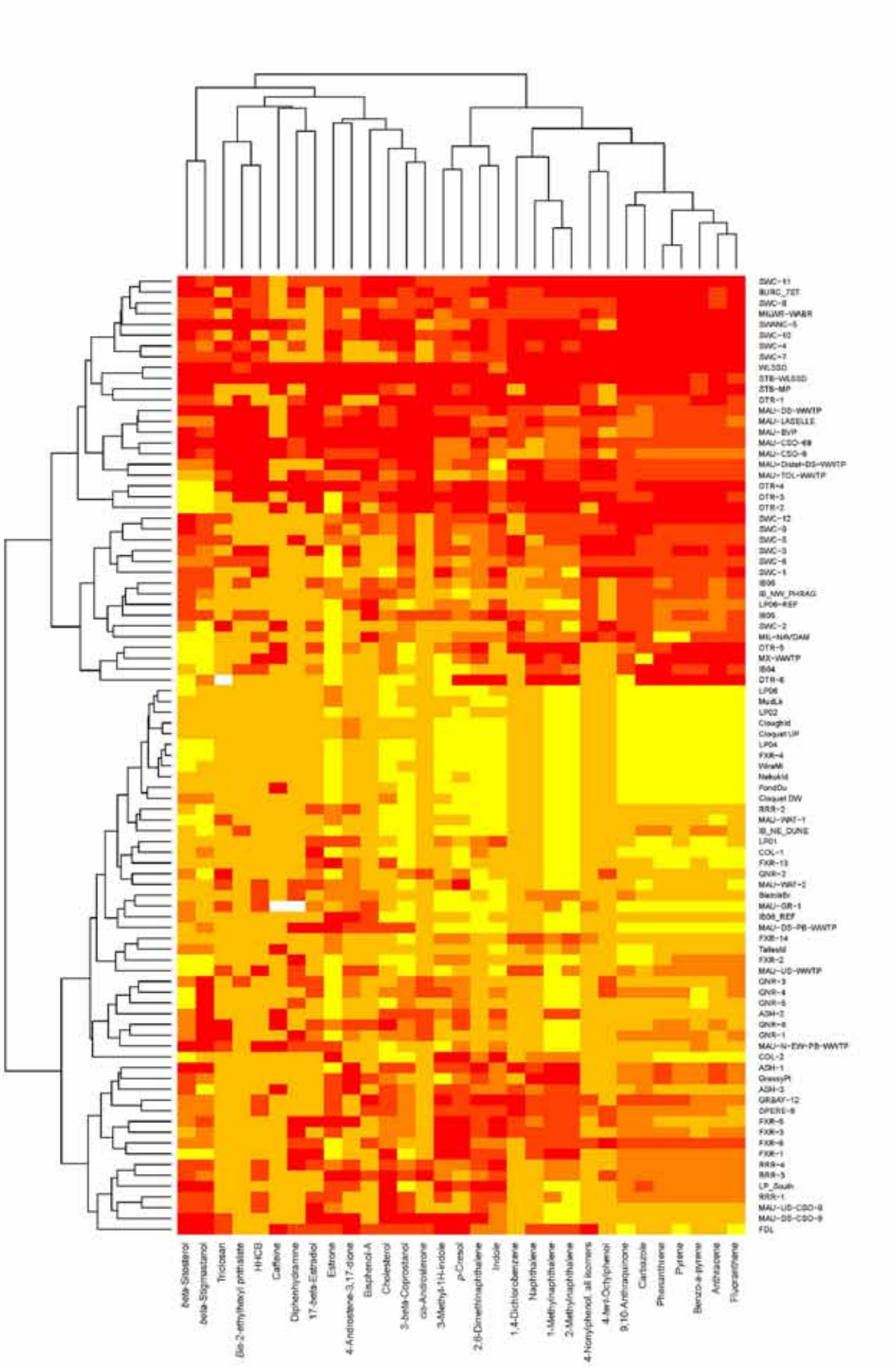

Figure 15. Output of the sediment chemistry cluster analysis. The heat map component indicates the ranked concentrations of CECs, and the dendrograms indicate the patterns of chemical occurrence or site chemical composition.

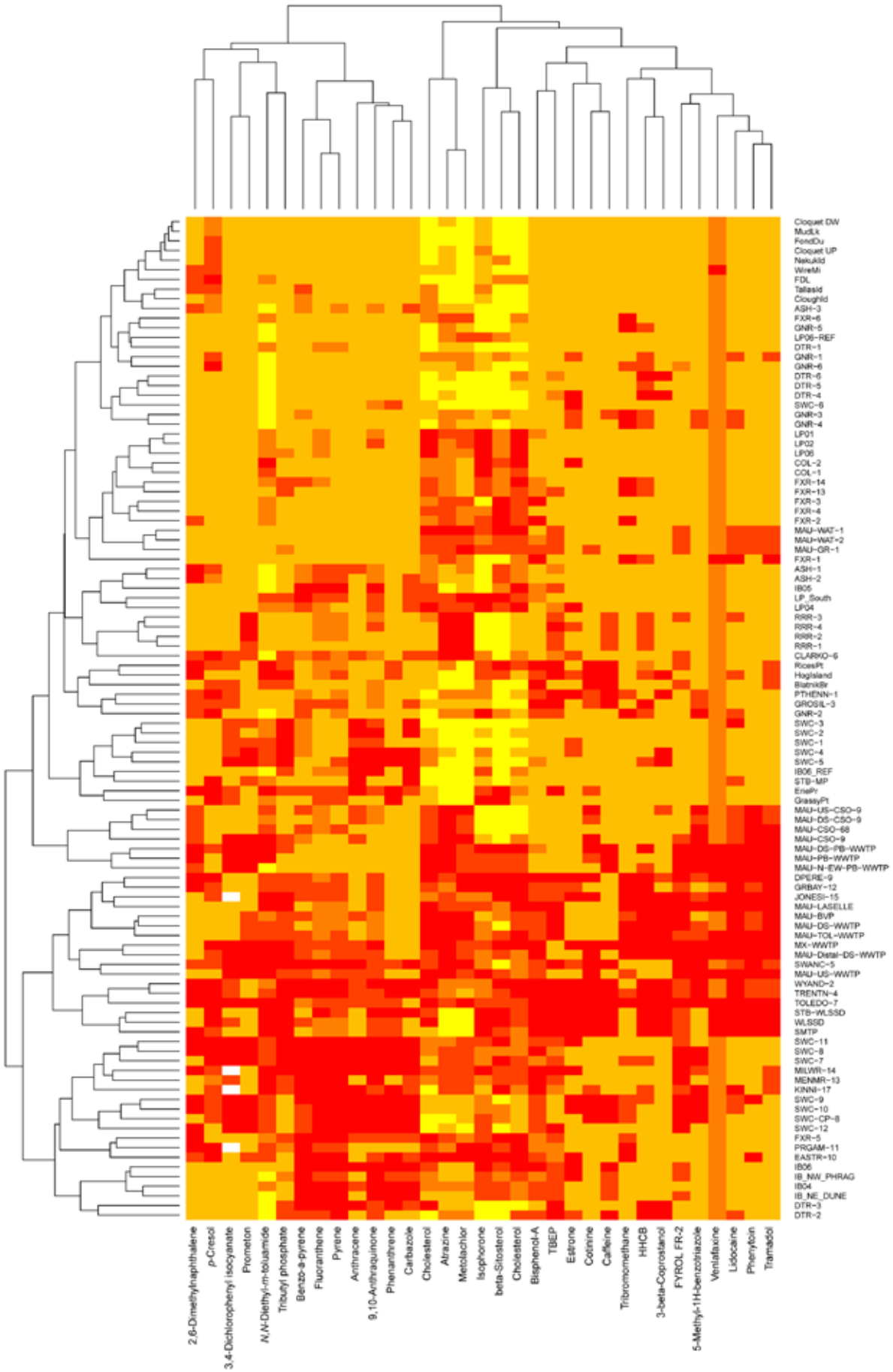

Figure 16. Output of the water chemistry cluster analysis. The heat map component indicates the ranked concentrations of CECs, and the dendrograms indicate the patterns of chemical occurrence or site chemical composition.

Temporal Variation

The samples collected at multiple times within a single sampling event at the St. Louis and Maumee River sites that were assessed visually did not reveal any consistent temporal pattern in the number or concentration of CECs detected in water. No pattern was expected because these grab samples represent a snapshot of the site in space and time. The chemical mixtures in the surface water at any site are expected to be in constant flux (Appendix C[7], Figures C9 through C15).

In spring of 2012, four samples were collected at various times of the day on different days at four sites in the St. Louis River location (Appendix C, Figures C9 through C12). At the most upstream site (EriePr), the samples collected in the morning and early evening generally yielded a greater number of detections. At the downstream site (RicesPt), the detections were highest in the samples collected later in the evening (i.e., after 7:00pm [20:00]). Similar to the most upstream site, number of chemicals detected seemed to be highest in the morning through mid-day, then again in the evening at site SMTP which was located downstream from site EriePr. The furthest downstream site (HogIsland) had similarly higher numbers of chemicals detected in the morning and afternoon and tapered off slightly in the evening sample. Because only two time series samples were collected at the St. Louis River location in fall 2012, these data points were left out of the analysis.

The Maumee River sites were sampled for daily variation in the autumn of only 2012. Similar to the St. Louis River, the results indicate no discernable temporal patterns. Of the four samples collected at different times of the day on different days, the sample collected just after mid-day at a site immediately upstream from a potential point source (MAU-US-WWTP) had the greatest number of chemical detections. At the site immediately downstream from the same potential point source (MX-WWTP), the morning sample had the greatest number of detections and highest concentrations of CECs. The samples collected in the late afternoon at a site further downstream from the potential point source (MAU-Distal) revealed higher concentrations and a greater number of CECs detected compared with the early afternoon and morning samples (Appendix C, Figures C13 through C15).

Location and Site Characterization

This section describes the patterns in the chemical concentration (i.e., appearances and increases) between individual sampling sites relative to potential CEC sources or land uses. Rather than evaluating the chemical gradients from the most upstream to the most downstream sites within a location, this analysis focused on pairs of sites that bracketed specific point sources and/or land uses. Known and suspected point sources of CECs (including WWTPs and CSOs), and known and suspected non-point sources of CECs (including urban and agricultural runoff) were the focus of the initial investigation and analysis (Gros et al., 2007; Vidal-Dorsch et al., 2012; Lee et al., 2011; Phillips and Chalmers, 2009; Phillips et al., 2012; Dodder et al., 2014; Shore and Shemesh, 2003, Fairbairn et al., 2016b, Van Metre et al., 2000; Lee et al., 2006; Abdel-Shafy and Mansour, 2016). Notably, this analysis was based on single grab samples that represent a "snapshot" of the chemical concentrations in space and time. The temporal analysis of CECs in water samples indicates that there was variability in the concentrations throughout the day. As a result, this analysis was limited to the sediment chemistry, which was assumed to provide more temporally stable chemical occurrence information than water because sediment is less mobile and adsorbs certain types of chemicals.

Generally, sites with the highest number of appearances or increases occurred immediately downstream from WWTPs, followed by CSOs and then other NPDES dischargers (Figures 17-18; Appendix C, Table C1). Polycyclic aromatic hydrocarbons (PAHs) appeared or increased more than any other CEC class downstream from the three studied types of point sources. These initial results were anticipated because developed areas that include WWTPs and CSOs were targeted as sampling locations during the first three years of the study. As a result, WWTPs and CSOs made up the majority of the sampled potential point sources.

With respect to the relationship between land use and CEC concentrations, most appearances and increases were observed at the downstream site of paired upstream/downstream sites between which the land use is primarily developed, followed by a mix of agricultural and developed land use, predominantly agricultural land use, and finally undeveloped land use (which included sites dominated by forests and wetlands; Figures 17 and 18; Appendix C, Table C1; Appendix D, Figures D1-D21). Similarly, PAHs appeared or increased more than any other CEC class at sites with predominantly developed land, a mix of developed and urban land, and undeveloped land. At sites characterized mainly by agricultural use, hormones exhibited the highest number of appearances and increases.

7 Although all CECs were used to evaluate temporal variation, Appendix C presents a subset of figures for demonstration purposes; chemicals were sorted by frequency of detection, and the first four chemical classes that had two chemicals with the highest detection were chosen for Appendix C. In some cases, sterols were omitted to avoid distortion of the y-axis scale.

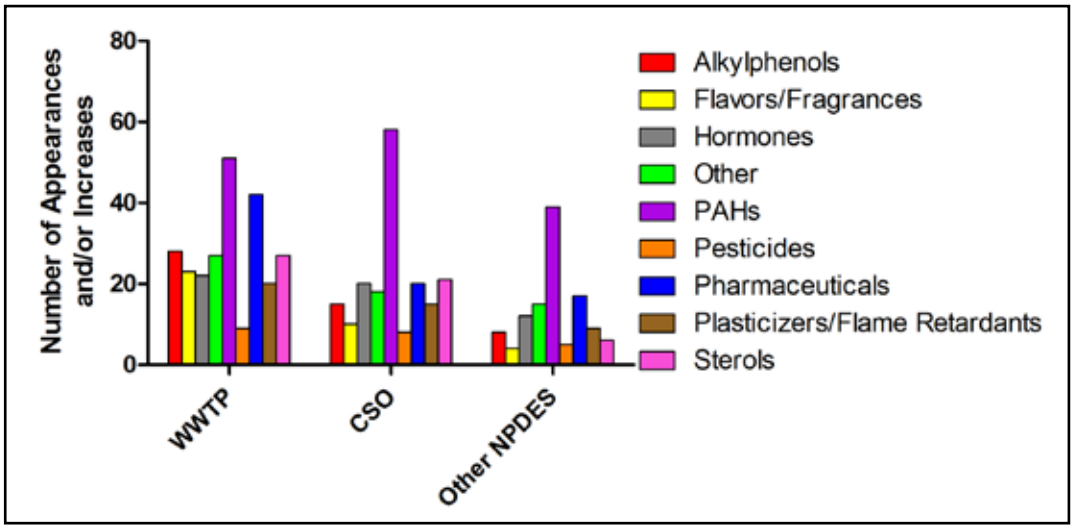

Figure 17. Number of appearances and increases in sediment by chemical class and point source type.

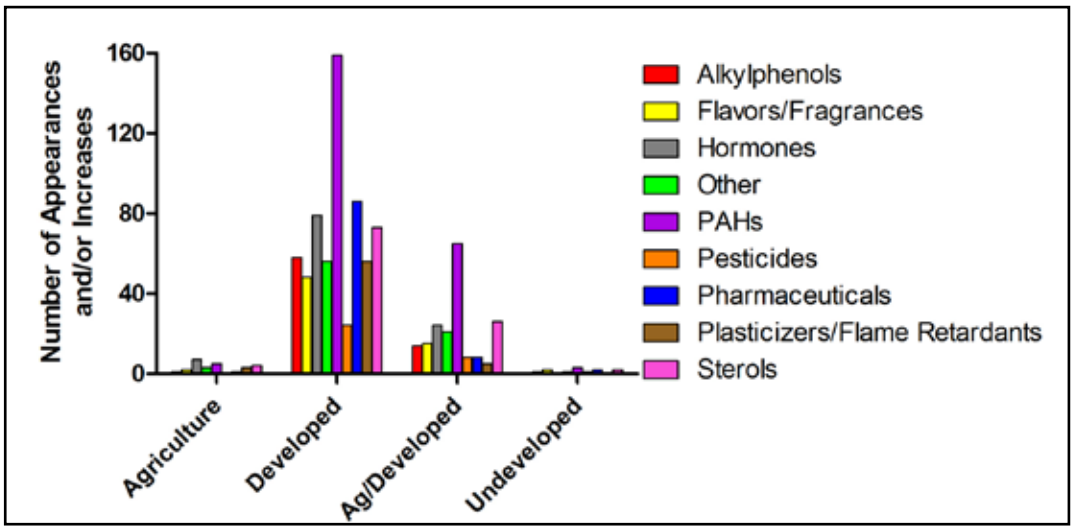

Figure 18. Number of appearances and increases in sediment by chemical class and land use grouping.

St. Louis River

In the St. Louis River, the WLSSD site had the highest number of appearances and increases in all three years in which sediment was sampled. The MP site had the second highest number of appearances and increases in 2010 and 2011, and GrassyPt site had the second highest number of appearances and increases in 2012. All nine PAHs analyzed appeared or increased at these sites. A coal and biomass-fueled power plant and developed land use may be contributing to these patterns in CEC concentrations at MP and GrassyPt sites because PAHs are associated with the combustion of organic materials such as coal (Van Metre et al., 2000; Abdel-Shafy and Mansour, 2016). Appearances and increases were observed in all classes of CECs at WLSSD site in 2010 and 2011. Furthermore, increases and appearances occurred more at the WLSSD site relative to any other site in all CEC classes except PAHs. In addition to the increase in developed land use, a municipal WWTP may be a contributing source to the large number of appearances and increases in CEC concentrations (Gros et al., 2007; Vidal-Dorsch et al., 2012; Lee et al., 2011; Dodder et al., 2014; Fairbairn et al., 2016b; Van Metre et al., 2000).

Green Bay and Lower Fox River

Appearances and increases in a variety of chemicals were observed in sediments at all sites within the Fox River and Green Bay sampling locations, except FXR-6 site. The greatest number of appearances and increases in 2010 and 2011 were observed at FXR-3 site. The FXR-3 site is located in Green Bay and may be in a depositional area of the bay; sediments contaminated with CECs may have been carried to this site by the Fox River over time (Manchester-

Neesvig et al., 1996). In 2012, the most appearances and increases occurred at DPERE-9 site in the alkylphenol, flavor/fragrance, "other" CEC, PAH, pesticide, and sterol chemical classes. The DPERE-9 site is located immediately downstream from a WWTP and areas of primarily agricultural land use, which could account for these observations (Gros et al., 2007; Vidal-Dorsch et al., 2012; Lee et al., 2011; Dodder et al., 2014; Fairbairn et al., 2016b). The greatest number of appearances and increases in hormones relative to any other site at the Fox River and Green Bay location was observed at FXR-13 site, which is below the confluence of a stream that drains agricultural land including CAFOs, which are potential sources of hormones (Shore and Shemesh, 2003; Lee et al., 2006).

Milwaukee River

Inferences regarding the potential trends in CEC concentrations and possible sources were limited because there were only three sediment sampling sites in the Milwaukee, Kinnickinnic, and Menomonee Rivers. A number of CECs appeared in Milwaukee River sediment at MILWR-WABR site, including alkylphenols, hormones, PAHs, pesticides, pharmaceuticals, and plasticizers/flame retardants. Potential upstream sources include several CSOs and other developed land uses. These sources may be a factor in the appearances and increases observed (Phillips and Chalmers, 2009; Phillips et al., 2012; Dodder et al., 2014; Van Metre et al., 2000).

Detroit River

Appearances and increases in Detroit River sediments were most commonly observed at DTR-2, DTR-3, and DTR-4 site in 2010 and DTR-11 and DTR-4 sites in 2011. The DTR-2 site experienced appearances and increases in PAHs, hormones, and "other" CECs. This site is located near the confluence of the Rouge River, which drains primarily developed lands (83%; Fry et al., 2011) and receives discharges from CSOs, a steel coating facility and an auto plant. Potential influences on the main stem of the Detroit River at DTR-2 site include a WWTP, coal-fired power plant, and steelmaking and finishing facility. A number of appearances and increases in pharmaceuticals were also observed at DTR-4 site, which may be explained by the two WWTPs upstream from DTR-4 (Gros et al., 2007; Vidal-Dorsch et al., 2012; Lee et al., 2011; Fairbairn et al., 2016b).

River Raisin

Appearances and increases in alkylphenols, flavors/fragrances, hormones, "Other" CECs, PAHs, and sterols were observed in sediment from RRR-3 site. In contrast to sites downstream from WWTPs at other locations, the appearances and increases were observed in all CEC classes at RRR-3 sites except pharmaceuticals. Developed land use surrounding the sampling reach and a WWTP located upstream from RRR-3 site are possible contributors to the pattern of CEC concentrations observed at the River Raisin location (Gros et al, 2007; Vidal-Dorsch et al., 2012; Lee et al., 2011; Dodder et al., 2014; Fairbairn, et al., 2016b; Van Metre et al., 2000).

Maumee River and Swan Creek

At the Maumee River location, sites with multiple increases and appearances in CEC concentrations were located in the vicinity of CSOs and WWTPs. The most appearances and increases were observed at MAU-LASALLE site in spring 2012. Appearances and increases were observed in all CEC classes at MAU-LASALLE site, in particular hormones, pharmaceuticals and plasticizers/flame retardants. Although MAU-LASALLE site is located upstream from a WWTP, appearances and increases were also prevalent adjacent to and downstream from the WWTP. The occurrence of large numbers of appearances and increases in pharmaceuticals and plasticizers/flame retardants relative to other sites follows the observed pattern at WWTPs located in large urban areas of other locations, including the WLSSD site in the St. Louis River watershed and the DTR-4 site in the Detroit River watershed. At CSO sites, including MAU-CSO-9 and MAU-CSO-68 sites, the greatest number of appearances and increases were observed for PAHs and hormones. It is possible that CSO overflows during rain events are contributing to this pattern (Phillips and Chalmers, 2009; Phillips et al., 2012).

Similar to the CSO sites in the Maumee River watershed, appearances and increases were observed downstream from CSOs in the Swan Creek watershed. In Swan Creek, SWC-3 and SWC-10 sites had the highest number of appearances and increases in CEC concentrations in 2010, followed by SWC-11 site in 2011. Hormone and PAH appearances were common, suggesting that CSOs and the large percentage of developed land use in the watershed are contributing to the observed patterns (Phillips et al., 2009; Phillips et al., 2012; Dodder et al., 2014; Van Metre et al., 2000).

Ashtabula River

The most notable observation in Ashtabula River sediments consisted of the appearances and increases in PAHs at ASH-1 site. This observation may be attributed to the high proportion of developed land use surrounding the sampling area, which includes a large rail yard that sits adjacent to an embayment in which ASH-1 site is located (Dodder et al., 2014; Van Metre et al., 2000).

Long Pond, Genesee River and Irondequoit Bay

For the analysis of the Long Pond location, all samples were compared to a single reference location (LP06-REF) located upstream from WWTP influences in the tributary, as opposed to the sample collected immediately upstream at riparian sites because Long Pond consists of open water with different patterns of flow compared to the river . The two sampling sites with the greatest number of CEC increases or appearances in Long Pond sediments were both located at the southern (most upstream) end of the

pond. Hormones appeared and increased the most at LP01 site relative to any other site, whereas flavors/fragrances and sterols increased and appeared at LP-South site. No currently known active point sources that may account for the observed patterns in CEC concentrations are located in the immediate area. The agricultural and developed land surrounding the sampling location may be partially contributing factors to these patterns (Dodder et al., 2014; Shore and Shemesh et al., 2003; Fairbairn et al., 2016b).

The majority of increases or appearances in CEC concentrations in Genesee River sediments occurred at GNR-3 and GNR-6 sites. The classes of CECs that appeared or increased at these sites include "other" CECs, PAHs, pharmaceuticals and plasticizers/flame retardants at GNR-3 site and hormones, PAHs, plasticizers/flame retardants, and sterols at GNR-6 site. Potential influences include the developed land use surrounding the sampling reach, two CSOs, and a WWTP that discharges upstream from GNR-3 site (Gros et al., 2007; Vidal-Dorsch et al., 2012; Lee et al., 2011; Phillips and Chalmers, 2009; Phillips et al., 2012; Fairbairn et al., 2016b; Van Metre et al., 2000). Although GNR-1 and GNR-2 sites are closer to these potential point sources than GNR-3 site, it is possible that the discharge is downstream from these sites or that the river flow transports any contaminants downstream before settling into the sediment.

Similar to Long Pond, Irondequoit Bay sediment samples were compared to a single reference sample (IB06_REF) located in a small tributary with no known CEC sources. Appearances and increases in CEC concentrations were observed in PAHs at every site relative to the reference site. Hormones were observed to appear and increase at IB06 and IB_NW_PHRAG sites. The concentrated, developed land use to the west of the bay may be a contributing factor (Van Metre et al., 2000).

Concentrations of CECs in Fish Tissue

The concentrations of CECs in fish tissue were measurable for some chemicals, but many chemicals were not detected. The small sampling size per site, small liver mass, and current laboratory detection limits led to challenges with data interpretation. Even with these limitations, some patterns were identified. Non-detects of chemicals in all classes except for plasticizers/flame retardants were reported. Atrazine, 17-alpha-ethynylestradiol, 17-alpha-estradiol, androstenedione, carbamazepine, diazepam, diclofenac, estrone, meprobamate, naproxen, sulfamethoxazole, and estriol were not detected in any benthic or pelagic fish samples. Perfluorinated compounds (PFCs), which were only analyzed in fish tissue, were the most frequently detected class of contaminant in fish liver tissues. These chemicals are commonly used in a number of applications including non-stick cookware, stain resistant carpeting, and cosmetics amongst others and do not readily breakdown in the environment (Minnesota Pollution Control Agency, 2016). These properties may account for the high detection frequencies of PFCs in fish tissue. One or more PFCs were detected in every tissue sample collected in both benthic and pelagic species. Perfluoroheptanoic acid was the least frequently detected PFC, with a 4% detection rate in benthic species and a 7% detection rate in pelagic species. Perfluorodecanoic acid, perfluorooctanesulfonate, and perfluoroundecanoic acid were detected at a 100% detection rate in benthic and pelagic species (Appendix B, Tables B3 and B4; Appendix C, Figures C16 and C17).

The frequency of detection appeared to be similar among benthic and pelagic fish species, with a few exceptions. Benthic species had a higher frequency of detection of perfluorononanoic, perfluorooctanoic, and perfluoropentanoic acids than their pelagic counterparts. Conversely, pelagic species had higher rates of detection of progesterone, perfluorohexanoic acid, and oxybenzone (Appendix B, Tables B3 and B4; Appendix C, Figures C16 and C17). Additional data from subsequent sampling years will be combined with these data for further, more in-depth statistical evaluations.

Summary of Principal Findings

The data collected during the first three years of our study indicate that contaminants were more frequently detected in sediment compared to water. The chemicals classified as alkylphenols, flavors/fragrances, hormones, PAHs, and sterols had higher average detection frequencies in sediment compared to water, whereas the opposite was observed for pesticides, pharmaceuticals, and plasticizers/flame retardants. The St. Louis River and Maumee River sampling locations had the highest number of detections in water and sediment, relative to the other sites, as well as the largest number of maximum detected concentrations across all sites in the basin. There were no consistent temporal CEC occurrence patterns observed at locations sampled multiple times each day. Most concentration appearances and increases in sediments occurred at sites immediately downstream from WWTPs and at sites with predominantly developed land use. The location with the greatest number of observed appearances and increases was the St. Louis River. Perfluorinated compounds were commonly detected in fish liver tissues with detections of 100% in both benthic and pelagic species. The occurrence of these chemicals in the liver tissue of benthic and pelagic species was generally similar.

Next Steps

This report provides an initial summary of the presence and distribution of CECs in the Great Lakes Basin and represents an important step in achieving the goals of the project: evaluating the risks to fish and wildlife and developing management recommendations to mitigate or eliminate those risks. This study indicates that CECs are prevalent throughout the environment and composed of wide and varying classes of chemicals. Currently, the methodologies and technologies needed to detect and quantify environmentally relevant levels of some compounds are not available. Importantly, a high number of non-detects were present in the dataset, which does not mean that the contaminant in question was absent from the environment or from fish tissues but rather concentrations were below a laboratory reporting level. The analyte may or may not be present at concentrations that could impact fish and wildlife resources. However, this question cannot be addressed for many chemicals because the chemical detection limits do not necessarily reflect the biological effect concentrations.

In-depth statistical analyses and continued sampling during 2013 and 2014 will help to further characterize the spatial and temporal trends in CECs across sites in order to evaluate the biological uptake and effects across fish guilds. Empirical data to interpret how such chemical concentrations would specifically impact fish and wildlife are sparse, which is confounded by the fact that many laboratory studies are based on a single chemical and do not take into account the interactive effects of real world exposures to chemical mixtures. Additional steps are planned (2015-2019) to refine toxicity-based screening levels and to understand the effects of mixtures on laboratory-exposed fish. These steps will build upon this current study and allow for a better definition of the effects of CECs on aquatic organism exposure and adverse outcomes. Those studies, along with an ongoing refinement of toxicity-based screening values, will provide much needed guidance to fish and wildlife managers in determining the best practices to protect and enhance fish, wildlife, and their habitats.

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Appendix A. Analyte Properties

Table A1. Analyte properties, including Chemical Abstract Service Registry Numbers (CASRN), class, laboratory reporting level for sediment samples (in nanograms per gram (ng/g)), reporting level for water samples (in micrograms per liter (μg/L)), octanol-water partition coefficient (log K_{ow}), and in what media analytes were sampled (S=sediment; W=water).

CASRN[1]	Analyte	Class	Sediment laboratory reporting level (ng/g)[2,3]	Water laboratory reporting level (ug/L)[2,3]	log K_{ow}[4]	Media
599-64-4	4-Cumylphenol	Alkyphenol	50	0.04	4.17^	S, W
1806-26-4	4-n-Octylphenol	Alkyphenol	50	0.02	5.66^	S, W
84852-15-3	4-Nonylphenol (sum of all isomers)	Alkyphenol	750	1.6	5.92*	S, W
20427-84-3	4-Nonylphenol diethoxylate, (sum of all isomers) aka NP2EO	Alkyphenol	1,000	1.6	5.79^	S, W
104-35-8	4-Nonylphenol monoethoxylate, (sum of all isomers) aka NP1EO	Alkyphenol	500	1.6	5.87^	S, W
140-66-9	4-tert-Octylphenol	Alkyphenol	50	0.4	5.28*	S, W
2315-61-9	4-tert-Octylphenol diethoxylate, aka OP2EO	Alkyphenol	50	0.6	4.53^	S, W
2315-67-5	4-tert-Octylphenol monoethoxylate OP1EO	Alkyphenol	250	0.2	5.52^	S, W
106-44-5	p-Cresol	Alkyphenol	250	0.08	1.94	S, W
83-34-1	3-Methyl-1(H)-indole (Skatole)	Flavor/Fragrance	50	0.04	2.6	S, W
98-86-2	Acetophenone	Flavor/Fragrance	150	0.4	1.58	S, W
21145-77-7	Acetyl hexamethyl tetrahydronaphthalene (AHTN)	Flavor/Fragrance	50	0.04	6.37^	S, W
76-22-2	Camphor	Flavor/Fragrance	50	0.08	2.38	S, W
5989-27-5	d-Limonene	Flavor/Fragrance	50	0.16	4.57	S, W
1222-05-5	Hexahydrohexamethylcyclopentabenzopyran (HHCB)	Flavor/Fragrance	50	0.04	6.23^	S, W
120-72-9	Indole	Flavor/Fragrance	100	0.04, 0.16	2.14	S, W
89-78-1	Menthol	Flavor/Fragrance	50	0.32	3.4	S, W
564-35-2	11-Ketotestosterone	Hormone	0.26	0.002	1.67^	S, W
57-91-0	17-alpha-Estradiol	Hormone	0.1	0.0008	3.94*	S, W
57-63-6	17-alpha-Ethynylestradiol	Hormone	0.1	0.0008	3.67	S, W
50-28-2	17-beta-Estradiol	Hormone	0.1	0.0008	4.01	S, W
63-05-8	4-Androstene-3,17-dione	Hormone	0.1	0.0008	2.75	S, W
53-41-8	cis-Androsterone	Hormone	0.1	0.0008	3.69	S, W
521-18-6	Dihydrotestosterone	Hormone	0.1	0.004	3.55	S, W
481-30-1	Epitestosterone	Hormone	0.5	0.004	3.47^	S, W
517-09-9	Equilenin	Hormone	0.26	0.002	3.93*	S, W
474-86-2	Equilin	Hormone	0.5	0.004	3.35*	S, W
50-27-1	Estriol	Hormone	0.26	0.002	2.45	S, W
53-16-7	Estrone	Hormone	0.1	0.0008	3.13	S, W
72-33-3	Mestranol	Hormone	0.1	0.0008	4.68*	S, W
68-22-4	Norethindrone	Hormone	0.1	0.0008	2.97	S, W
57-83-0	Progesterone	Hormone	0.5	0.008	3.87	S, W
58-22-0	Testosterone	Hormone	0.1	0.0008	3.32	S, W
56-53-1	trans-Diethylstilbestrol	Hormone	0.1	0.0008	5.93^	S, W
106-46-7	1,4-Dichlorobenzene	Other	50	0.08	3.44	S, W
102-36-3	3,4-Dichlorophenyl isocyanate	Other	N/A	0.32	3.88*	W
121-00-6	3-tert-Butyl-4-hydroxy anisole (BHA)	Other	150	0.16	3^	S, W

[1] This report contains Chemical Abstracts Services Registry Numbers (CASRN)®, which is a Registered Trademark of the American Chemical Society. The CASRN
[2] Laboratory reporting levels separated by "/" indicate 2 different laboratory methods used to measure the concentration in the sample. Two different methods were used for bisphenol A, cholesterol and 3-beta-coprostanol.
[3] N/A = not applicable

CASRN[1]	Analyte	Class	Sediment laboratory reporting level (ng/g)[2,3]	Water laboratory reporting level (ug/L)[2,3]	log K_{ow}[4]	Media
136-85-6	5-Methyl-1H-benzotriazole	Other	N/A	0.32	1.8^	W
84-65-1	9,10-Anthraquinone	Other	50	0.04	3.39	S, W
119-61-9	Benzophenone	Other	50	0.08	3.18	S, W
124-76-5	Isoborneol	Other	50	0.9	3.24	S, W
78-59-1	Isophorone	Other	50	0.05	1.7	S, W
98-82-8	Isopropylbenzene	Other	100	0.04	3.66	S, W
119-65-3	Isoquinoline	Other	100	0.04, 0.2	2.08	S, W
119-36-8	Methyl salicylate	Other	N/A	0.08	2.55	W
108-95-2	Phenol	Other	50	0.16	1.46	S, W
127-18-4	Tetrachloroethylene	Other	N/A	0.16	3.4	W
72-25-2	Tribromomethane	Other	N/A	0.16		W
3380-34-5	Triclosan	Other	50	0.32	4.76	S, W
77-93-0	Triethyl citrate (ethyl citrate)	Other	N/A	0.04	0.33*	W
1912-24-9	Atrazine	Pesticide	100	0.16	2.61	S, W
314-40-9	Bromacil	Pesticide	500	0.16	2.11	S, W
63-25-2	Carbaryl	Pesticide	N/A	0.06	2.36	W
86-74-8	Carbazole	Pesticide	50	0.02	3.72	S, W
2921-88-2	Chlorpyrifos	Pesticide	50	0.12	4.96	S, W
333-41-5	Diazinon	Pesticide	50	0.32	3.81	S
62-73-7	Dichlorvos	Pesticide	N/A	0.08, 0.32	1.47	W
57837-19-1	Metalaxyl	Pesticide	N/A	0.16	1.65	W
51218-45-2	Metolachlor	Pesticide	50	0.04	3.13	S, W
134-62-3	N,N-diethyl-meta-toluamide (DEET)	Pesticide	100	0.04	2.18	S, W
87-86-5	Pentachlorophenol	Pesticide	N/A	1.6	5.12	W
1610-18-0	Prometon	Pesticide	50	0.16	2.99	S, W
611-59-6	1,7-Dimethylxanthine	Pharmaceutical	4.1	N/A	-2.08^	S
7206-76-0	2-Ethyl-2-phenylmalonamide	Pharmaceutical	N/A	0.1	0.13^	W
103-90-2	Acetaminophen	Pharmaceutical	1.5	0.64	0.46	S, W
18559-94-9	Albuterol	Pharmaceutical	2.2	N/A	0.64*	S
50-48-6	Amitriptyline	Pharmaceutical	N/A	0.16	4.92	W
60-80-0	Antipyrine	Pharmaceutical	N/A	0.32	0.38	W
83905-01-5	Azithromycin	Pharmaceutical	1.7	N/A	4.02	S
34911-55-2	Bupropion	Pharmaceutical	0.25	N/A	3.47^	S
77-26-9	Butalbital	Pharmaceutical	N/A	0.16	1.87*	W
58-08-2	Caffeine	Pharmaceutical	2.6	0.08	-0.07	S, W
298-46-4	Carbamazepine	Pharmaceutical	0.25/3.3	0.16	2.45	S, W
78-44-4	Carisoprodol	Pharmaceutical	N/A	0.16	2.36*	W
169590-42-5	Celecoxib	Pharmaceutical	N/A	0.64	3.47*	W
38345-66-3	Chirald	Pharmaceutical	N/A	0.16	3.83^	W
88-04-0	Chloroxylenol	Pharmaceutical	N/A	0.08	3.27	W
132-22-9	Chlorpheniramine	Pharmaceutical	N/A	0.08	3.38	W
51481-61-9	Cimetidine	Pharmaceutical	0.25	N/A	0.4	S
59729-33-8	Citalopram	Pharmaceutical	1.76	0.08	3.74*	S, W
76-57-3	Codeine	Pharmaceutical	2.6	0.32	1.19	S, W
486-56-6	Cotinine	Pharmaceutical	2.6	0.08	0.07	S, W
67035-22-7	Dehydronifedipine	Pharmaceutical	3.4	N/A	3.04^	S
125-71-3	Dextromethorphan	Pharmaceutical	N/A	0.16	4.11^	W
439-14-5	Diazepam	Pharmaceutical	N/A	0.16	2.82	W
125-28-0	Dihydrocodeine	Pharmaceutical	N/A	0.16	1.49*	W
42399-41-7	Diltiazem	Pharmaceutical	3	0.04	2.79*	S, W
147-24-0	Diphenhydramine	Pharmaceutical	2.7	0.08		S, W
116539-59-4	Duloxetine	Pharmaceutical	0.25	N/A	3.73^	S
154598-52-4	Efavirenz	Pharmaceutical	N/A	0.32	3.72^	W
114-07-8	Erythromycin	Pharmaceutical	3.32	N/A	3.06	S
86386-73-4	Fluconazole	Pharmaceutical	N/A	0.16	0.5^	W
54910-89-3	Fluoxetine	Pharmaceutical	1.5/1.5	0.64	4.05	S, W

Table A1 *(continued)*

CASRN[1]	Analyte	Class	Sediment laboratory reporting level (ng/g)[2,3]	Water laboratory reporting level (ug/L)[2,3]	log K_{ow}[4]	Media
54739-18-3	Fluvoxamine	Pharmaceutical	0.25	N/A	3.11^	S
126-07-8	Griseofulvin	Pharmaceutical	N/A	0.32	2.18	W
125-29-1	Hydrocodone	Pharmaceutical	N/A	0.32	2.16*	W
15687-27-1	Ibuprofen	Pharmaceutical	N/A	0.64	3.97	W
256-96-2	Iminostilbene	Pharmaceutical	N/A	0.08	4.11^	W
137-58-6	Lidocaine	Pharmaceutical	N/A	0.08	2.44	W
57-42-1	Meperidine	Pharmaceutical	N/A	0.08	2.72	W
57-53-4	Meprobamate	Pharmaceutical	N/A	0.32	0.7	W
1665-48-1	Metaxalone	Pharmaceutical	N/A	0.08	2.6*	W
76-99-3	Methadone	Pharmaceutical	N/A	0.08	3.93	W
532-03-6	Methocarbamol	Pharmaceutical	N/A	0.64	0.61	W
113-45-1	Methylphenidate	Pharmaceutical	N/A	0.08	0.2	W
22916-47-8	Miconazole	Pharmaceutical	0.25	N/A	6.25*	S
56161-73-0	Norfluoxetine	Pharmaceutical	0.25	N/A	4.36^	S
3376-94-1	Norpropoxyphene	Pharmaceutical	N/A	0.32	4^	W
87857-41-8	Norsertraline	Pharmaceutical	0.5	N/A	4.59^	S, W
28721-07-5	Oxcarbazepine	Pharmaceutical	N/A	0.32	1.11*	W
76-42-6	Oxycodone	Pharmaceutical	N/A	0.32	0.66*	W
61869-08-7	Paroxetine	Pharmaceutical	0.25	N/A	3.95*	S
76-74-4	Pentobarbital	Pharmaceutical	N/A	0.16	2.1	W
6493-05-6	Pentoxifylline	Pharmaceutical	N/A	0.32	0.29	W
634-03-7	Phendimetrazine	Pharmaceutical	N/A	0.04	1.7*	W
50-06-6	Phenobarbital	Pharmaceutical	N/A	0.16	1.47	W
57-41-0	Phenytoin	Pharmaceutical	N/A	0.16	2.47	W
51-03-6	Piperonyl butoxide	Pharmaceutical	N/A	0.08	4.75	W
125-33-7	Primidone	Pharmaceutical	N/A	0.32	0.91	W
2078-54-8	Propofol	Pharmaceutical	N/A	0.04	3.79	W
66357-35-5	Ranitidine	Pharmaceutical	2.22	N/A	0.27	S
79617-96-2	Sertraline	Pharmaceutical	0.25	N/A	5.29*	S
723-46-6	Sulfamethoxazole	Pharmaceutical	3.2	N/A	0.89	S
846-50-4	Temazepam	Pharmaceutical	N/A	0.32	2.19	W
148-79-8	Thiabendazole	Pharmaceutical	2.1	N/A	2.47	S
55142-85-3	Ticlopidine	Pharmaceutical	N/A	0.08	3.77^	W
27203-92-5	Tramadol	Pharmaceutical	N/A	0.04	3.01*	W
738-70-5	Trimethoprim	Pharmaceutical	2.9	N/A	0.91	S
93413-69-5	Venlafaxine	Pharmaceutical	0.25	0.04	3.28*	S, W
52-53-9	Verapamil	Pharmaceutical	N/A	0.08	3.79	W
81-81-2	Warfarin	Pharmaceutical	2.5	N/A	2.6	S
5436-43-1	2,2',4,4'-Tetrabromodiphenylether (PBDE 47)	Plasticizer/Flame Retardant	50	0.04	7.39^	S, W
117-81-7	Bis(2-Ethylhexyl) phthalate	Plasticizer/Flame Retardant	250	2.0	7.6	S, W
80-05-7	Bisphenol A	Plasticizer/Flame Retardant	0.2/50	0.04/0.2	3.32	S, W
84-66-2	Diethyl phthalate	Plasticizer/Flame Retardant	100	0.4	2.42	S, W
126-73-8	Tributyl phosphate	Plasticizer/Flame Retardant	50	0.064	4	S, W
115-86-6	Triphenyl phosphate	Plasticizer/Flame Retardant	50	0.08	4.59	S, W
78-51-3	Tris(2-butoxyethyl)phosphate	Plasticizer/Flame Retardant	150	0.64	3.75	S, W
b115-96-8	Tris(2-chloroethyl)phosphate	Plasticizer/Flame Retardant	100	0.16	1.44	S, W
13674-87-8	Tris(dichlorisopropyl)phosphate	Plasticizer/Flame Retardant	100	0.32	3.65	S, W
90-12-0	1-Methylnaphthalene	Polycylic Aromatic Hydrocarbon	50	0.04	3.87	S, W
581-42-0	2,6-Dimethylnaphthalene	Polycylic Aromatic Hydrocarbon	50	0.04	4.31	S, W

CASRN[1]	Analyte	Class	Sediment laboratory reporting level (ng/g)[2,3]	Water laboratory reporting level (ug/L)[2,3]	log K_{ow}[4]	Media
91-57-6	2-Methylnaphthalene	Polycylic Aromatic Hydrocarbon	50	0.04	3.86	S, W
120-12-7	Anthracene	Polycylic Aromatic Hydrocarbon	50	0.02	4.45	S, W
50-32-8	Benzo[a]pyrene	Polycylic Aromatic Hydrocarbon	50	0.02	6.13	S, W
206-44-0	Fluoranthene	Polycylic Aromatic Hydrocarbon	50	0.02	5.16	S, W
91-20-3	Naphthalene	Polycylic Aromatic Hydrocarbon	50	0.02	3.3	S, W
85-01-8	Phenanthrene	Polycylic Aromatic Hydrocarbon	50	0.02	4.46	S, W
129-00-0	Pyrene	Polycylic Aromatic Hydrocarbon	50	0.02	4.88	S, W
360-68-9	3-beta-Coprostanol	Sterol	25/500	0.2/1.6	8.82*	S, W
83-46-5	beta-Sitosterol	Sterol	500	4.8	9.65*	S, W
19466-47-8	beta-Stigmastanol	Sterol	500	3.4	11.1^	S, W
57-88-5	Cholesterol	Sterol	25/250	0.2/1.6	8.74*	S, W

Table A2. Analytes included in the analysis of fish tissue. This suite of chemicals includes 12 perfluorinated compounds (PFCs) and 17 brominated diphenyl ethers (BDEs).

CASRN[5]	Analyte[6]	Class
57-91-0	17-alpha-Estradiol	Hormone
57-63-6	17-alpha-Ethynylestradiol	Hormone
50-28-2	17-beta-Estradiol	Hormone
63-05-8	Androstenedione*	Hormone
50-27-1	Estriol	Hormone
53-16-7	Estrone	Hormone
56-53-1	Diethylstilbestrol*	Hormone
57-83-0	Progesterone	Hormone
58-22-0	Testosterone	Hormone
131-57-7	Oxybenzone*	Other
N/A	Perfluorinated compounds (PFCs)*	Other
1912-24-9	Atrazine	Pesticide
134-62-3	N,N-diethyl-meta-toluamide (DEET)	Pesticide
103-90-2	Acetaminophen	Pharmaceutical
58-08-2	Caffeine	Pharmaceutical
298-46-4	Carbamazepine	Pharmaceutical
439-14-5	Diazepam	Pharmaceutical
15307-86-5	Diclofenac*	Pharmaceutical
42399-41-7	Diltiazem	Pharmaceutical
147-24-0	Diphenhydramine	Pharmaceutical
25812-30-0	Gemfibrozil*	Pharmaceutical
125-29-1	Hydrocodone	Pharmaceutical
73334-07-3	Iopromide*	Pharmaceutical
57-53-4	Meprobamate	Pharmaceutical
76-99-3	Methadone	Pharmaceutical
22204-53-1	Naproxen*	Pharmaceutical
56161-73-0	Norfluoxetine	Pharmaceutical
6493-05-6	Pentoxifylline	Pharmaceutical
69-72-7	Salicylic acid*	Pharmaceutical
723-46-6	Sulfamethoxazole	Pharmaceutical
738-70-5	Trimethoprim	Pharmaceutical
80-05-7	Bisphenol A	Plasticizer/Flame Retardant
N/A	Brominated diphenyl ethers (BDEs)	Plasticizer/Flame Retardant

[5] This report contains Chemical Abstracts Services Registry Numbers (CASRN)®, which is a Registered Trademark of the American Chemical Society. The CASRN online database provides the latest registry number information: (http://www.cas.org/). Chemical Abstracts Services (CAS) recommends the verification of the CASRNs through CAS Client Services℠.

[6] * Indicates analytes only analyzed in fish tissue.

Appendix B. Summary Statistics

Table B1. Select summary statistics based on detections for sediment samples across all sites from 2010-2012 listed in order of detection frequency (i.e. percent detection) including analyte, CEC class, minimum concentration detected, maximum concentration detected, geometric mean, median, and detection frequency. All concentrations are reported in nanograms per gram (ng/g).

Analyte	Class	Minimum of Detections (ng/g)[7]	Maximum of Detections (ng/g)[7]	Geometric Mean of Detections (ng/g)[7]	Median of Detections(ng/g)[7]	Number of Detects	Percent Detects (n=107)
Indole	Flavor/Fragrance	10	888	172.9	199	106	99
Cholesterol	Sterol	148	24940	1746	1993	105	98
2,6-Dimethylnaphthalene	PAH	2	619	59.09	77	101	94
Fluoranthene	PAH	18	48700	779.3	757	97	91
Pyrene	PAH	9.63	40300	606.9	572	97	91
3-beta-Coprostanol	Sterol	29.5	23980	493.1	487	96	90
3-Methyl-1H-indole	Flavor/Fragrance	2	260	15.80	16.45	96	90
p-Cresol	Alkylphenol	10	4150	152.8	130	95	89
Benzo[a]-pyrene	PAH	2	5390	247.4	286.81	94	88
Carbazole	Pesticide	2	460	45.20	47	93	87
9,10-Anthraquinone	Other	4	1010	118.0	139	92	86
Phenanthrene	PAH	38.03	17300	403.0	343	92	86
Anthracene	PAH	3	3620	125.0	96	91	85
Estrone	Hormone	0.12	9.83	0.950	0.88	69	64
4-Androstene-3,17-dione	Hormone	0.05	6.64	0.400	0.42	63	59
beta-Sitosterol	Sterol	1670	22700	5408	5390	63	59
beta-Stigmastanol	Sterol	460	17200	2361	2150	63	59
Cholesterol	Sterol	911	18000	3025	2680	63	59
3-beta-Coprostanol	Sterol	89.48	13100	805.5	850	60	56
1-Methylnaphthalene	PAH	18.7	785	111.3	98.5	56	52
2-Methylnaphthalene	PAH	51.3	1160	189.2	170.5	56	52
Naphthalene	PAH	52	3080	323.4	278	54	50
17-beta-Estradiol	Hormone	0.04	5.16	0.360	0.39	46	43
Bisphenol A	Plasticizer/Flame Retardant	3.6	365.72	46.58	51	45	42
4-tert-Octylphenol	Alkylphenol	5.6	1910	40.12	30.55	42	39
Bisphenol A	Plasticizer/Flame Retardant	10.86	691	67.04	59.6	40	37
cis-Androsterone	Hormone	0.06	5.76	0.540	0.7	37	35
1,4-Dichlorobenzene	Other	11.3	270	48.59	43.8	36	34
4-Nonylphenol (sum of all isomers)	Alkylphenol	347	5180	1001	909.5	36	34
Diphenhydramine	Pharmaceutical	1.61	130.10	13.27	12.21	36	34
Triclosan	Other	7	518.17	69.31	80.4	35	33
Hexahydro-hexamethyl cyclopenta-benzopyran	Flavor/Fragrance	8.3	394	49.32	41.3	31	29
Bis(2-ethylhexyl) phthalate	Plasticizer/Flame Retardant	314	18200	1427	1085	24	22
Caffeine	Pharmaceutical	2.15	294.56	23.75	29	24	22
Isophorone	Other	0.92	25	4.46	5	21	20
Citalopram	Pharmaceutical	1.5	40.67	8.84	9.09	18	17
17-alpha-Estradiol	Hormone	0.07	2.05	0.300	0.21	17	16
Cotinine	Pharmaceutical	2.4	27.86	6.320	5.79	16	15
Acetyl hexamethyl tetrahydro naphthalene	Flavor/Fragrance	4.89	54	22.48	27	15	14
Tris(2-butoxyethyl) phosphate	Plasticizer/Flame Retardant	30	1220	198.0	242	15	14

[7] ND = Non-detect

Analyte	Class	Minimum of Detections (ng/g)[7]	Maximum of Detections (ng/g)[7]	Geometric Mean of Detections (ng/g)[7]	Median of Detections(ng/g)[7]	Number of Detects	Percent Detects (n=107)
Venlafaxine	Pharmaceutical	1.2	91.6	5.77	3.33	14	13
Isopropylbenzene	Other	7.6	56.8	29.53	33.23	12	11
Miconazole	Pharmaceutical	5.5	197.5	26.29	25.9	12	11
Thiabendazole	Pharmaceutical	2.3	58.04	8.85	9.97	12	11
Camphor	Flavor/Fragrance	8.40	92.90	29.85	31.56	9	8
4-Cumylphenol	Alkylphenol	15.44	234	67.58	70	8	7
Epitestosterone	Hormone	0.11	1.62	0.29	0.28	8	7
Sertraline	Pharmaceutical	5.8	22.7	10.62	9.6	8	7
4-Nonylphenol monoethoxylate (sum of all isomers)	Alkylphenol	208	3230	761.3	730	7	7
Equilenin	Hormone	0.53	9.71	2.16	2.7	6	6
Fluoxetine	Pharmaceutical	4.2	44.21	9.09	7.4	6	6
Triphenyl phosphate	Plasticizer/Flame Retardant	6.4	180	25.82	20.8	6	6
Warfarin	Pharmaceutical	0.59	92.7	22.76	44.51	6	6
4-tert-Octylphenol diethoxylate	Alkylphenol	15.6	126	40.59	38.4	5	5
Cimetidine	Pharmaceutical	2.35	37.10	7.66	5.27	5	5
d-Limonene	Flavor/Fragrance	31.1	378.42	119.7	110	5	5
Metolachlor	Pesticide	6	17	8.07	7	5	5
1,7-Dimethylxanthine	Pharmaceutical	28.86	43.69	34.08	32.74	4	4
Albuterol	Pharmaceutical	1.8	11.28	3.66	3.15	4	4
Progesterone	Hormone	0.23	4.41	1.01	1.01	4	4
4-tert-Octylphenol monoethoxylate	Alkylphenol	3.51	272	46.96	108.5	3	3
Codeine	Pharmaceutical	6.08	18.51	10.13	9.25	3	3
Estriol	Hormone	0.13	0.79	0.33	0.36	3	3
Mestranol	Hormone	0.12	0.83	0.29	0.24	3	3
Norsertraline	Pharmaceutical	14.7	25	18.27	16.6	3	3
Paroxetine	Pharmaceutical	6.5	18.7	10.16	8.64	3	3
Testosterone	Hormone	0.29	0.8	0.46	0.42	3	3
Trimethoprim	Pharmaceutical	10.7	17.8	14.19	15	3	3
Carbamazapine	Pharmaceutical	3.41	5.62	4.38	4.52	2	2
Carbamazepine	Pharmaceutical	3.41	5.62	4.38	4.52	2	2
Dihydrotestosterone	Hormone	0.07	0.14	0.100	0.1	2	2
trans-Diethylstilbestrol	Hormone	0.15	0.46	0.26	0.31	2	2
Tributyl phosphate	Plasticizer/Flame Retardant	7.84	82.1	25.37	44.97	2	2
17-alpha-Ethynyl estradiol	Hormone	0.37	0.37	0.37	0.37	1	1
Chlorpyrifos	Pesticide	305	305	305	305	1	1
Erythromycin	Pharmaceutical	9.12	9.12	9.12	9.12	1	1
Isoquinoline	Other	20.86	20.86	20.86	20.86	1	1
N,N-diethyl-meta-toluamide (DEET)	Pesticide	9.7	9.7	9.7	9.7	1	1
Phenol	Other	294	294	294	294	1	1
Prometon	Pesticide	2470	2470	2470	2470	1	1
Sulfamethoxazole	Pharmaceutical	3.45	3.45	3.45	3.45	1	1
Tris(2-chloroethyl) phosphate	Plasticizer/Flame Retardant	120	120	120	120	1	1
Tris(dichloroisopropyl) phosphate	Plasticizer/Flame Retardant	123	123	123	123	1	1
11-Ketotestosterone	Hormone	ND	ND	ND	ND	0	0
2,2',4,4'-Tetrabromodiphenyl ether (BDE congener 47 BDE)	Plasticizer/Flame Retardant	ND	ND	ND	ND	0	0
3-tert-Butyl-4-hydroxy-anisole	Other	ND	ND	ND	ND	0	0
4-n-Octylphenol	Alkylphenol	ND	ND	ND	ND	0	0
4-Nonylphenol diethoxylate (sum of all isomers)	Alkylphenol	ND	ND	ND	ND	0	0

Table B1 *(continued)*

Analyte	Class	Minimum of Detections (ng/g)[7]	Maximum of Detections (ng/g)[7]	Geometric Mean of Detections (ng/g)[7]	Median of Detections(ng/g)[7]	Number of Detects	Percent Detects (n=107)
Acetaminophen	Pharmaceutical	ND	ND	ND	ND	0	0
Acetephenone	Flavor/Fragrance	ND	ND	ND	ND	0	0
Atrazine	Pesticide	ND	ND	ND	ND	0	0
Azithromycin	Pharmaceutical	ND	ND	ND	ND	0	0
Benzophenone	Other	ND	ND	ND	ND	0	0
Bromacil	Pesticide	ND	ND	ND	ND	0	0
Bupropion	Pharmaceutical	ND	ND	ND	ND	0	0
Dehydronifedipine	Pharmaceutical	ND	ND	ND	ND	0	0
Diazinon	Pesticide	ND	ND	ND	ND	0	0
Diethyl phthalate	Plasticizer/Flame Retardant	ND	ND	ND	ND	0	0
Diltiazem	Pharmaceutical	ND	ND	ND	ND	0	0
Duloxetine	Pharmaceutical	ND	ND	ND	ND	0	0
Equilin	Hormone	ND	ND	ND	ND	0	0
Fluoxetine	Pharmaceutical	ND	ND	ND	ND	0	0
Fluvoxamine	Pharmaceutical	ND	ND	ND	ND	0	0
Isoborneol	Other	ND	ND	ND	ND	0	0
Menthol	Flavor/Fragrance	ND	ND	ND	ND	0	0
Norethindrone	Hormone	ND	ND	ND	ND	0	0
Norfluoxetine	Pharmaceutical	ND	ND	ND	ND	0	0
Ranitidine	Pharmaceutical	ND	ND	ND	ND	0	0

Table B2. Select summary statistics based on detections for water samples across all sites from 2010-2012 listed in order of detection frequency (i.e. percent detection) including analyte, CEC class, minimum concentration detected, maximum concentration detected, geometric mean, median, and detection frequency. All concentrations are reported in micrograms per liter (μg/L).

Analyte	Class	Minimum of Detections (µg/L)[8]	Maximum of Detections (µg/L)[8]	Geometric Mean of Detections (µg/L)[8]	Median of Detections (µg/L)[8]	Number of Detections	Percent Detection (n=127)
Cholesterol	Sterol	0.286	18.5	1.955	1848.69	124	98
Metolachlor	Pesticide	0.005	1.56	0.034	0.03	84	66
N,N-diethyl-meta-toluamide (DEET)	Pesticide	0.01	0.714	0.04	0.04	82	65
Atrazine	Pesticide	0.01	2.6	0.074	0.07	76	60
Cholesterol	Sterol	0.2	5	0.625	0.7	58	46
Isophorone	Other	0.004	0.046	0.012	0.01	58	46
9,10-Anthraquinone	Other	0.005	0.534	0.047	0.05	56	44
beta-Sitosterol	Sterol	0.1	1.57	0.492	0.5	51	40
Tributyl phosphate	Plasticizer/Flame Retardant	0.008	0.283	0.042	0.04	48	38
Fluoranthene	PAH	0.005	0.26	0.023	0.02	44	35
Tris(dichloro-isopropyl) phosphate	Plasticizer/Flame Retardant	0.02	0.21	0.058	0.06	42	33
Tris(2-butoxyethyl) phosphate	Plasticizer/Flame Retardant	0.106	1.466	0.372	0.29	40	32
Estrone	Hormone	0	0.002	0.001	0.8	39	31
Prometon	Pesticide	0.007	0.18	0.043	0.05	37	29
Bisphenol A	Plasticizer/Flame Retardant	0.018	0.629	0.046	0.04	36	28
3,4-Dichlorophenyl isocyanate	Other	0.01	0.442	0.082	0.09	35	28
Caffeine	Pharmaceutical	0.02	0.769	0.111	0.11	34	27
Carbaryl	Pesticide	0.002	0.99	0.059	0.08	33	26
Pyrene	PAH	0.01	0.2	0.024	0.02	33	26
Tramadol	Pharmaceutical	0.013	0.304	0.045	0.05	33	26
Lidocaine	Pharmaceutical	0.002	0.078	0.01	0.01	31	24
Hexahydrohexamethyl cyclopentabenzopyran	Flavor/Fragrance	0.01	0.58	0.058	0.07	30	24
3-beta-Coprostanol	Sterol	0.071	5.935	0.556	515.12	29	23
Benzo[a]pyrene	PAH	0.005	0.12	0.014	0.01	28	22
Phenytoin	Pharmaceutical	0.014	0.148	0.041	0.04	27	21
Oxycodone	Pharmaceutical	0.017	0.638	0.129	0.16	25	20
Bromacil	Pesticide	0.01	0.118	0.051	0.07	24	19
p-Cresol	Alkylphenol	0.004	0.1	0.017	0.02	24	19
Cotinine	Pharmaceutical	0.02	0.104	0.038	0.04	22	17
Carbamazepine	Pharmaceutical	0.014	0.135	0.04	0.04	21	17
Fluconazole	Pharmaceutical	0.008	0.086	0.026	0.03	21	17
5-Methyl-1H-benzotriazole	Other	0.07	0.45	0.192	0.2	19	15
Iminostilbene	Pharmaceutical	0.006	0.084	0.02	0.02	19	15
Triphenyl phosphate	Plasticizer/Flame Retardant	0.01	0.059	0.023	0.03	19	15
Celecoxib	Pharmaceutical	0.009	0.124	0.055	0.06	17	13
Ibuprofen	Pharmaceutical	0.025	22.041	0.252	0.24	17	13
Carbazole	Pesticide	0.005	0.159	0.021	0.02	16	13
Diphenhydramine	Pharmaceutical	0.007	0.147	0.036	0.04	16	13
Tribromomethane	Other	0.004	0.18	0.033	0.04	16	13
Venlafaxine	Pharmaceutical	0.009	0.102	0.037	0.04	16	13
1-Methyl-naphthalene	PAH	0.01	0.071	0.026	0.02	15	12
Phenanthrene	PAH	0.01	0.08	0.029	0.03	14	11
Phenobarbital	Pharmaceutical	0.007	0.055	0.022	0.02	14	11
2-Methylnaphthalene	PAH	0.01	0.116	0.05	0.06	13	10
Anthracene	PAH	0.005	0.03	0.013	0.02	13	10
Citalopram	Pharmaceutical	0.003	0.063	0.012	0.01	13	10

[8] ND = Non-detect

Table B2 *(continued)*

Analyte	Class	Minimum of Detections (µg/L)[a]	Maximum of Detections (µg/L)[a]	Geometric Mean of Detections (µg/L)[a]	Median of Detections (µg/L)[a]	Number of Detections	Percent Detection (n=127)
Triethyl citrate	Other	0.01	0.169	0.062	0.08	13	10
3-beta-Coprostanol	Sterol	0.044	1.030	0.178	0.2	12	9
4-Nonylphenol (sum of all isomers)	Alkylphenol	0.04	1.2	0.176	0.2	12	9
Methocarbamol	Pharmaceutical	0.062	0.329	0.17	0.21	11	9
2,6-Dimethylnaphthalene	PAH	0.005	0.02	0.014	0.02	10	8
4-Androstene-3,17-dione	Hormone	0	0.002	0.001	0.9	10	8
Bisphenol A	Plasticizer/Flame Retardant	0.004	0.724	0.084	104	10	8
Chloroxylenol	Pharmaceutical	0.012	0.07	0.035	0.04	10	8
Piperonyl butoxide	Pharmaceutical	0.006	0.03	0.015	0.02	10	8
4-tert-Octylphenol diethoxylate	Alkylphenol	0.029	0.123	0.062	0.07	9	7
Benzophenone	Other	0.026	0.492	0.162	0.19	9	7
cis-Androsterone	Hormone	0	0.006	0.001	1.06	9	7
1,4-Dichlorobenzene	Other	0.01	0.07	0.019	0.02	8	6
4-Nonylphenol diethoxylate (sum of all isomers)	Alkylphenol	0.12	0.813	0.383	0.6	8	6
Acetyl hexamethyl tetrahydro naphthalene	Flavor/Fragrance	0.01	0.07	0.015	0.01	8	6
Diltiazem	Pharmaceutical	0.004	0.028	0.012	0.02	8	6
Metaxalone	Pharmaceutical	0.006	0.052	0.023	0.03	8	6
Primidone	Pharmaceutical	0.014	0.049	0.027	0.03	8	6
Triclosan,	Other	0.02	0.104	0.041	0.04	8	6
Tetrachloroethene,	Other	0.01	0.05	0.013	0.01	7	6
17-beta-Estradiol	Hormone	0	0.001	0	0.67	6	5
4-Nonylphenol monoethoxylate (sum of all isomers)	Alkylphenol	0.094	0.438	0.212	0.22	6	5
Hydrocodone	Pharmaceutical	0.013	0.104	0.039	0.06	6	5
Menthol	Flavor/Fragrance	0.036	0.230	0.102	0.17	5	4
Oxcarbazepine	Pharmaceutical	0.062	0.281	0.098	0.09	5	4
Tris(2-chloroethyl) phosphate	Plasticizer/Flame Retardant	0.042	0.130	0.076	0.1	5	4
beta-Stigmastanol	Sterol	0.14	0.245	0.192	0.2	4	3
Chirald	Pharmaceutical	0.001	0.012	0.004	0.01	4	3
Dichlorvos	Pesticide	0.005	0.120	0.042	0.1	4	3
Methadone	Pharmaceutical	0.002	0.031	0.008	0.02	4	3
3-Methyl-1H-indole	Flavor/Fragrance	0.002	0.02	0.005	0.01	3	2
Butalbital	Pharmaceutical	0.006	0.046	0.018	0.03	3	2
Camphor	Flavor/Fragrance	0.1	0.32	0.152	0.24	3	2
Diethyl phthalate	Plasticizer/Flame Retardant	0.6	1.9	0.893	1.4	3	2
Efavirenz	Pharmaceutical	0.005	0.033	0.013	0.02	3	2
Estriol	Hormone	0	0.001	0.001	0.97	3	2
Indole	Flavor/Fragrance	0.01	0.012	0.011	0.01	3	2
Meperidine	Pharmaceutical	0.002	0.192	0.018	0.11	3	2
Naphthalene	PAH	0.05	0.055	0.052	0.05	3	2
Pentachlorophenol	Pesticide	0.04	0.2	0.117	0.2	3	2
Propofol	Pharmaceutical	0.014	0.047	0.029	0.04	3	2
trans-Diethyl-stilbestrol	Hormone	0	0.002	0.001	1.43	3	2
2-Ethyl-2-phenylmalonamide	Pharmaceutical	0.009	0.012	0.01	0.01	2	2
4-Cumylphenol	Alkylphenol	0.003	0.01	0.005	0.01	2	2
Bis(2-ethylhexyl) phthalate	Plasticizer/Flame Retardant	1.780	36	8.005	2	2	2
Carisoprodol	Pharmaceutical	0.016	0.086	0.037	0.09	2	2
Chlorpheniramine	Pharmaceutical	0.001	0.015	0.004	0.01	2	2
Codeine	Pharmaceutical	0.013	0.041	0.023	0.04	2	2
Epitestosterone	Hormone	0.001	0.001	0.001	0.98	2	2
Pentobarbital	Pharmaceutical	0.01	0.019	0.014	0.02	2	2
Verapamil	Pharmaceutical	0.015	0.017	0.016	0.02	2	2
17-alpha-Estradiol	Hormone	1.27	1.27	1.27	1.27	1	1

Analyte	Class	Minimum of Detections (µg/L)[a]	Maximum of Detections (µg/L)[a]	Geometric Mean of Detections (µg/L)[a]	Median of Detections (µg/L)[a]	Number of Detections	Percent Detection (n=127)
17-alpha-Ethynyl estradiol	Hormone	1.31	1.31	1.31	1.31	1	1
3-tert-Butyl-4-hydroxyanisole	Other	0.04	0.04	0.04	0.04	1	1
4-tert-Octylphenol monoethoxylate	Alkylphenol	0.1	0.1	0.1	0.1	1	1
Amitriptyline	Pharmaceutical	0.004	0.004	0.004	0.004	1	1
Antipyrine	Pharmaceutical	0.018	0.018	0.018	0.018	1	1
Dextromethorphan	Pharmaceutical	008	0.008	008	008	1	1
Dihydrotestosterone	Hormone	1.71	1.71	1.71	1.71	1	1
Griseofulvin	Pharmaceutical	0.031	0.031	0.031	0.031	1	1
Mestranol	Pharmaceutical	1.38	1.38	1.38	1.38	1	1
Metalaxyl	Pesticide	0.04	0.04	0.04	0.04	1	1
Pentoxifylline	Pharmaceutical	0.034	0.034	0.034	0.034	1	1
Phenol	Other	0.14	0.14	0.14	0.14	1	1
Ticlopidine	Pharmaceutical	0.002	0.002	0.002	0.002	1	1
11-Ketotestosterone	Hormone	ND	ND	ND	ND	0	0
2,2',4,4'-Tetrabromodiphenyl ether (BDE congener 47)	Plasticizer/Flame Retardant	ND	ND	ND	ND	0	0
4-n-Octylphenol	Alkylphenol	ND	ND	ND	ND	0	0
4-tert-Octylphenol	Alkylphenol	ND	ND	ND	ND	0	0
Acetaminophen	Pharmaceutical	ND	ND	ND	ND	0	0
Acetophenone	Flavor/Fragrance	ND	ND	ND	ND	0	0
Chlorpyrifos	Pesticide	ND	ND	ND	ND	0	0
Diazepam	Pharmaceutical	ND	ND	ND	ND	0	0
Diazinon	Pesticide	ND	ND	ND	ND	0	0
Dihydrocodeine	Pharmaceutical	ND	ND	ND	ND	0	0
d-Limonene	Flavor/Fragrance	ND	ND	ND	ND	0	0
Equilenin	Hormone	ND	ND	ND	ND	0	0
Equilin	Hormone	ND	ND	ND	ND	0	0
Fluoxetine	Pharmaceutical	ND	ND	ND	ND	0	0
Isoborneol	Other	ND	ND	ND	ND	0	0
Isopropylbenzene	Other	ND	ND	ND	ND	0	0
Isoquinoline	Other	ND	ND	ND	ND	0	0
Meprobamate	Pharmaceutical	ND	ND	ND	ND	0	0
Methyl salicylate	Other	ND	ND	ND	ND	0	0
Methylphenidate	Pharmaceutical	ND	ND	ND	ND	0	0
Norethindrone	Pharmaceutical	ND	ND	ND	ND	0	0
Norpropoxyphene	Pharmaceutical	ND	ND	ND	ND	0	0
Phendimetrazine	Pharmaceutical	ND	ND	ND	ND	0	0
Progesterone	Hormone	ND	ND	ND	ND	0	0
Temazepam	Pharmaceutical	ND	ND	ND	ND	0	0
Testosterone	Hormone	ND	ND	ND	ND	0	0

Table B3. Select summary statistics for CEC concentrations in benthic species liver tissue. All concentrations are reported in nanograms per gram (ng/g). Laboratory detection limits are listed in an unpublished laboratory report and can be made available upon request.

Analyte	Minimum of Detections (ng/g)[9]	Geometric Mean of Detections (ng/g)[9]	Maximum of Detections (ng/g)[9]	Number of Liver Samples Analyzed	Number of Detects	Percent Detection
17-alpha-Estradiol	ND	ND	ND	61	0	0
17-alpha-Ethynylestradiol	ND	ND	ND	61	0	0
17-beta-Estradiol	0.01	0.03	0.04	61	3	5
Androstenedione	ND	ND	ND	61	0	0
Caffeine	0.004	0.01	0.01	61	4	7
Carbamazepine	ND	ND	ND	61	0	0
Diazepam	ND	ND	ND	61	0	0
Diclofenac	ND	ND	ND	61	0	0
Diethylstilbestrol	ND	ND	ND	61	0	0
Diltiazem	0.01	0.01	0.01	61	1	2
Diphenhydramine	0.02	0.02	0.02	61	1	2
Estrone	ND	ND	ND	61	0	0
Gemfibrozil	ND	ND	ND	61	0	0
Iopromide	ND	ND	ND	61	0	0
Meprobamate	ND	ND	ND	61	0	0
Methadone	0.01	0.01	0.01	61	1	2
Naproxen	ND	ND	ND	61	0	0
Norfluoxetine	0.01	0.01	0.02	61	3	5
Oxybenzone	ND	ND	ND	61	0	0
Pentoxifylline	ND	ND	ND	61	0	0
Progesterone	0.09	0.09	0.09	61	2	3
Sulfamethoxazole	ND	ND	ND	61	0	0
Testosterone	0.02	0.06	0.13	61	23	38
Acetaminophen	ND	ND	ND	61	0	0
Estriol	ND	ND	ND	61	0	0
Salicylic Acid	0.06	0.09	0.16	61	26	43
Bisphenol A	0.02	0.02	0.04	61	6	10
DEET	0.003	0.003	0.003	61	1	2
Hydrocodone	0.01	0.01	0.01	61	1	2
Perfluoro-n-tridecanoic acid	0.0006	0.01	4.40	46	41	89
Perfluorobutanesulfonate	0.0003	0.003	0.25	46	3	7
Perfluorodecanoic acid	0.001	0.03	9.80	46	46	100
Perfluorododecanoic acid	0.0007	0.01	4.40	46	40	87
Perfluoroheptanoic acid	0.0002	0.0003	0.0003	46	2	4
Perfluorohexanesulfonate	0.0003	0.004	2.20	46	23	50
Perfluorohexanoic acid	0.0002	0.002	1.80	46	7	15
Perfluorononanoic acid	0.0004	0.004	2.70	46	31	67
Perfluorooctanesulfonate	0.01	0.73	710	46	46	100
Perfluorooctanoic acid	0.0003	0.002	3.20	46	17	37
Perfluoropentanoic acid	0.001	0.01	0.02	46	16	35
Perfluoroundecanoic acid	0.001	0.03	8.70	46	46	100
Trimethoprim	0.004	0.004	0.004	61	1	2
Atrazine	ND	ND	ND	61	0	0
BDE# 100	ND	ND	ND	0	0	0
BDE# 128	ND	ND	ND	0	0	0
BDE# 138	ND	ND	ND	0	0	0
BDE# 153	ND	ND	ND	0	0	0
BDE# 154	ND	ND	ND	0	0	0
BDE# 17	ND	ND	ND	0	0	0
BDE# 183	ND	ND	ND	0	0	0
BDE# 190	ND	ND	ND	0	0	0
BDE# 203	ND	ND	ND	0	0	0

[9] ND = Non-detect

Analyte	Minimum of Detections (ng/g)[9]	Geometric Mean of Detections (ng/g)[9]	Maximum of Detections (ng/g)[9]	Number of Liver Samples Analyzed	Number of Detects	Percent Detection
BDE# 206	ND	ND	ND	0	0	0
BDE# 209	ND	ND	ND	0	0	0
BDE# 28	ND	ND	ND	0	0	0
BDE# 47	ND	ND	ND	0	0	0
BDE# 66	ND	ND	ND	0	0	0
BDE# 71	ND	ND	ND	0	0	0
BDE# 85	ND	ND	ND	0	0	0
BDE# 99	ND	ND	ND	0	0	0

Table B4. Select summary statistics for CEC concentrations in pelagic species liver tissue. All concentrations are reported in nanograms per gram (ng/g). Laboratory detection limits are listed in an unpublished laboratory report and can be made available upon request.

Analyte	Minimum of Detections (ng/g)[10]	Geometric Mean of Detections (ng/g)[10]	Maximum of Detections (ng/g)[10]	Number of Liver Samples Analyzed	Number of detects	Percent detection
17-alpha-Estradiol	ND	ND	ND	89	0	0
17-alpha-Ethynylestradiol	ND	ND	ND	89	0	0
17-beta-Estradiol	0.01	0.02	0.15	89	13	15
Androstenedione	ND	ND	ND	89	0	0
Caffeine	0.01	0.03	0.15	89	4	4
Carbamazepine	ND	ND	ND	89	0	0
Diazepam	ND	ND	ND	89	0	0
Diclofenac	ND	ND	ND	89	0	0
Diethylstilbestrol	0.11	0.12	0.13	89	2	2
Diltiazem	ND	ND	ND	89	0	0
Diphenhydramine	0.003	0.003	0.003	89	1	1
Estrone	ND	ND	ND	89	0	0
Gemfibrozil	0.01	0.01	0.01	89	1	1
Iopromide	0.01	0.01	0.01	89	2	2
Meprobamate	ND	ND	ND	89	0	0
Methadone	0.003	0.01	0.01	89	8	9
Naproxen	ND	ND	ND	89	0	0
Norfluoxetine	0.01	0.01	0.01	89	1	1
Oxybenzone	0.06	0.18	0.83	89	9	10
Pentoxifylline	0.04	0.04	0.04	89	1	1
Progesterone	0.02	0.04	0.14	89	15	17
Sulfamethoxazole	ND	ND	ND	89	0	0
Testosterone	0.03	0.06	0.21	89	41	46
Acetaminophen	0.06	0.06	0.06	89	1	1
Estriol	ND	ND	ND	89	0	0
Salicylic Acid	0.05	0.13	0.42	89	41	46
Bisphenol A	0.01	0.03	11.00	89	10	11
DEET	0.003	0.004	0.01	89	2	2
Hydrocodone	ND	ND	ND	89	0	0
Perfluoro-n-tridecanoic acid	0.0006	0.005	4.70	68	63	93
Perfluorobutanesulfonate	0.0003	0.0005	0.001	68	7	10
Perfluorodecanoic acid	0.001	0.01	6.60	68	68	100
Perfluorododecanoic acid	0.0008	0.01	6.10	68	65	96
Perfluoroheptanoic acid	0.0002	0.0004	0.0009	68	5	7
Perfluorohexanesulfonate	0.0003	0.001	0.96	68	29	43
Perfluorohexanoic acid	0.0003	0.0006	0.002	68	18	26
Perfluorononanoic acid	0.0002	0.0003	0.0008	68	7	10
Perfluorooctanesulfonate	0.002	0.15	170.00	68	68	100
Perfluorooctanoic acid	0.0003	0.0007	0.02	68	8	12
Perfluoropentanoic acid	0.002	0.004	0.01	68	14	21
Perfluoroundecanoic acid	0.001	0.01	8.60	68	68	100
Trimethoprim	ND	ND	ND	89	0	0
Atrazine	ND	ND	ND	89	0	0
BDE# 100	4.70	12.27	130.00	8	7	88
BDE# 128	ND	ND	ND	8	0	0
BDE# 138	ND	ND	ND	8	0	0
BDE# 153	3.10	10.15	100.00	8	4	50
BDE# 154	2.90	8.83	77.00	8	4	50
BDE# 17	ND	ND	ND	8	0	0
BDE# 183	ND	ND	ND	8	0	0
BDE# 190	ND	ND	ND	8	0	0
BDE# 203	ND	ND	ND	8	0	0

[10] ND = Non-detect

Analyte	Minimum of Detections (ng/g)[10]	Geometric Mean of Detections (ng/g)[10]	Maximum of Detections (ng/g)[10]	Number of Liver Samples Analyzed	Number of detects	Percent detection
BDE# 206	ND	ND	ND	8	0	0
BDE# 209	ND	ND	ND	8	0	0
BDE# 28	ND	ND	ND	8	0	0
BDE# 47	ND	ND	ND	8	0	0
BDE# 66	ND	ND	ND	8	0	0
BDE# 71	150.00	150.00	150.00	8	1	13
BDE# 85	ND	ND	ND	8	0	0
BDE# 99	3.00	14.46	280.00	8	6	75

Appendix C. Summary Figures and Tables

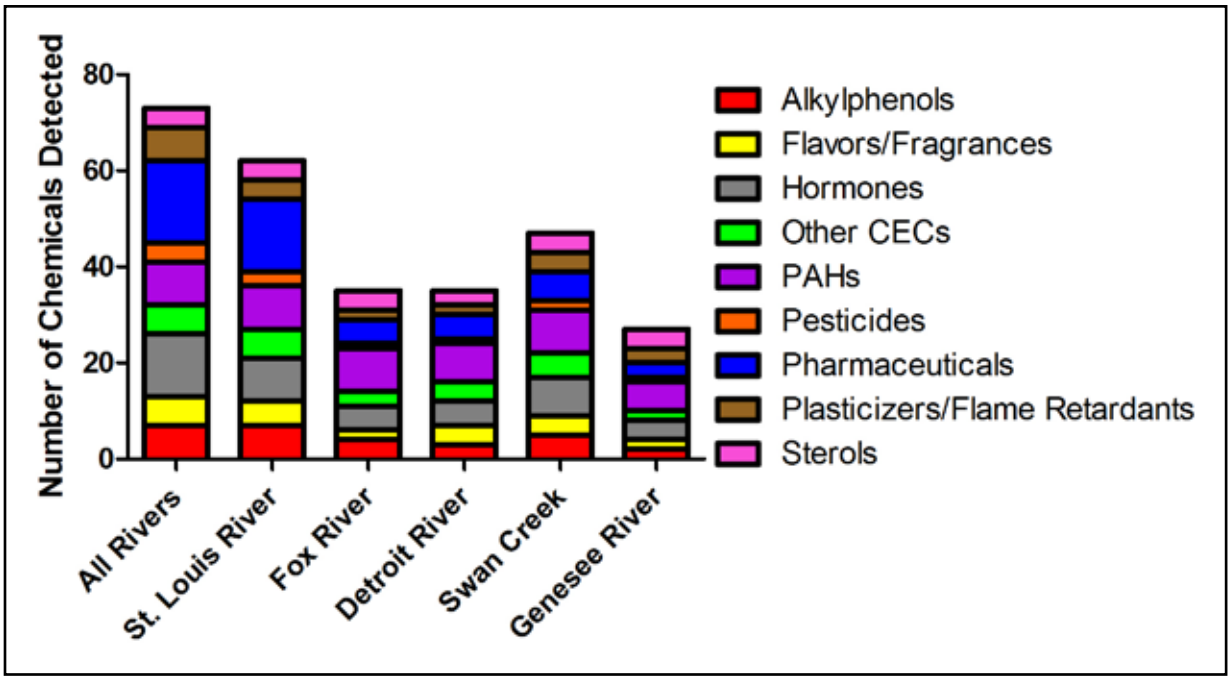


Figure C1. Number of chemicals detected in sediment samples collected in fall 2010 by sampling location and chemical class.

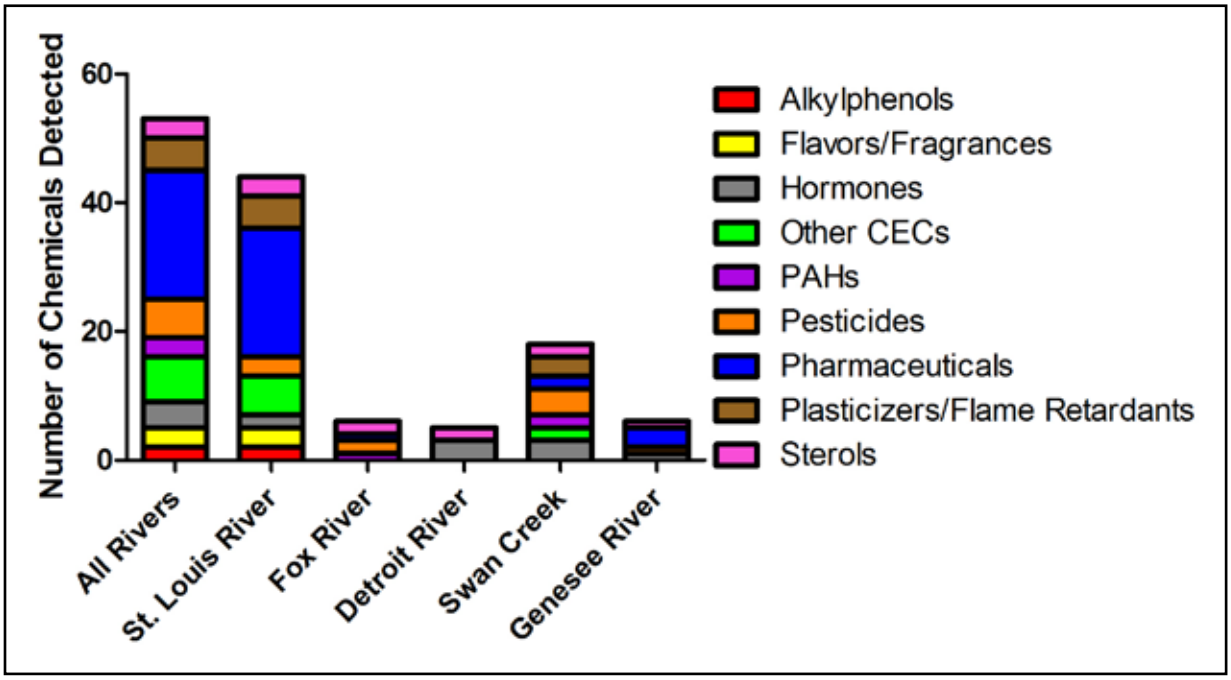


Figure C2. Number of chemicals detected in water samples collected in fall 2010 by sampling location and chemical class.

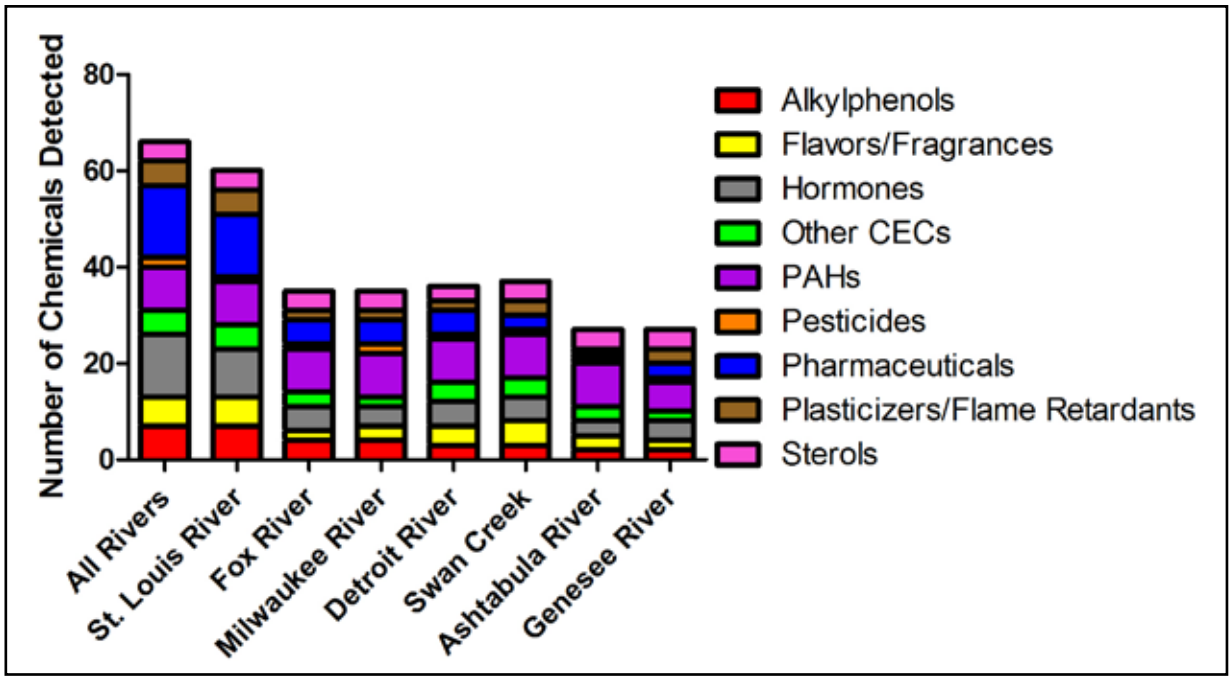


Figure C3. Number of chemicals detected in sediment samples collected in spring 2011 by sampling location and chemical class.

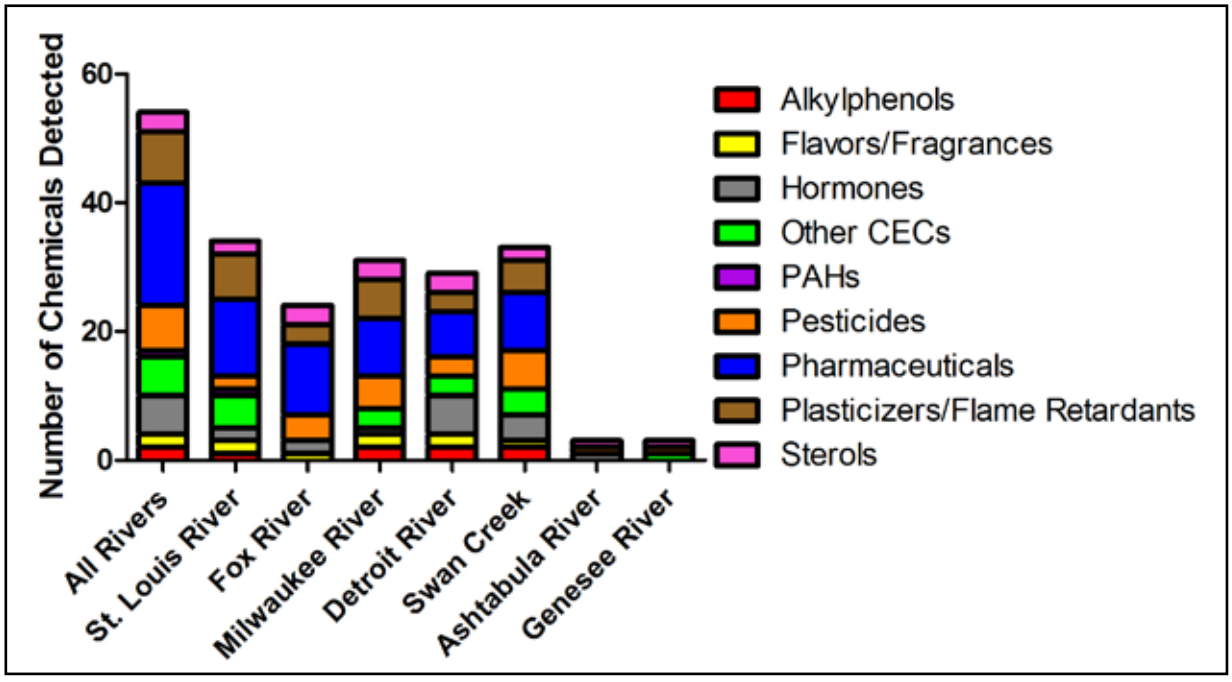


Figure C4. Number of chemicals detected in water samples collected in spring 2011 by sampling location and chemical class.

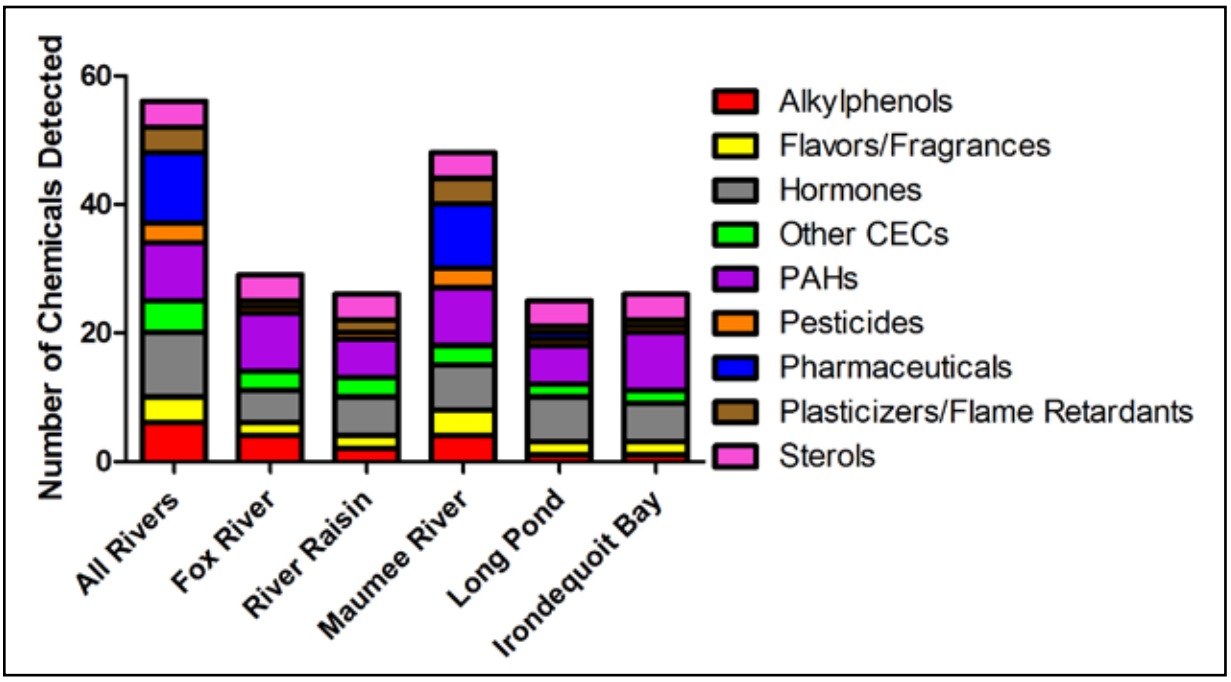


Figure C5. Number of chemicals detected in sediment samples collected in spring 2012 by sampling location and chemical class.

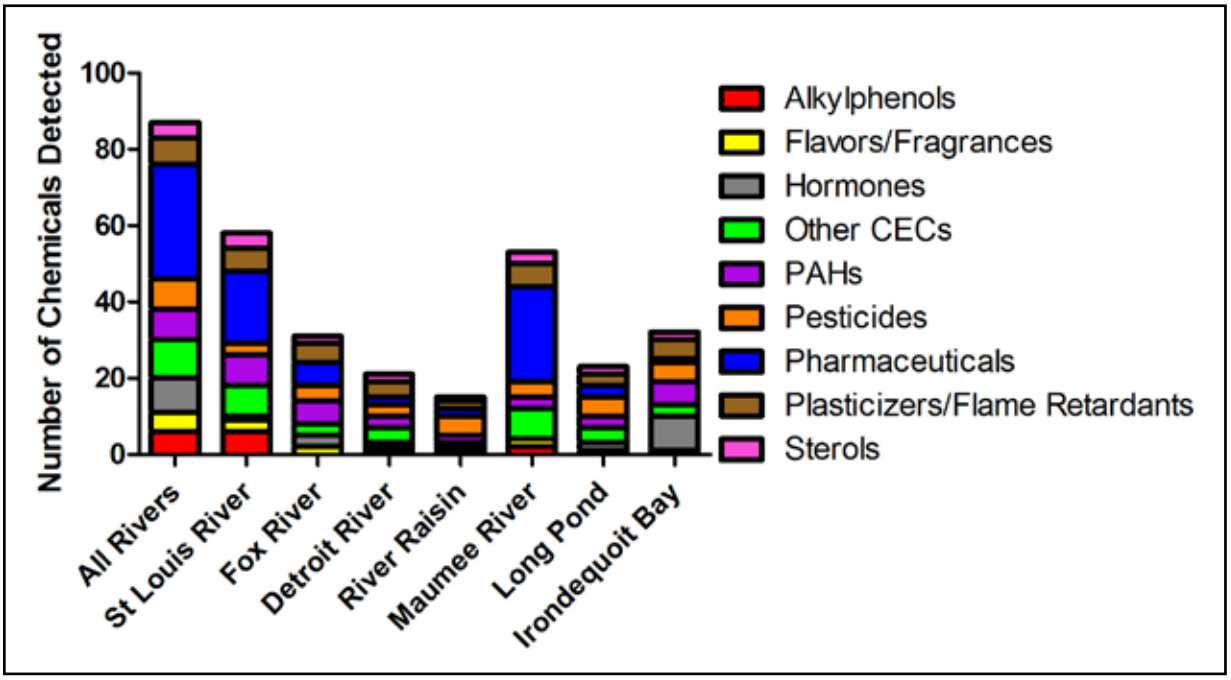


Figure C6. Number of chemicals detected in water samples collected in spring 2012 by sampling location and chemical class.

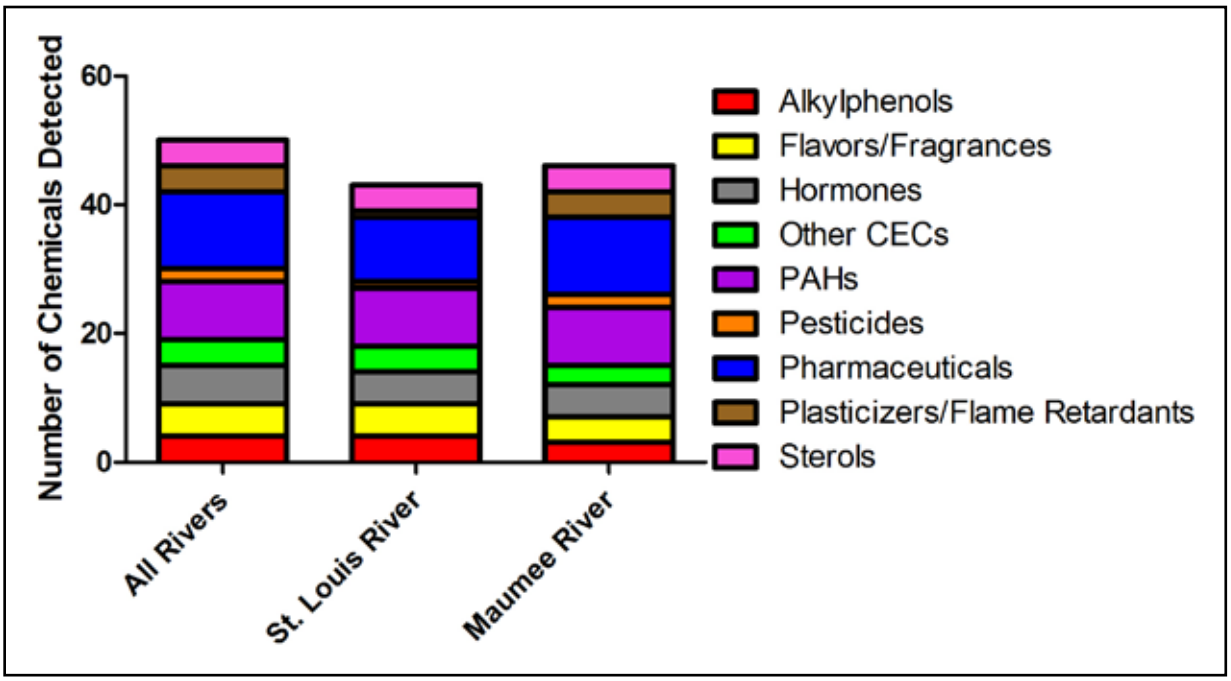


Figure C7. Number of chemicals detected in sediment samples collected in fall 2012 by sampling location and chemical class.

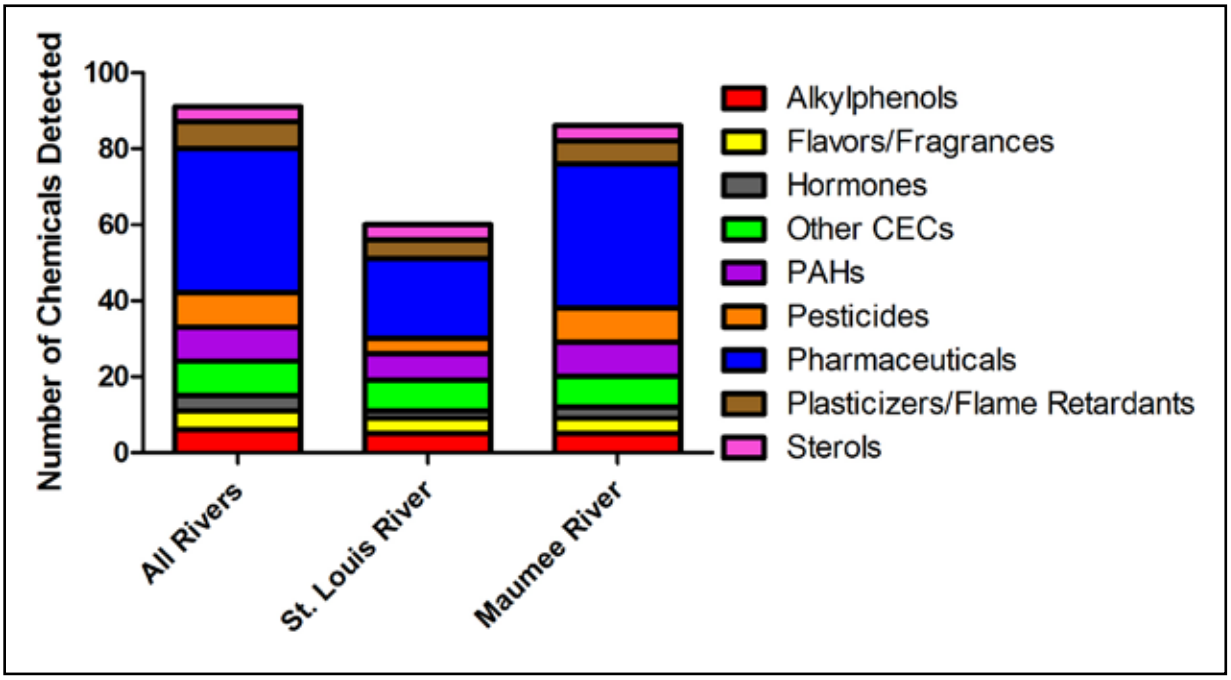


Figure C8. Number of chemicals detected in water samples collected in fall 2012 by sampling location and chemical class.

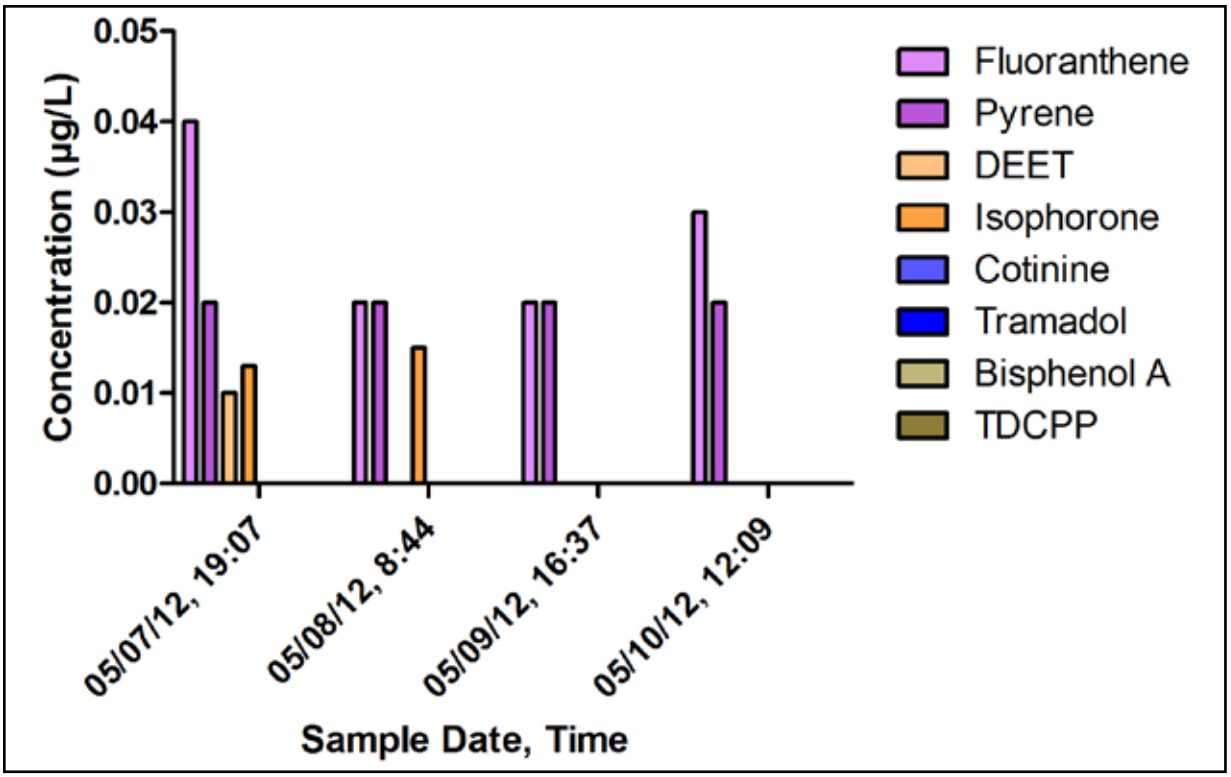


Figure C9. Time series graph of water samples collected in spring 2012 at the EriePr sampling site in the St. Louis River location (TDCPP = tris(dichloroisopropyl) phosphate).

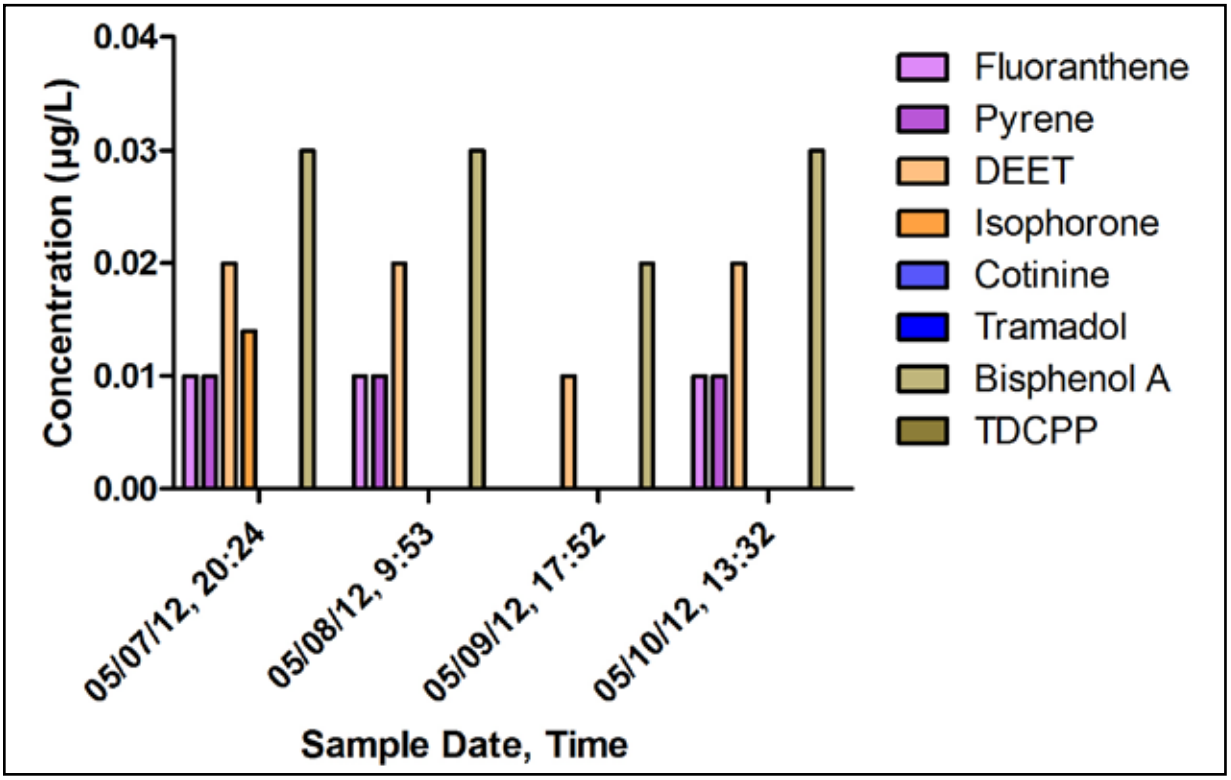


Figure C10. Time series graph of water samples collected in spring 2012 at the RicesPt sampling site in the St. Louis River location (TDCPP = tris(dichloroisopropyl) phosphate).

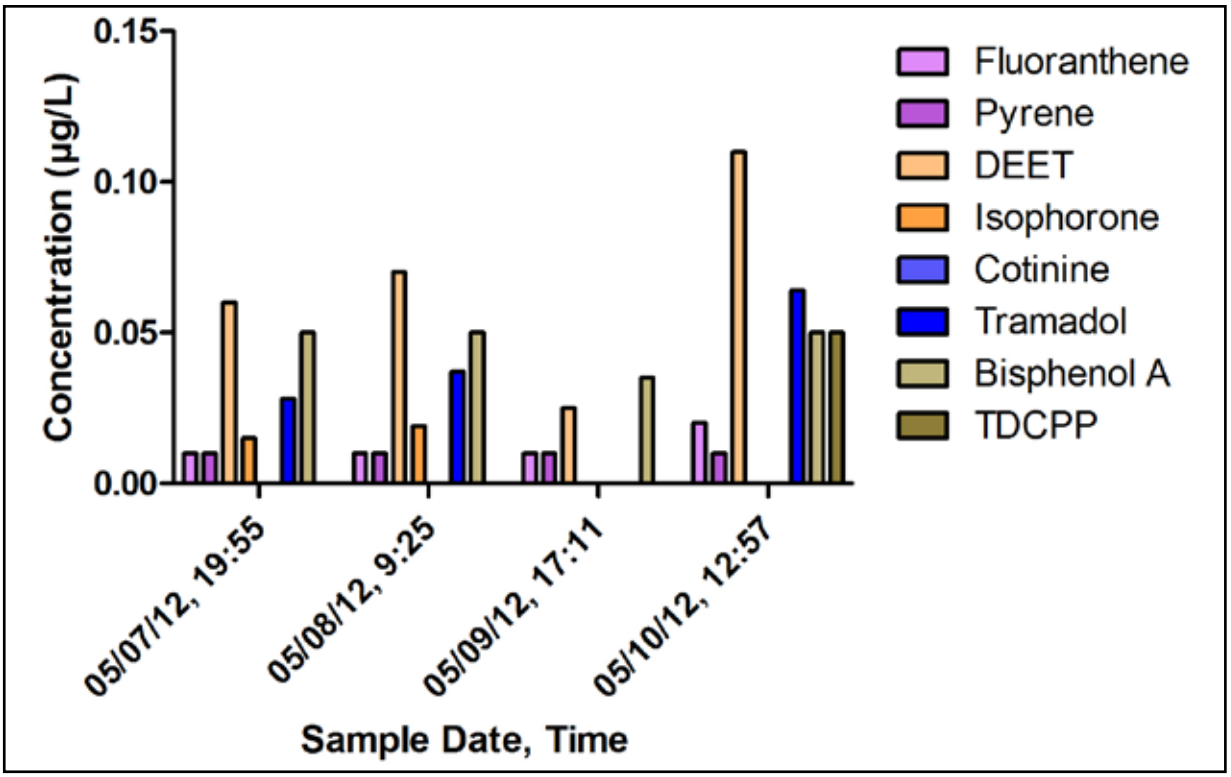


Figure C11. Time series graph of water samples collected in spring 2012 at the SMTP sampling site in the St. Louis River location (TDCPP = tris(dichloroisopropyl) phosphate).

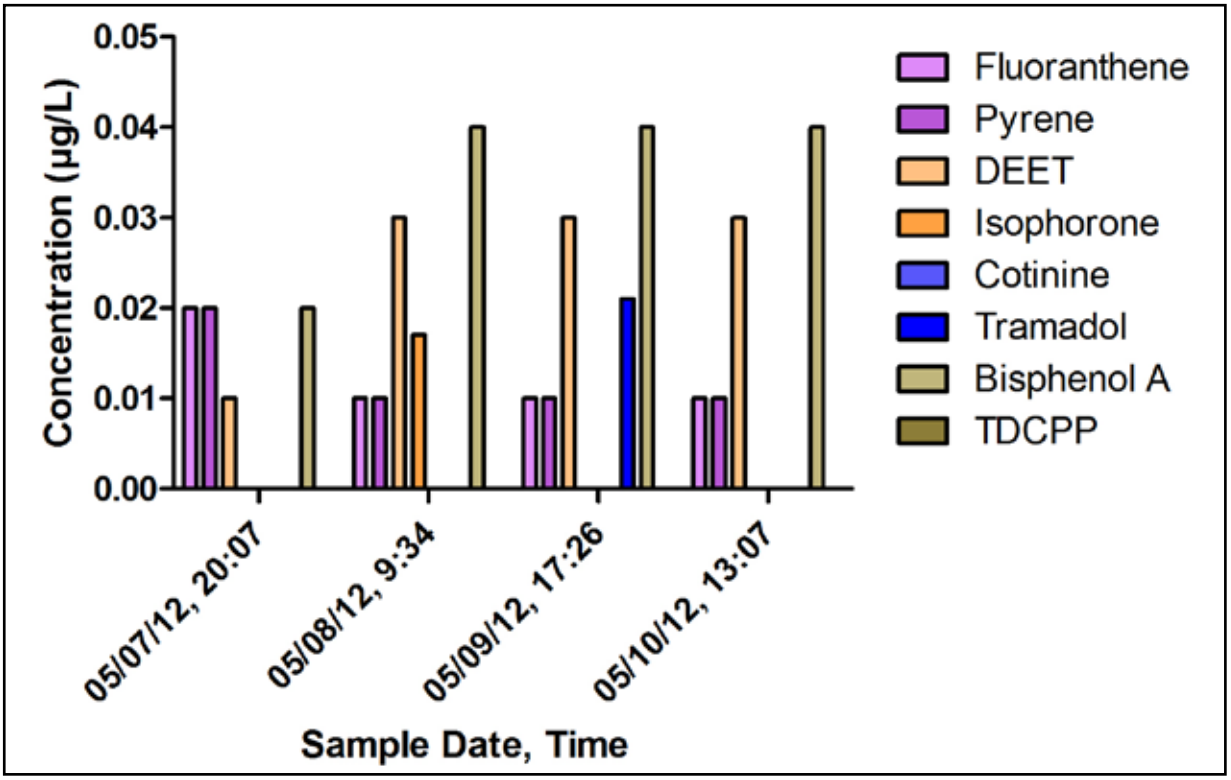


Figure C12. Time series graph of water samples collected in spring 2012 at the HogIsland sampling site in the St. Louis River location (TDCPP = tris(dichloroisopropyl) phosphate).

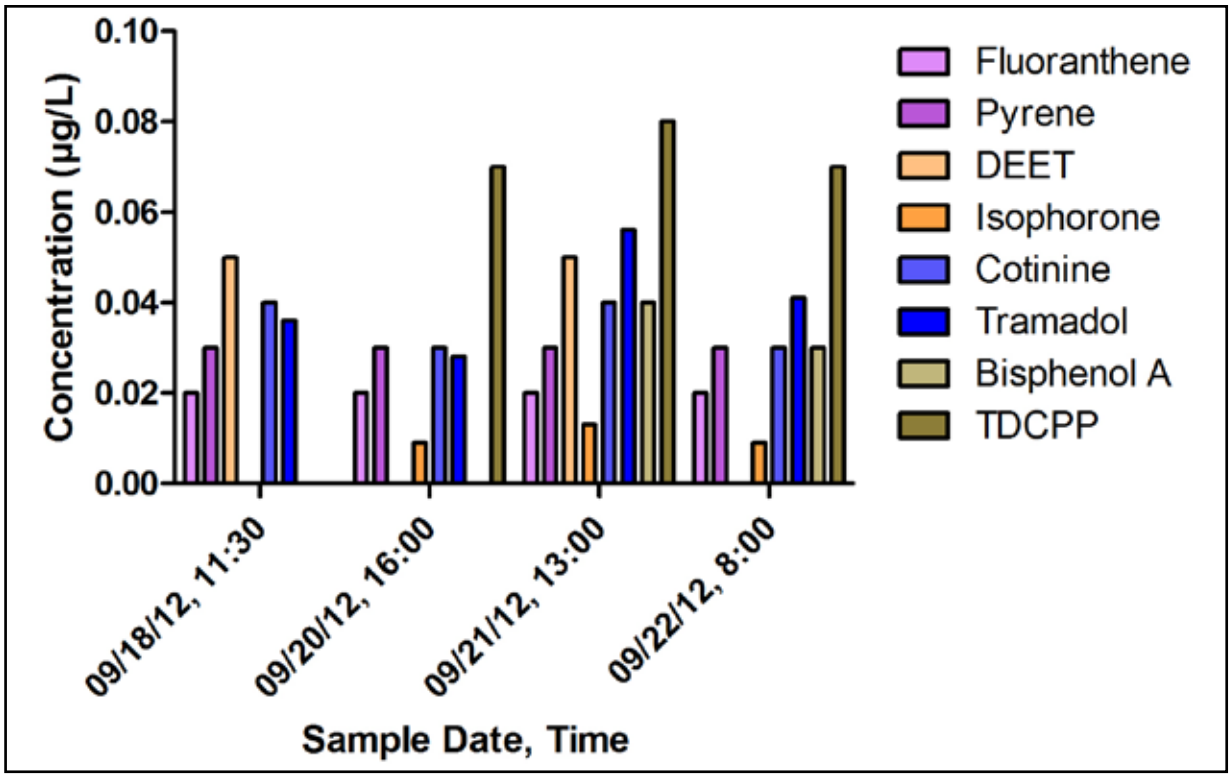


Figure C13. Time series graph of water samples collected in fall 2012 at the MAU-US-WWTP sampling site in the Maumee River (TDCPP = tris(dichloroisopropyl) phosphate).

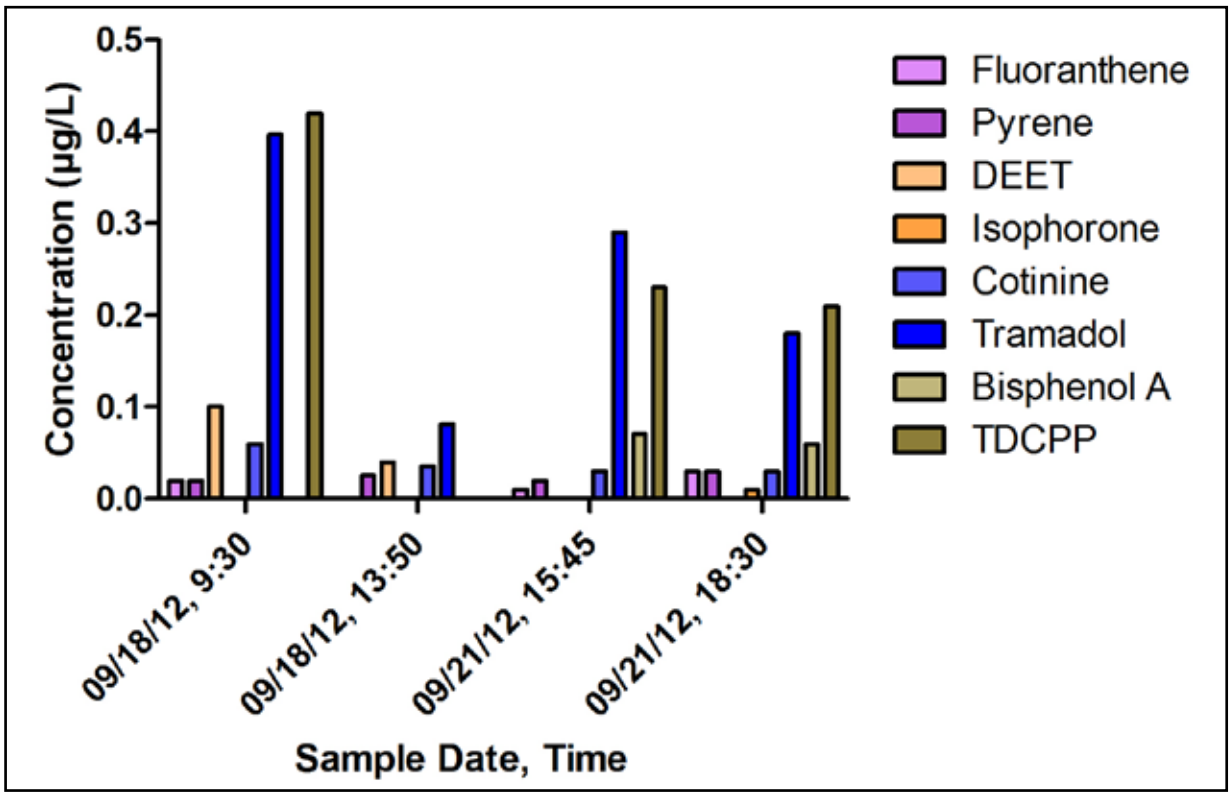


Figure C14. Time series graph of water samples collected in fall 2012 at the MX-WWTP sampling site in the Maumee River (TDCPP = tris(dichloroisopropyl) phosphate).

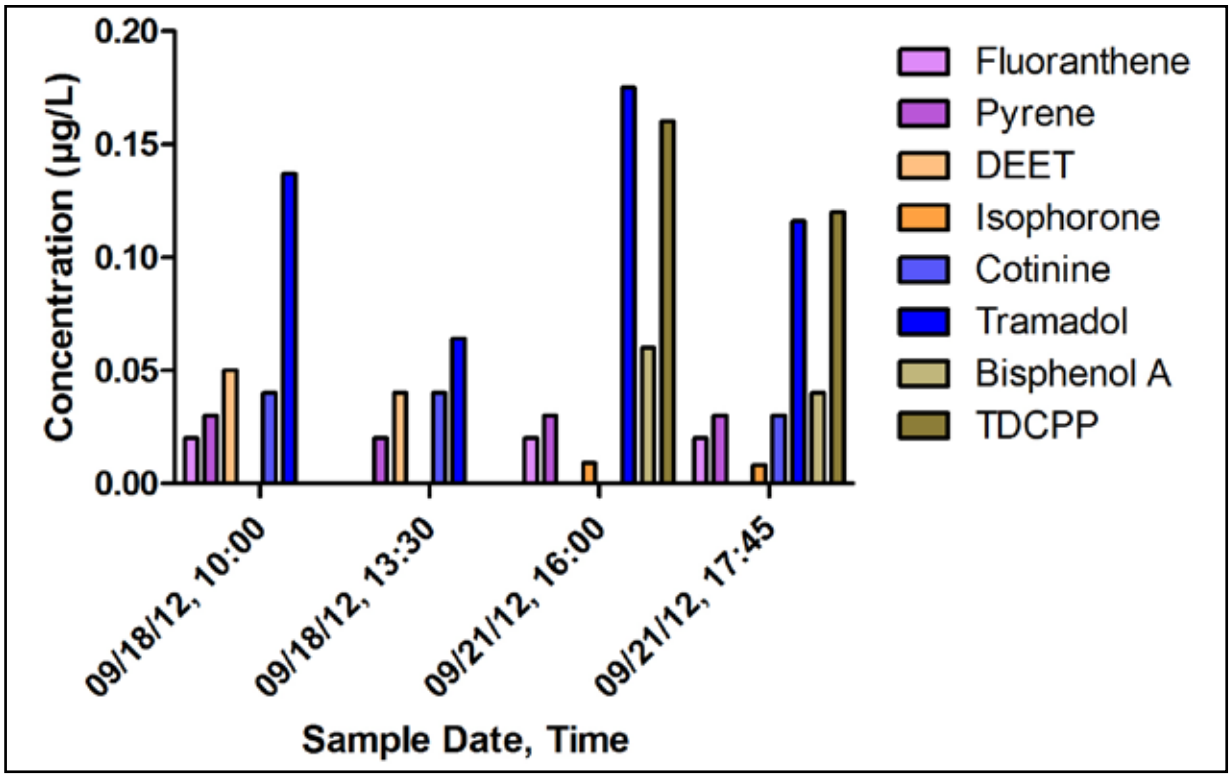


Figure C15. Time series graph of water samples collected in fall 2012 at the MAU-Distal sampling site in the Maumee River (TDCPP = tris(dichloroisopropyl) phosphate).

Table C1. Number of appearances or increases observed in sediment at each sampling location by sampling period and chemical class.

Sediment	Fall 2010	Spring 2011	Fall 2012	Fall 2010	Spring 2011	Spring 2012	Spring 2011	Fall 2010	Spring 2011	Spring 2012	Fall 2010	Spring 2011	Fall 2012	Spring 2012	Fall 2012	Spring 2011	Spring 2012	Fall 2010	Spring 2011	Spring 2012	Total
	St. Louis River			Fox River			Milwaukee, Kinnickinnic, and Menomonee Rivers	Detroit River		River Raisin	Swan Creek			Maumee River		Ashtabula River	Long Pond	Genesee River		Irondequoit Bay	
Alkylphenols	8	8	7	4	2	4	2	3	2	2	10	2	0	9	6	1	0	3	2	1	76
Flavors/Fragrances	4	3	11	3	2	3	0	3	1	2	4	3	2	10	8	1	2	1	3	3	69
Hormones	10	6	6	4	1	5	3	3	2	5	13	3	0	17	12	2	6	4	3	5	110
Other	7	5	6	5	2	5	0	6	3	3	9	1	1	6	10	2	2	3	2	3	81
PAHs	13	10	26	10	2	11	3	12	8	5	34	6	0	17	26	1	4	6	1	29	224
Pesticides	3	1	3	1	0	2	1	2	1	1	4	0	0	2	5	0	0	1	1	4	32
Pharmaceuticals	10	9	13	6	2	0	1	8	7	1	6	4	6	9	9	1	0	5	1	0	98
Plasticizer/Flame Retardants	4	6	3	1	1	2	1	2	3	2	13	3	3	9	5	1	0	4	0	2	65
Sterols	5	2	7	6	2	6	4	4	1	4	11	4	2	11	14	0	7	3	4	4	101
Total	64	50	82	40	14	38	15	43	28	25	104	26	14	90	95	9	21	30	17	51	856

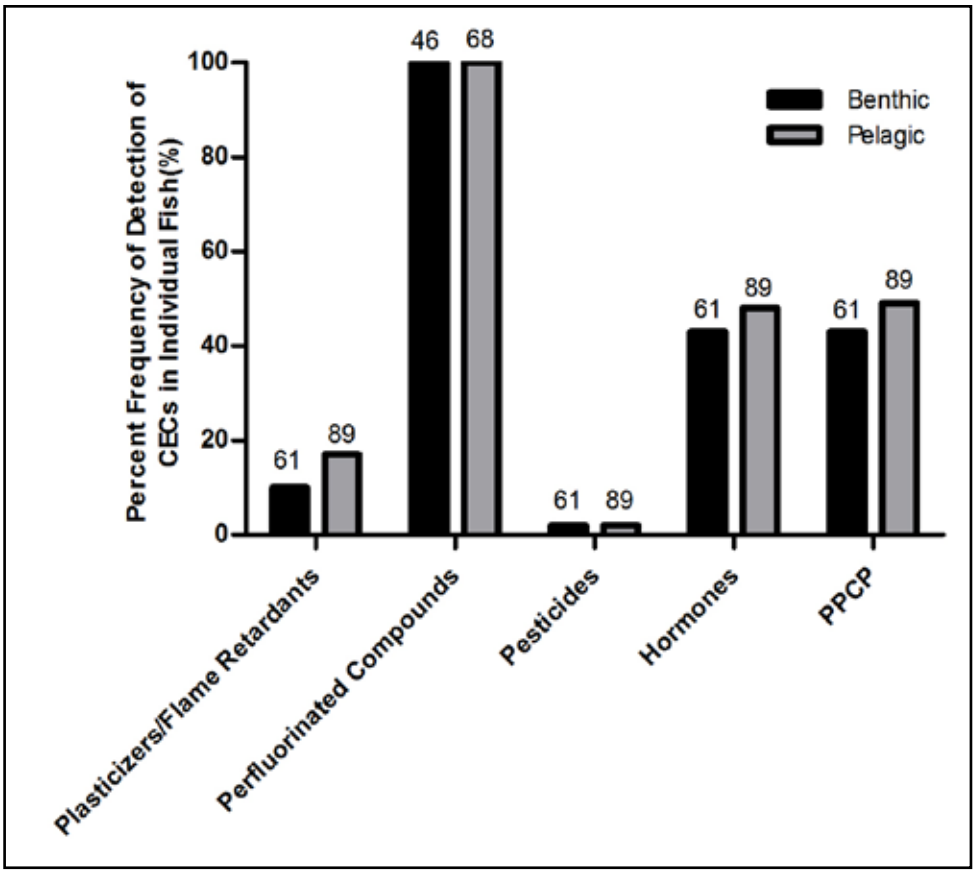


Figure C16. Frequency of detections of CECs by chemical class and species community. Numbers over chart bars indicate number of samples.

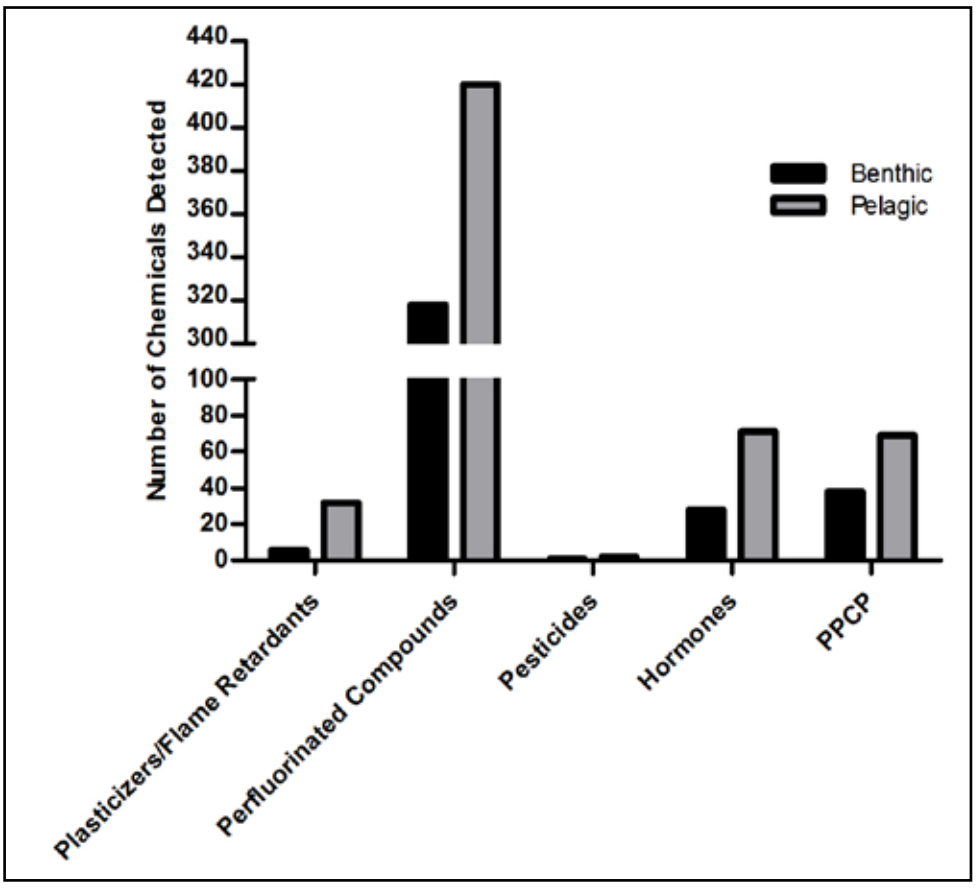


Figure C17. Number of CECs detected by CEC class and species community.

Appendix D. Location and Site Information

Table D1. Locations of sampled sites and types of samples collected (ID=identifier; S=sediment; W=water; DD=decimal degrees; --= not sampled).

State	Area	Field ID	Fall 2010	Spring 2011	Spring 2012	Fall 2012	Latitude (DD)	Longitude (DD)
MN	Duluth	STR-FDL-1	W, S	S	--	--	46.659306	-92.283667
MN	Duluth	STR-FDL-2	W, S	--	--	--	46.660194	-92.283250
MN	Duluth	STR-FDL-3	W, S	S	--	--	46.660778	-92.285250
MN	Duluth	STR-FDL-4	W, S	--	--	--	46.658750	-92.283611
MN	Duluth	STR-FDL-5	W, S	S	--	--	46.659639	-92.285889
MN	Duluth	STR-FDL-6	W, S	--	--	--	46.660306	-92.286750
MN	Duluth	FDL	W	--	--	--	46.658611	-92.282500
MN	Duluth	STB-MP-1	W, S	S	--	--	46.734500	-92.152361
MN	Duluth	STB-MP-2	W, S	--	--	--	46.733056	-92.155278
MN	Duluth	STB-MP-3	W, S	--	--	--	46.730972	-92.155000
MN	Duluth	STB-MP-4	W, S	S	--	--	46.730361	-92.152756
MN	Duluth	STB-MP-5	W, S	--	--	--	46.731000	-92.150972
MN	Duluth	STB-MP-6	W, S	S	--	--	46.732389	-92.151583
MN	Duluth	STB-WLSSD-1	W, S	W, S	--	--	46.754806	-92.120528
MN	Duluth	STB-WLSSD-2	W, S	--	--	--	46.755778	-92.119694
MN	Duluth	STB-WLSSD-3	W, S	S	--	--	46.756333	-92.121361
MN	Duluth	STB-WLSSD-4/WLSSD-DISTAL	W, S	W	W	W, S	46.755278	-92.121111
MN	Duluth	STB-WLSSD-5	W, S	--	--	--	46.757583	-92.121278
MN	Duluth	STB-WLSSD-6/WLSSD-PROXIMAL	W, S	W, S	W	W, S	46.757778	-92.120000
MN	Duluth	SMTP	W	--	W	--	46.728611	-92.068333
MN	Duluth	WLSSD-EFF	W	W	--	--	46.760556	-92.123889
MN	Duluth	GrsyPt	--	--	W	W, S	46.726667	-92.148333
MN	Duluth	EriePr	--	--	W	W	46.740000	-92.148056
MN	Duluth	RicesPt	--	--	W	W	46.773056	-92.103889
MN	Duluth	HogIsland	--	--	W	--	46.707778	-92.036667
MN	Duluth	BlatnikBr	--	--	--	W, S	46.751111	-92.097500
MN	Duluth	TallasId	--	--	--	W, S	46.710000	-92.197500
MN	Duluth	CloughId	--	--	--	W, S	46.696111	-92.184444
MN	Duluth	WireMi	--	--	--	W, S	46.675833	-92.196944
MN	Duluth	MudLk	--	--	--	W, S	46.658333	-92.202778
MN	Duluth	NekukId	--	--	--	W, S	46.655833	-92.273056
MN	Duluth	CloquetDw	--	--	--	W, S	46.848611	-92.576667
MN	Duluth	CloquetUp	--	--	--	W, S	46.854444	-92.573056
MN	Duluth	FondDu	--	--	--	W,S	46.667500	-92.287500
MN	Duluth	KnifeR	--	--	W	--	46.945278	-91.776944
MN	Duluth	EPAMED	--	--	W	--	46.838611	-92.003333
WI	Green Bay	FXR-1	W, S	--	--	--	44.538583	-88.003944
WI	Green Bay	FXR-2	W, S	--	--	--	44.541139	-87.991806
WI	Green Bay	FXR-3	W, S	S	--	--	44.546722	-87.959389
WI	Green Bay	FXR-4	W, S	--	--	--	44.573250	-87.978972
WI	Green Bay	FXR-5	W, S	S	W, S	--	44.590806	-87.999167
WI	Green Bay	FXR-6	W, S	S	--	--	44.533861	-88.006667
WI	Green Bay	DPERE-9	--	W	W, S	--	44.461944	-88.059444
WI	Green Bay	EASTR-10	--	W	S	--	44.517222	-88.006667
WI	Green Bay	PRGAM-11	--	W	--	--	44.528611	-88.010000
WI	Green Bay	GRBAY-12	--	W	W, S	--	44.539444	-88.004444
WI	Green Bay	FXR-13	--	--	W, S	--	44.333056	-88.156389
WI	Green Bay	FXR-14	--	--	W, S	--	44.357222	-88.143889
WI	Milwaukee	MENMR-13	--	W	--	--	43.032500	-87.929167
WI	Milwaukee	MILWR-14	--	W	--	--	43.034444	-87.910278
WI	Milwaukee	JISLA-15	--	W	--	--	43.023056	-87.893889
WI	Milwaukee	KINNI-17	--	W	--	--	43.008056	-87.909167
WI	Milwaukee	MILWR-WABR	--	S	--	--	43.038056	-87.909722
WI	Milwaukee	MIL-2	--	S	--	--	43.028611	-87.920833

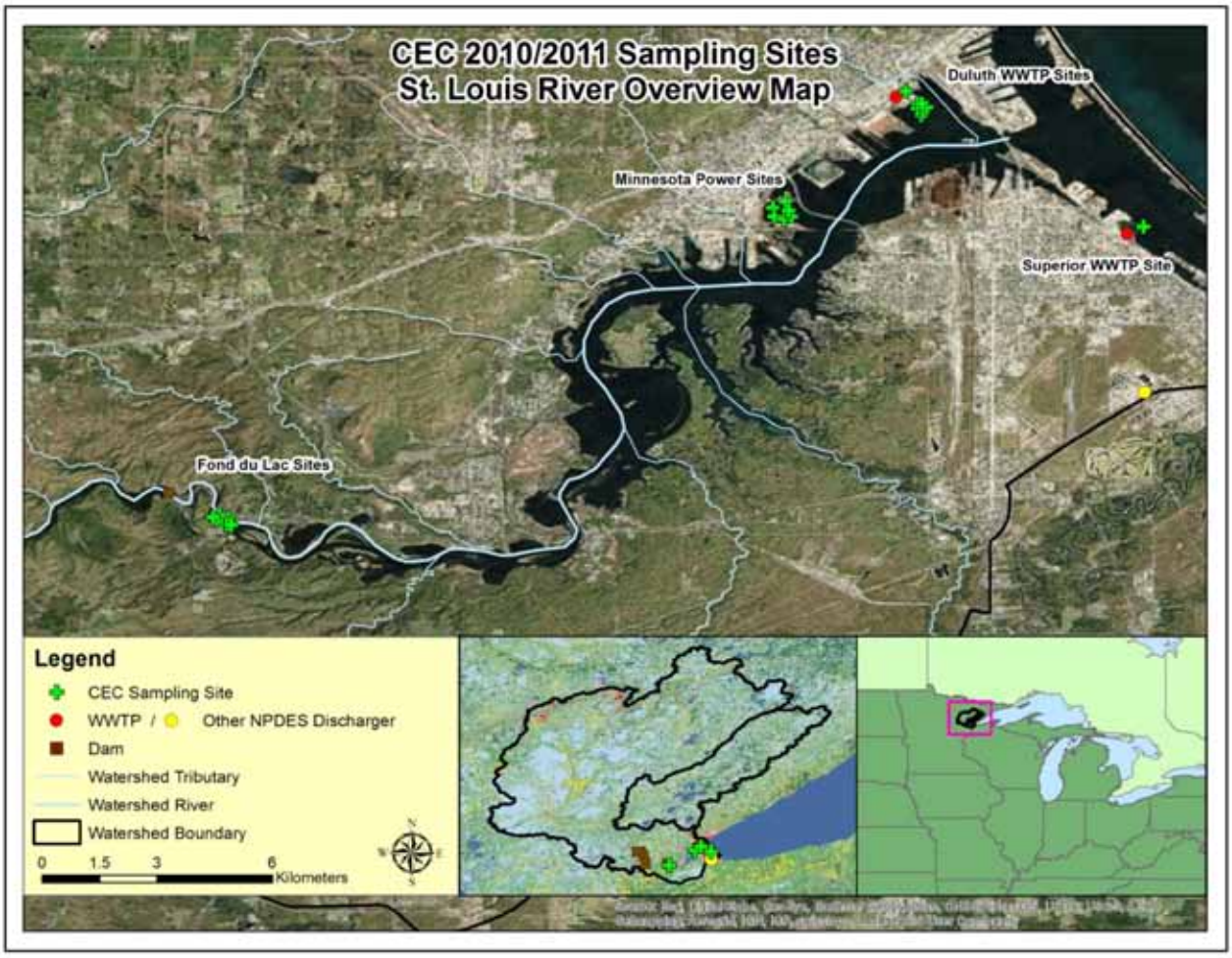
State	Area	Field ID	Fall 2010	Spring 2011	Spring 2012	Fall 2012	Latitude (DD)	Longitude (DD)
WI	Milwaukee	MIL-NAVDAM	--	S	--	--	43.057222	-87.897222
WI	Waupaca	COL-1	--	--	W, S	--	44.338056	-89.148056
WI	Waupaca	COL-2	--	--	W, S	--	44.346389	-89.151944
MI	Detroit	DTR-1	W, S	S	W	--	42.293778	-83.098778
MI	Detroit	DTR-2	W, S	--	W	--	42.273500	-83.110056
MI	Detroit	DTR-3	W, S	--	--	--	42.205194	-83.146000
MI	Detroit	DTR-4	W, S	S	--	--	42.113833	-83.183250
MI	Detroit	DTR-5	W, S	--	--	--	42.085833	-83.177444
MI	Detroit	DTR-6	W, S	--	--	--	42.073306	-83.184444
MI	Detroit	PTHENN-1	--	W	--	--	42.202500	-83.142222
MI	Detroit	WYAND-2	--	W	--	--	42.183333	-83.135556
MI	Detroit	GROSIL-3	--	W	--	--	42.127222	-83.173056
MI	Detroit	TRENTN-4	--	W	--	--	42.120556	-83.180000
MI	Detroit	DTR-11	--	S	--	--	42.184444	-83.150556
MI	Detroit	DTR–12–GRSS	--	--	W	--	42.222917	-83.140000
MI	Monroe	RRR-1	--	--	W, S	--	41.923750	-83.421556
MI	Monroe	RRR-3	--	--	W, S	--	41.900528	-83.361889
MI	Monroe	RRR-4	--	--	W, S	--	41.894556	-83.344806
MI	Monroe	RRR-2	--	--	W, S	--	41.909806	-83.377278
OH	Toledo	SWC-1	W, S	--	--	--	41.636861	-83.570667
OH	Toledo	SWC-2	W, S	--	--	--	41.636861	-83.569500
OH	Toledo	SWC-3	W, S	--	--	--	41.636944	-83.568194
OH	Toledo	SWC-4	W, S	--	--	--	41.636583	-83.566806
OH	Toledo	SWC-5	W, S	--	--	--	41.637333	-83.563139
OH	Toledo	SWC-6	W, S	--	--	--	41.641250	-83.562750
OH	Toledo	SWC-7	W, S	W, S	--	--	41.643028	-83.562250
OH	Toledo	SWC-8	W, S	W, S	--	--	41.641500	-83.557306
OH	Toledo	SWC-9	W, S	--	--	W	41.642611	-83.552056
OH	Toledo	SWC-10	W, S	--	--	W	41.642917	-83.549639
OH	Toledo	SWC-11	W, S	W, S	--	--	41.641861	-83.545611
OH	Toledo	SWC-12	W, S	--	--	--	41.644500	-83.543083
OH	Toledo	SWANC-5	--	W	--	W,S	41.647778	-83.534167
OH	Toledo	CLARKO-6	--	W	--	--	41.683056	-83.484722
OH	Toledo	TOLEDO-7	--	W	--	--	41.688611	-83.475000
OH	Ashtabula	ASH-1	--	W, S	--	--	41.897778	-80.793333
OH	Ashtabula	ASH-2	--	W, S	--	--	41.895833	-80.796111
OH	Ashtabula	ASH-3	--	W, S	--	--	41.891111	-80.798056
OH	Waterville	MAU-WAT-1	--	--	W, S	--	41.476472	-83.749056
OH	Waterville	MAU-WAT-2	--	--	W, S	--	41.477472	-83.748167
OH	Toledo	MAU-BVP	--	--	W, S	--	41.693361	-83.471944
OH	Toledo	MAU-TOL-WWTP	--	--	W, S	--	41.687250	-83.479611
OH	Grand Rapids	MAU-GR-1	--	--	W, S	--	41.430333	-83.827056
OH	Toledo	MAU-DS-WWTP	--	--	W, S	--	41.690556	-83.476472
OH	Toledo	MAU-LASALLE	--	--	W, S	--	41.685250	-83.482389
OH	Toledo	MAU-US-WWTP	--	--	--	W, S	41.683611	-83.485556
OH	Toledo	MX-WWTP	--	--	--	W, S	41.688889	-83.477222
OH	Toledo	MAU-Distal-DS-WWTP	--	--	--	W, S	41.691056	-83.474528
OH	Toledo	MAU-CSO-68	--	--	--	W, S	41.655639	-83.523917
OH	Toledo	MAU-DS-CSO-9	--	--	--	W, S	41.627500	-83.532222
OH	Toledo	MAU-US-CSO-9	--	--	--	W, S	41.623611	-83.538056
OH	Toledo	MAU-CSO-9	--	--	--	W, S	41.624444	-83.533889
OH	Perrysburg	MAU-DS-PB-WWTP	--	--	--	W, S	41.559806	-83.639167
OH	Maumee	MAU-N-EW-PB-WWTP	--	--	--	W, S	41.570417	-83.637611
OH	Perrysburg	MAU-PB-WWTP	--	--	--	W, S	41.557500	-83.649722
OH	Toledo	SWC-CP-8	--	--	--	W	41.642222	-83.547778
NY	Rochester	GNR-1	W, S	W, S	--	--	43.198086	-77.621519
NY	Rochester	GNR-2	W, S	W, S	--	--	43.201333	-77.623833
NY	Rochester	GNR-3	W, S	--	--	--	43.207278	-77.626500
NY	Rochester	GNR-4	W, S	--	--	--	43.227750	-77.616417
NY	Rochester	GNR-5	W, S	--	--	--	43.234028	-77.617917
NY	Rochester	GNR-6	W, S	W, S	--	--	43.256556	-77.605972
NY	Rochester	IB04	--	--	W, S	--	43.184083	-77.518556

Table D1 *(continued)*

State	Area	Field ID	Fall 2010	Spring 2011	Spring 2012	Fall 2012	Latitude (DD)	Longitude (DD)
NY	Rochester	IB05	--	--	W, S	--	43.179222	-77.528222
NY	Rochester	IB06	--	--	W, S	--	43.177667	-77.527833
NY	Rochester	IB_NE_DUNE	--	--	W, S	--	43.192361	-77.517444
NY	Rochester	IB_NW_PHRAG	--	--	W, S	--	43.191417	-77.528944
NY	Rochester	IB06_REF	--	--	W, S	--	43.173333	-77.519667
NY	Rochester	LP01	--	--	W, S	--	43.288250	-77.706917
NY	Rochester	LP02	--	--	W, S	--	43.283861	-77.697778
NY	Rochester	LP04	--	--	W, S	--	43.291194	-77.677833
NY	Rochester	LP06	--	--	W, S	--	43.296944	-77.683778
NY	Rochester	LP-South	--	--	W, S	--	43.284722	-77.704528
NY	Rochester	LP06-REF	--	--	W, S	--	43.255472	-77.791056

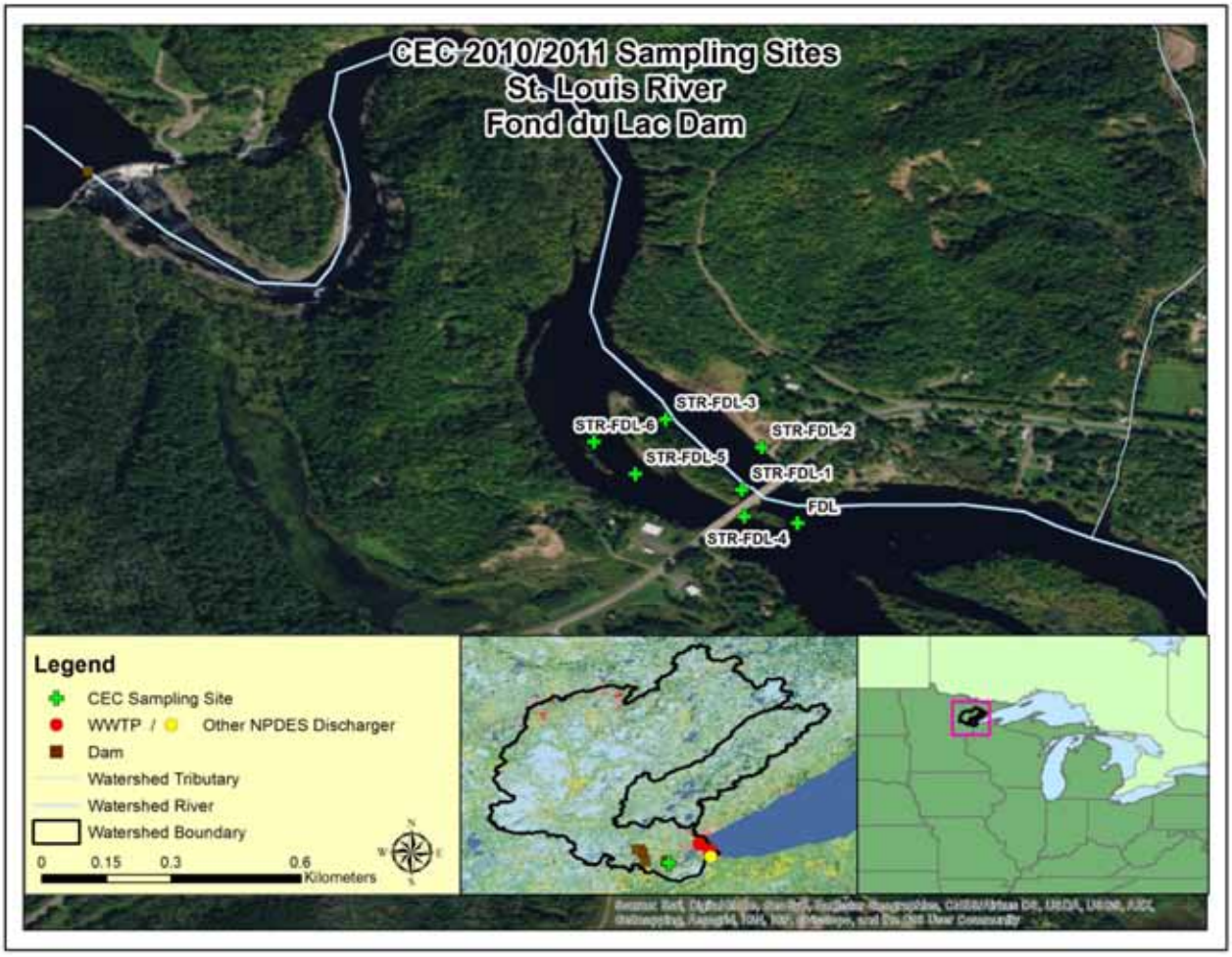
Table D2. USGS 2006 National Land Cover Database descriptions (Fry et al., 2011).

Class/Type (Value)	Classification Description
WATER	
Open (11)	Areas of open water, generally with less than 25% cover of vegetation or soil.
Perennial Ice/Snow (12)	Areas characterized by a perennial cover of ice and /or snow, generally greater than 25% of total cover.
DEVELOPED	
Open Space (21)	Areas with a mixture of some constructed materials, but mostly vegetation in the form of lawn grasses, impervious surfaces account for less than 20% of total cover. Includes greenspaces, parks, golf courses, and single family housing units on large lots.
Low Density (22)	Areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 20-49% of total cover. Areas include single housing family units.
Medium Density (23)	Areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 50-79% of total cover. Areas include single housing family units
High Density (24)	Areas where people work and live in high numbers. Impervious surfaces account for 80-100% of total cover. Includes apartment complexes and industrial and commercial developments.
BARREN	
Rock/Sand/Clay (31)	Areas of bedrock, desert pavement, scarps, talus, slides, volcanic material, glacial debris, sand dunes, strip mines, gravel pits, and other accumulation of earthen material. Generally, vegetation accounts for less than 15% of total cover.
FOREST	
Deciduous (41)	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. More than 75% of the tree species shed foliage simultaneously in response to seasonal change.
Evergreen (42)	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of the total vegetation cover. More than 75% of the trees species maintain their leaves all year. Canopy is never without green foliage.
Mixed (43)	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. Neither deciduous nor evergreen species are greater than 75% of total tree cover.
SHURBLAND	
Dwarf (51)	Alaska only areas dominated by shrubs less than 20 centimeters tall with shrub canopy typically greater than 20% of the total vegetation. Associated with grasses, sedges, herbs, and non-vascular vegetation.
Scrub (52)	Areas dominated by shrubs, less than 5 meters tall with shrub canopy typically greater than 20% of total vegetation. This class includes true shrubs, young trees, and stunted trees.
HERBACEOUS	
Grassland (71)	Areas dominated by gramanoid or herbaceous vegetation, generally greater than 80% of total vegetation. These areas are not subject to intensive management.
Sedge (72)	Alaska only areas dominated by sedges and forbs, generally greater than 80% of total vegetation. This type can occur with significant other grasses or other grass-like plants, and includes sedge tundra and sedge-tussock tundra.
Lichens (73)	Alaska only areas dominated by fruticose or foliose lichens generally greater than 80% of total vegetation.
Moss (74)	Alaska only areas dominated by mosses, generally greater than 80% of total vegetation.
PLANTED/CULTIVATED	
Pasture/Hay (81)	Areas of grasses, legumes, or grass-legume mixtures planted for livestock grazing or the production of seed or hay crops, typically on ta perennial cycle, pasture/hay vegetation accounts for greater than 20% of total vegetation.
Cultivated Crops (82)	Areas used for the production of annual crops, such as corn, soybeans, vegetables, tobacco, and cotton, and also perennial woody crops such as orchards and vineyards. Crop vegetation accounts for greater than 20% of total vegetation.
WETLANDS	
Woody (90)	Areas where forest or shrubland vegetation accounts for greater than 20% of vegetative cover and the soil or substrate is periodically saturated with or covered with water.
Emergent Herbaceous (95)	Areas where perennial herbaceous vegetation accounts for greater than 80% of vegetative cover and the soil or substrate is periodically saturate with or covered with water.



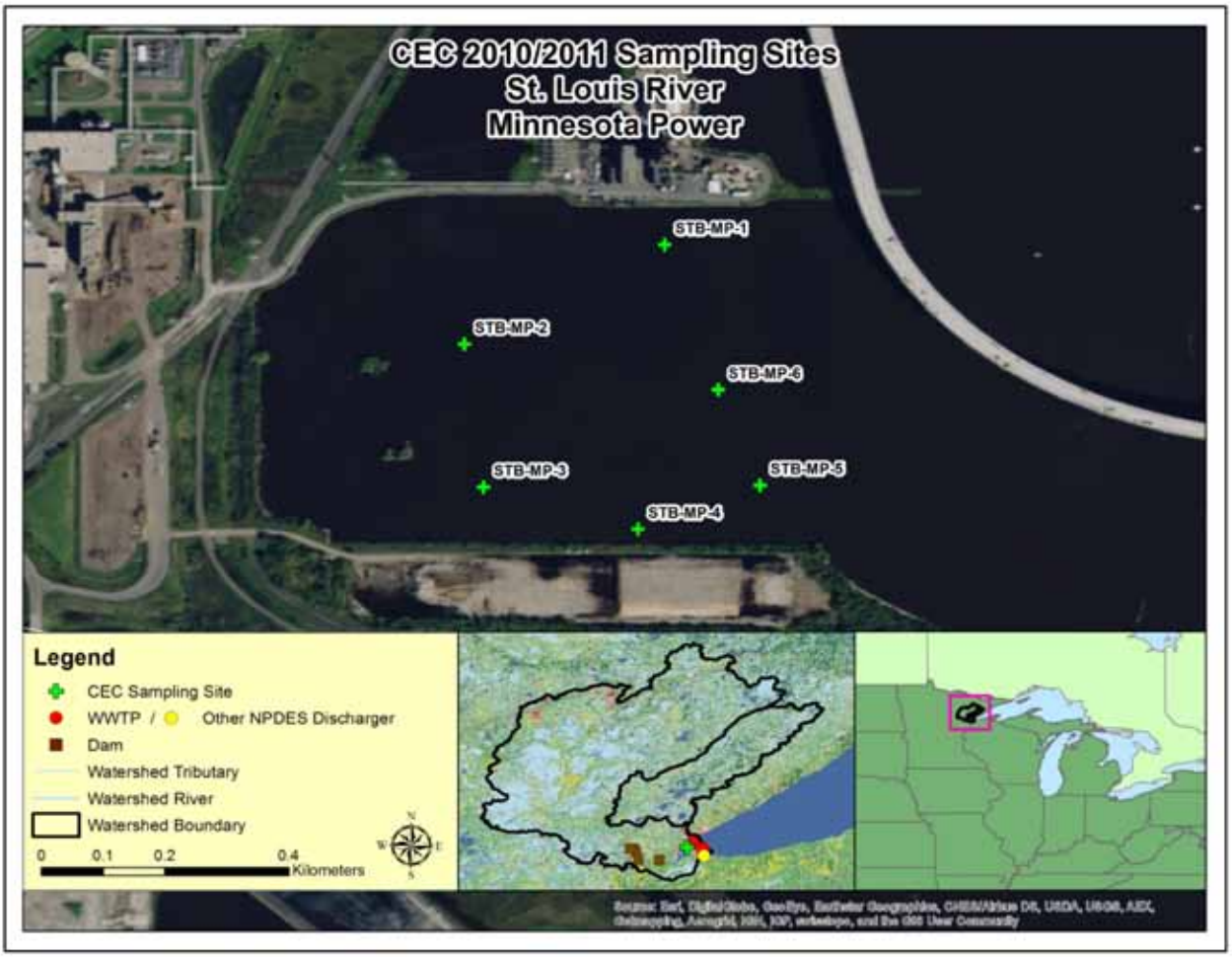
St. Louis and Cloquet Watershed (8-digit HUC)	
Drainage Area (km^2)	9665.56
WTTPs	4
CSOs	0
Land Use Class	**% Cover**
Water	3.74
Developed	4.02
Barren	1.1
Forest	34.87
Shrubland	6.44
Herbaceous	7.37
Agriculture	3.19
Wetland	45.71

Figure D1. Map of St. Louis River sites sampled in fall 2010 and spring 2011.



St. Louis and Cloquet Watershed (8-digit HUC)	
Drainage Area (km^2)	9665.56
WTTPs	4
CSOs	0
Land Use Class	**% Cover**
Water	3.74
Developed	4.02
Barren	1.1
Forest	34.87
Shrubland	6.44
Herbaceous	7.37
Agriculture	3.19
Wetland	45.71

Figure D2. Map of Fond du Lac sampling sites within the Saint Louis River location in fall 2010 and spring 2011.



St. Louis and Cloquet Watershed (8-digit HUC)	
Drainage Area (km^2)	9665.56
WTTPs	4
CSOs	0
Land Use Class	**% Cover**
Water	3.74
Developed	4.02
Barren	1.1
Forest	34.87
Shrubland	6.44
Herbaceous	7.37
Agriculture	3.19
Wetland	45.71

Figure D3. Map of Minnesota Power sampling sites within the Saint Louis River location in fall 2010 and spring 2011.

St. Louis and Cloquet Watershed (8-digit HUC)	
Drainage Area (km^2)	9665.56
WTTPs	4
CSOs	0
Land Use Class	**% Cover**
Water	3.74
Developed	4.02
Barren	1.1
Forest	34.87
Shrubland	6.44
Herbaceous	7.37
Agriculture	3.19
Wetland	45.71

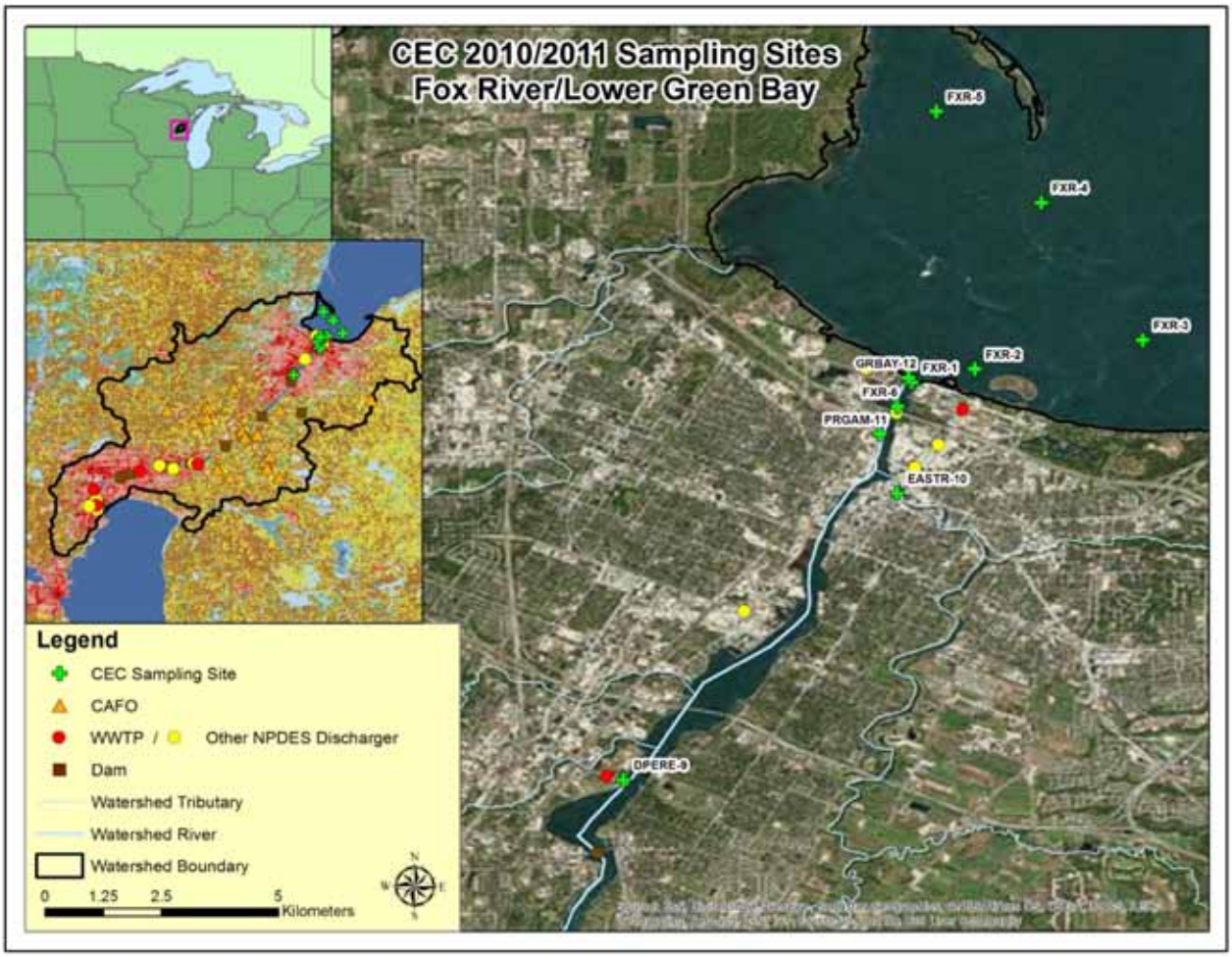
Figure D4. Map of Duluth Wastewater Treatment Plant sampling sites within the Saint Louis River location in fall 2010 and spring 2011.

St. Louis and Cloquet Watershed (8-digit HUC)	
Drainage Area (km^2)	9665.56
WTTPs	4
CSOs	0
Land Use Class	**% Cover**
Water	3.74
Developed	4.02
Barren	1.1
Forest	34.87
Shrubland	6.44
Herbaceous	7.37
Agriculture	3.19
Wetland	45.71

Figure D5. Map of Superior Wastewater Treatment Plant sampling site within the Saint Louis River location in fall 2010 and spring 2011.

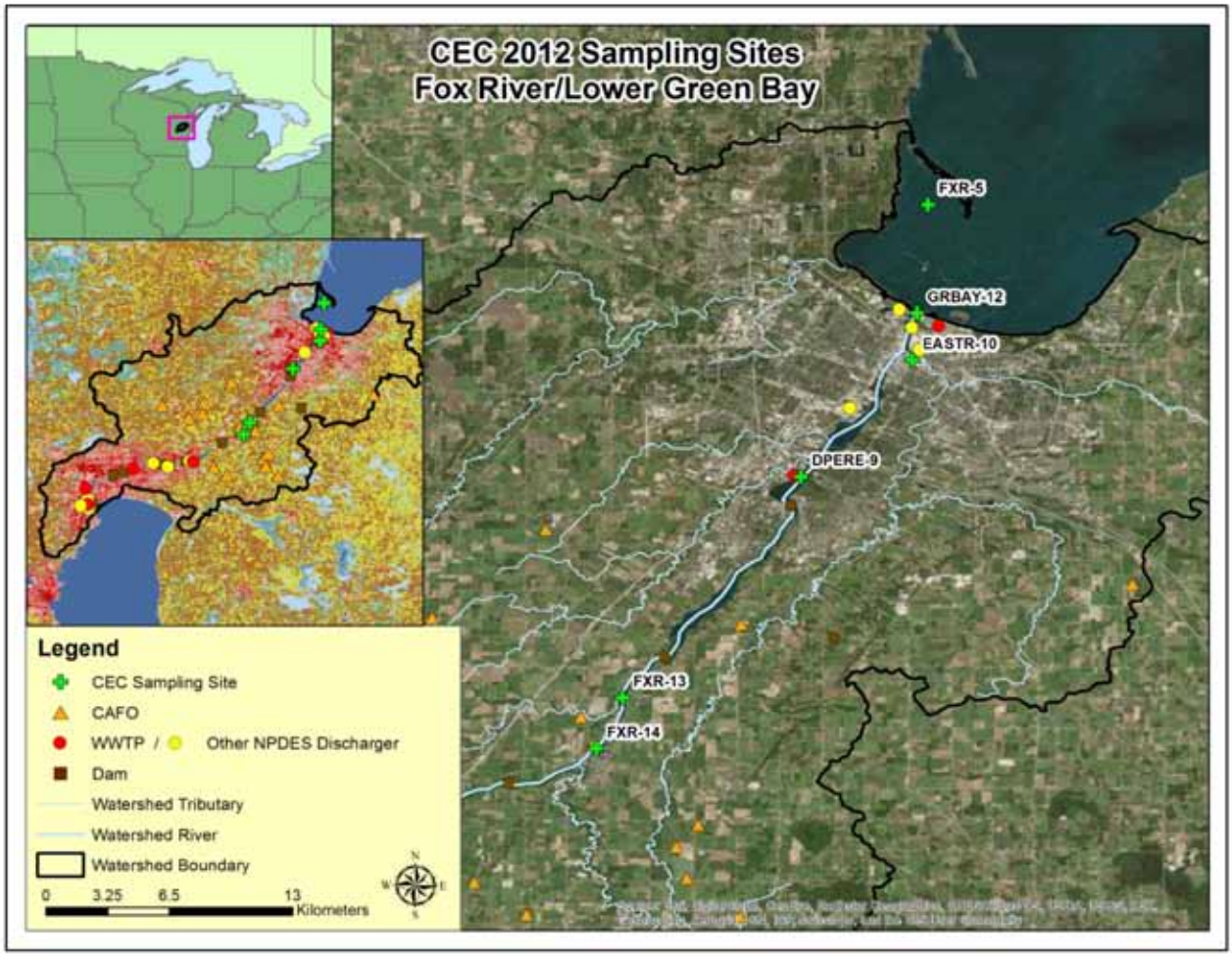
St. Louis and Cloquet Watershed (8-digit HUC)	
Drainage Area (km^2)	9665.56
WTTPs	4
CSOs	0
Land Use Class	**% Cover**
Water	3.74
Developed	4.02
Barren	1.1
Forest	34.87
Shrubland	6.44
Herbaceous	7.37
Agriculture	3.19
Wetland	45.71

Figure D6. Map of Saint Louis River sites sampled in spring and fall 2012.



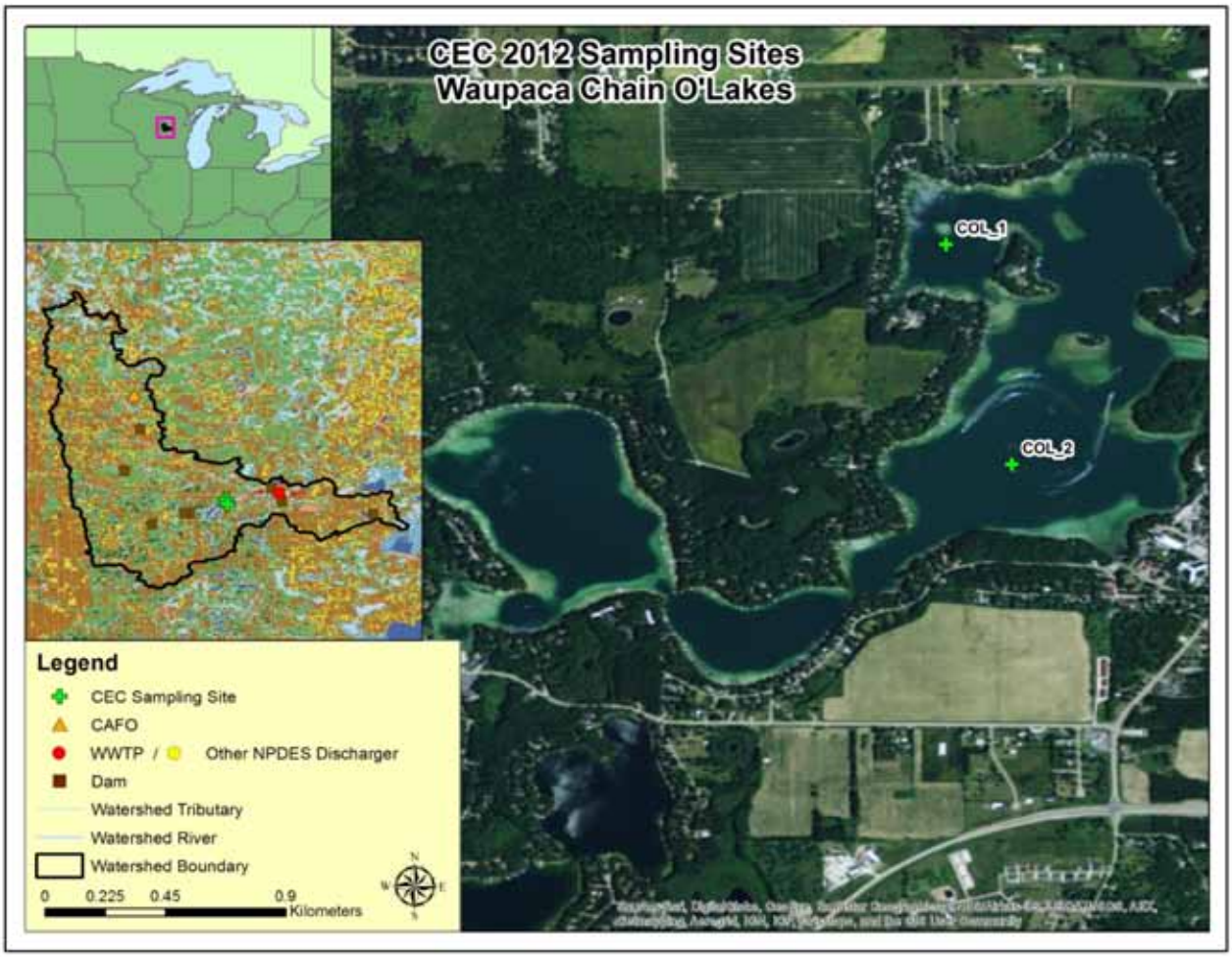
Lower Fox River Watershed (8-digit HUC)	
Drainage Area (km^2)	1678.62
WTTPs	6
CSOs	0
Land Use Class	**% Cover**
Water	1.55
Developed	29.92
Barren	0.21
Forest	7.79
Shrubland	0.3
Herbaceous	0.58
Agriculture	55.35
Wetland	4.29

Figure D7. Map of Fox River sites sampled in fall 2010 and spring 2011.



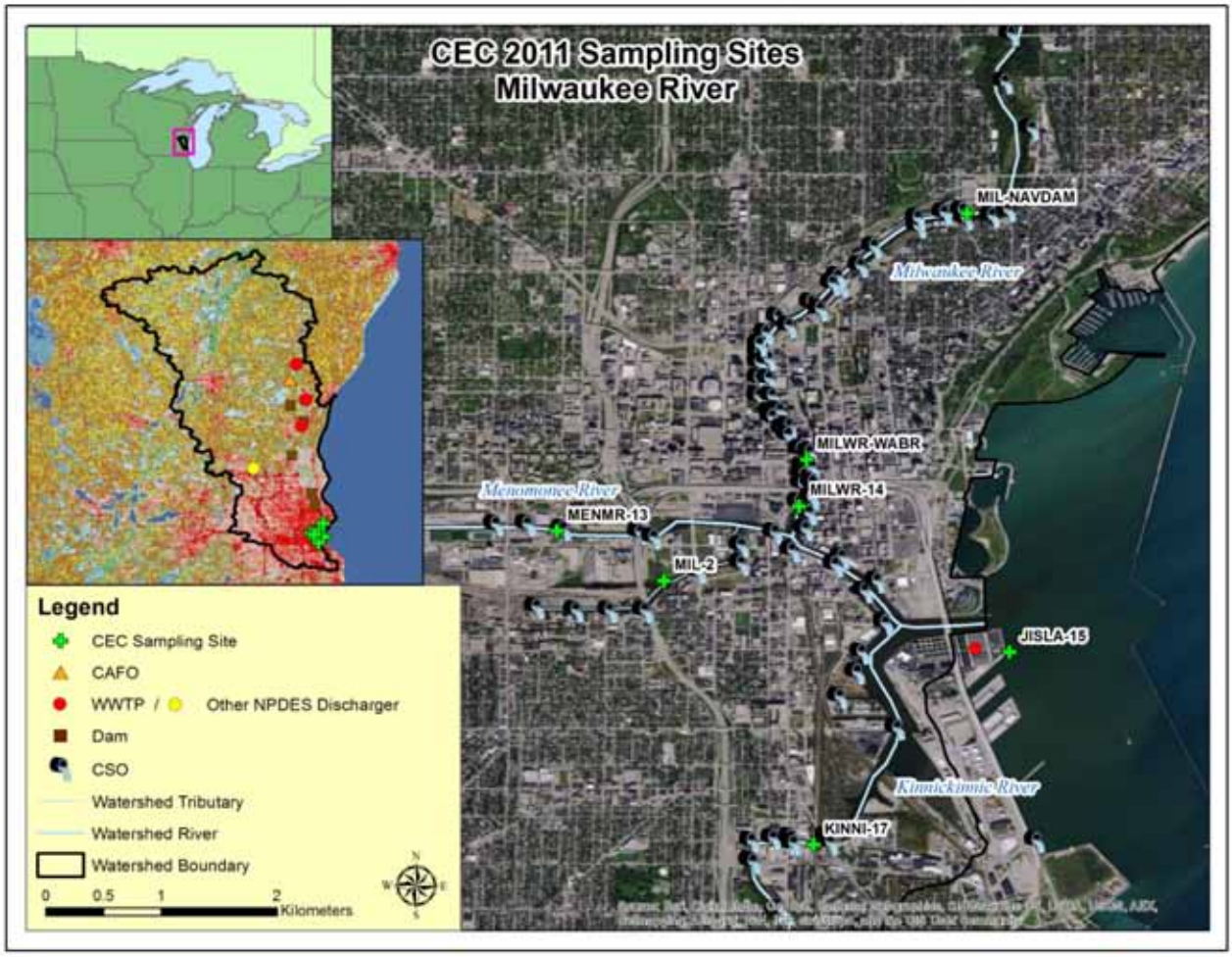
Lower Fox River Watershed (8-digit HUC)	
Drainage Area (km^2)	1678.62
WTTPs	6
CSOs	0
Land Use Class	**% Cover**
Water	1.55
Developed	29.92
Barren	0.21
Forest	7.79
Shrubland	0.3
Herbaceous	0.58
Agriculture	55.35
Wetland	4.29

Figure D8. Map of Fox River sites sampled in spring 2012.



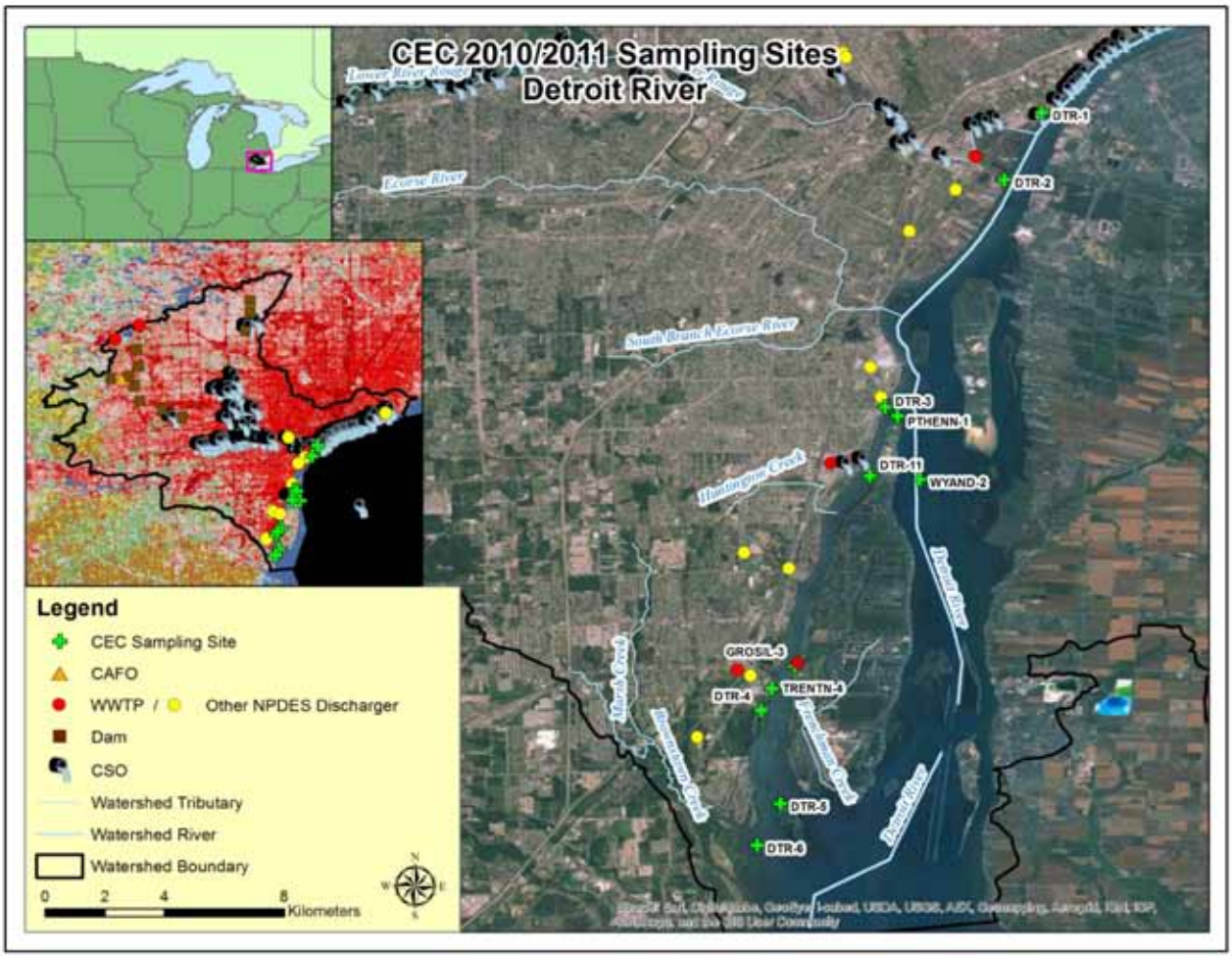
Waupaca River Watershed (10-digit HUC)	
Drainage Area (km^2)	745.98
WTTPs	1
CSOs	0
Land Use Class	**% Cover**
Water	1.67
Developed	7.13
Barren	0.07
Forest	32.78
Shrubland	0.04
Herbaceous	0.28
Agriculture	51.35
Wetland	6.68

Figure D9. Map of Waupaca Chain O'Lakes sites sampled in spring 2012.



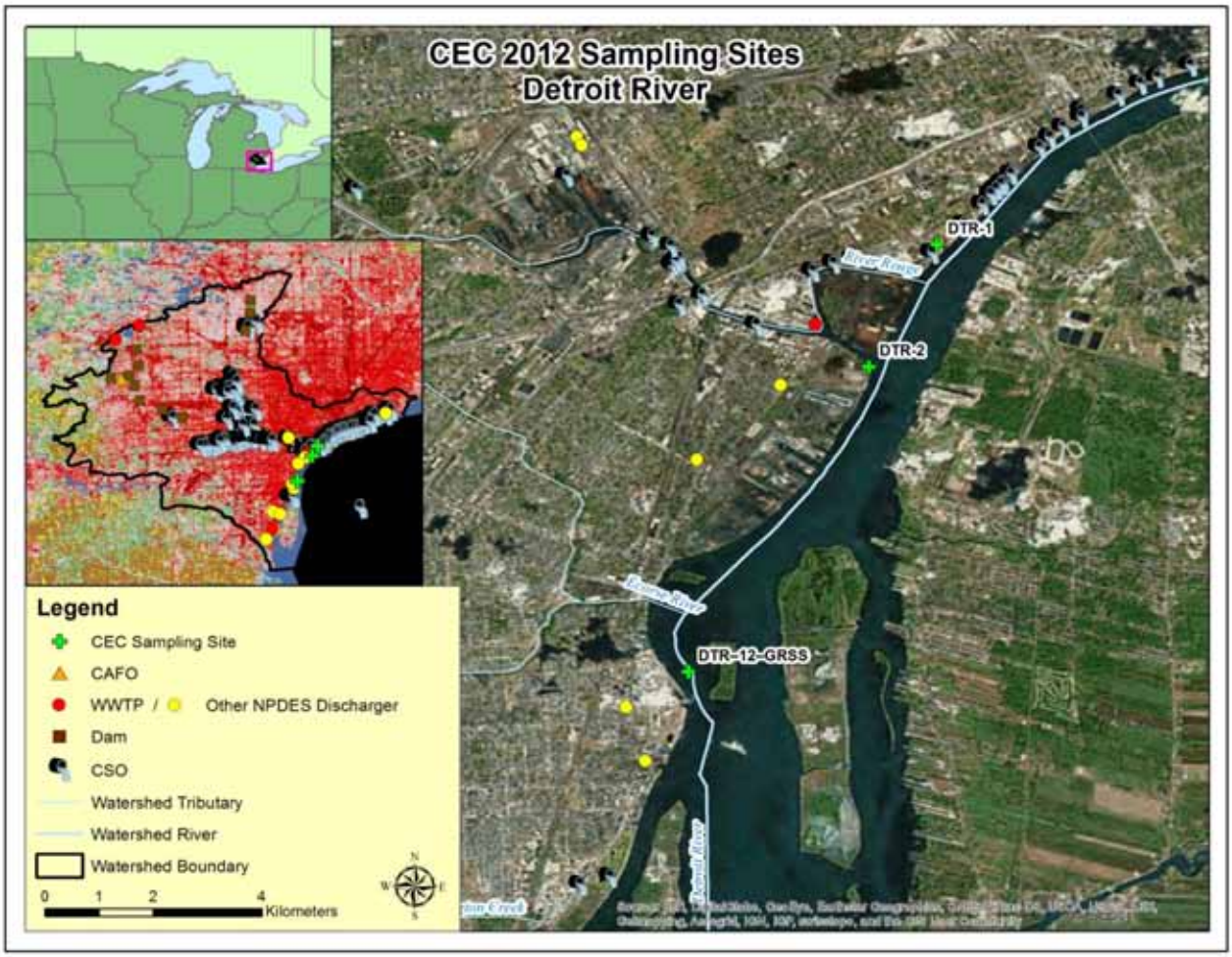
Milwaukee Watershed (8-digit HUC)	
Drainage Area (km^2)	2276.51
WTTPs	6
CSOs	113
Land Use Class	**% Cover**
Water	1.01
Developed	29.62
Barren	0.14
Forest	12.04
Shrubland	0.77
Herbaceous	0.85
Agriculture	43.37
Wetland	12.19

Figure 10. Map of Milwaukee River sites sampled in spring 2011.



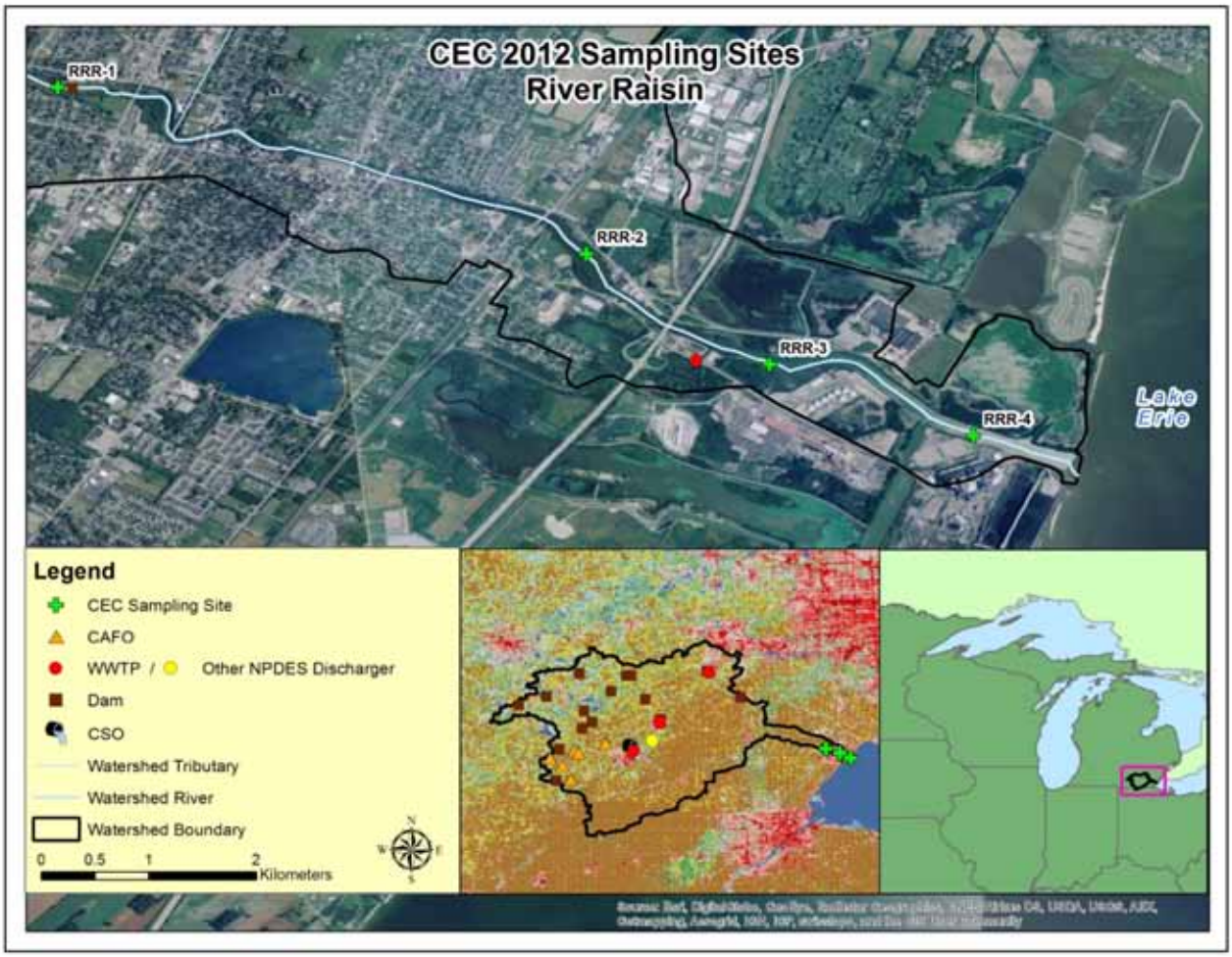
Detroit River Watershed (8-digit HUC)			
Drainage Area (km^2)		2298.10	
WTTPs		6	
CSOs		123	
Land Use Class (U.S.)	**% Cover**	**Land Use Class (Canada)**	**% Cover**
Water	0.86	Water	0.01
Developed	85.05	Developed	1.55
Barren	0.31	Barren	0.04
Forest	6.61	Forest	0.16
Shrubland	0.05	Agriculture	98.19
Herbaceous	0.53	Marshes	0.05
Agriculture	3.90		
Wetlands	2.68		

Figure 11. Map of Detroit River sites sampled in fall 2010 and spring 2011.



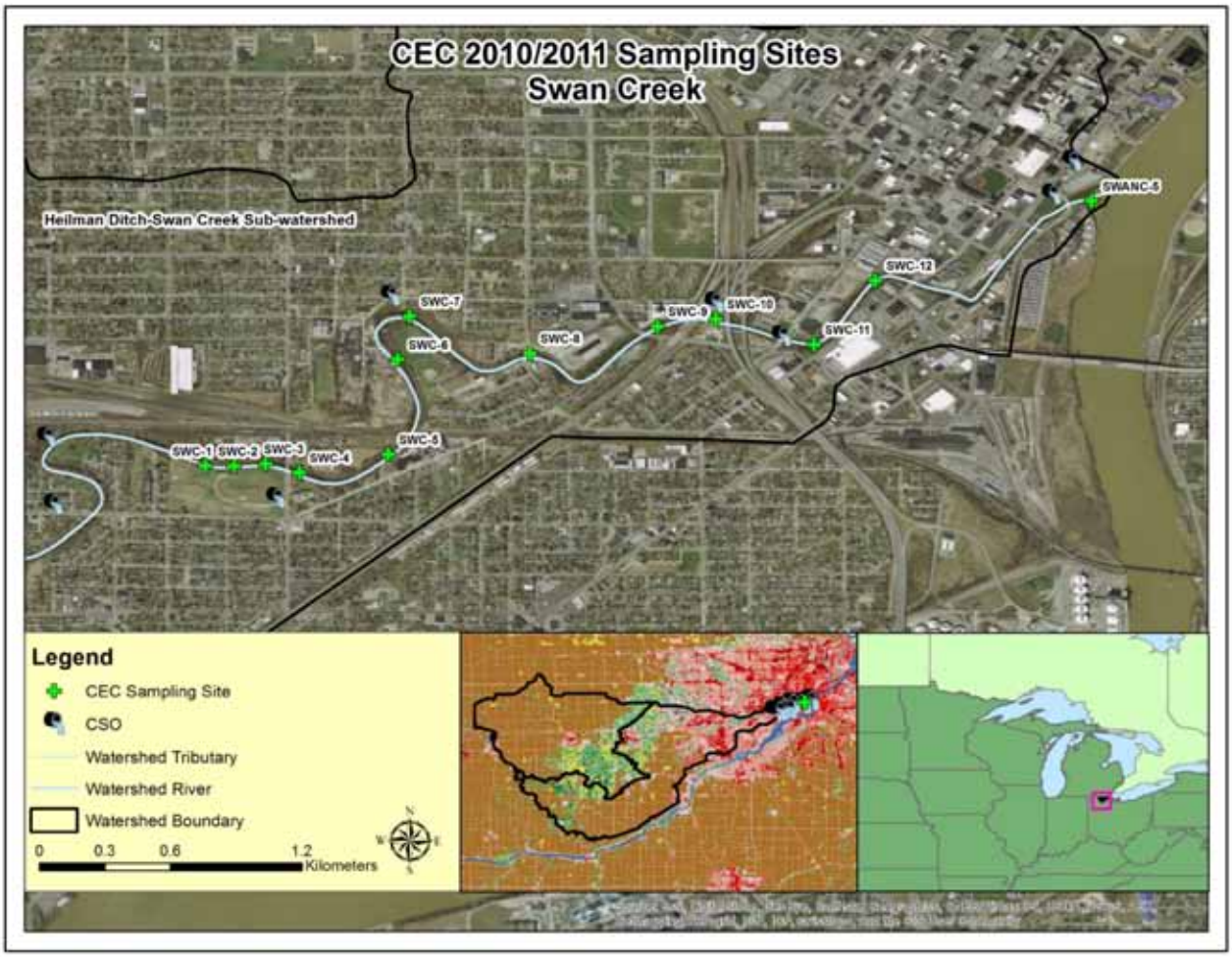
Detroit River Watershed (8-digit HUC)				
Drainage Area (km^2)			2298.10	
WTTPs			6	
CSOs			123	
Land Use Class (U.S.)	% Cover		Land Use Class (Canada)	% Cover
Water	0.86		Water	0.01
Developed	85.05		Developed	1.55
Barren	0.31		Barren	0.04
Forest	6.61		Forest	0.16
Shrubland	0.05		Agriculture	98.19
Herbaceous	0.53		Marshes	0.05
Agriculture	3.90			
Wetlands	2.68			

Figure 12. Map of Detroit River sites sampled in spring 2012.



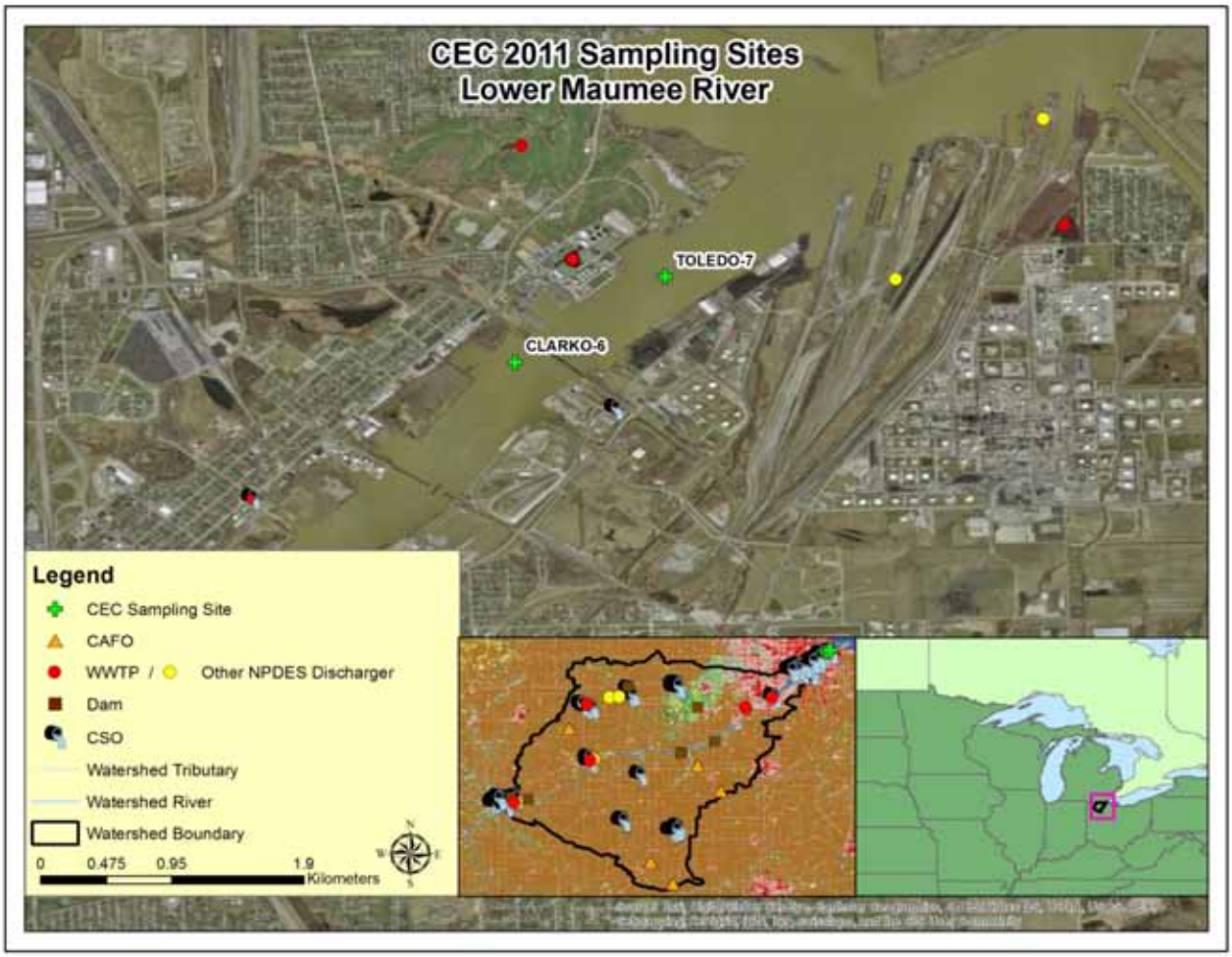
River Raisin Watershed (8-digit HUC)	
Drainage Area (km^2)	2753.30
WTTPs	4
CSOs	1
Land Use Class	**% Cover**
Water	1.42
Developed	11.24
Barren	0.24
Forest	10.91
Shrubland	0.18
Herbaceous	0.64
Agriculture	67.25
Wetland	8.10

Figure 13. Map of River Raisin sites sampled in spring 2012



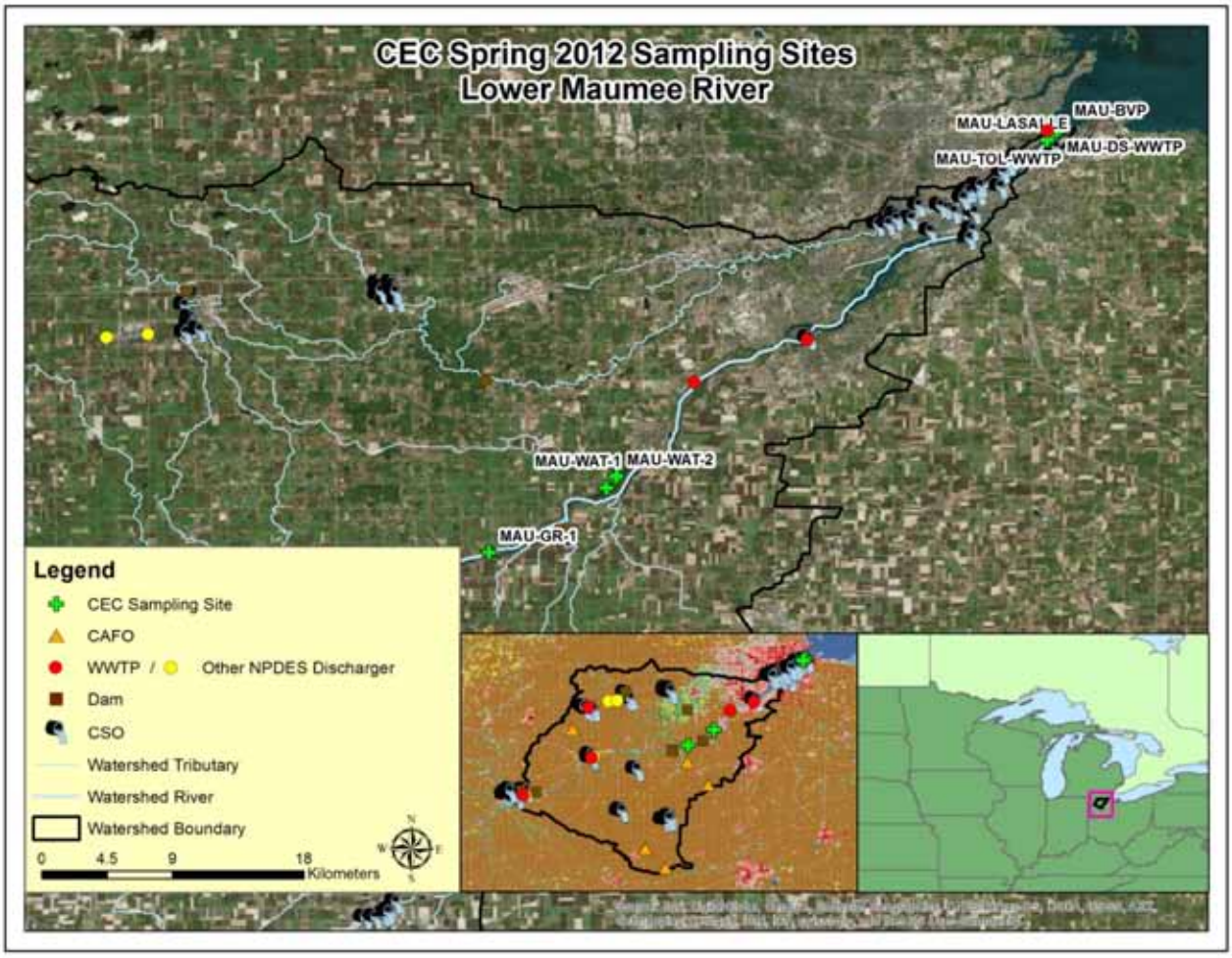
Upper and Lower Swan Creek Watersheds (10-digit HUC)	
Drainage Area (km^2)	529.93
WTTPs	0
CSOs	19
Land Use Class	**% Cover**
Water	0.47
Developed	23.18
Barren	0.16
Forest	18.54
Shrubland	0
Herbaceous	2.059
Agriculture	54.72
Wetland	0.87

Figure 14. Map of Swan Creek sites sampled in fall 2010 and spring 2011.



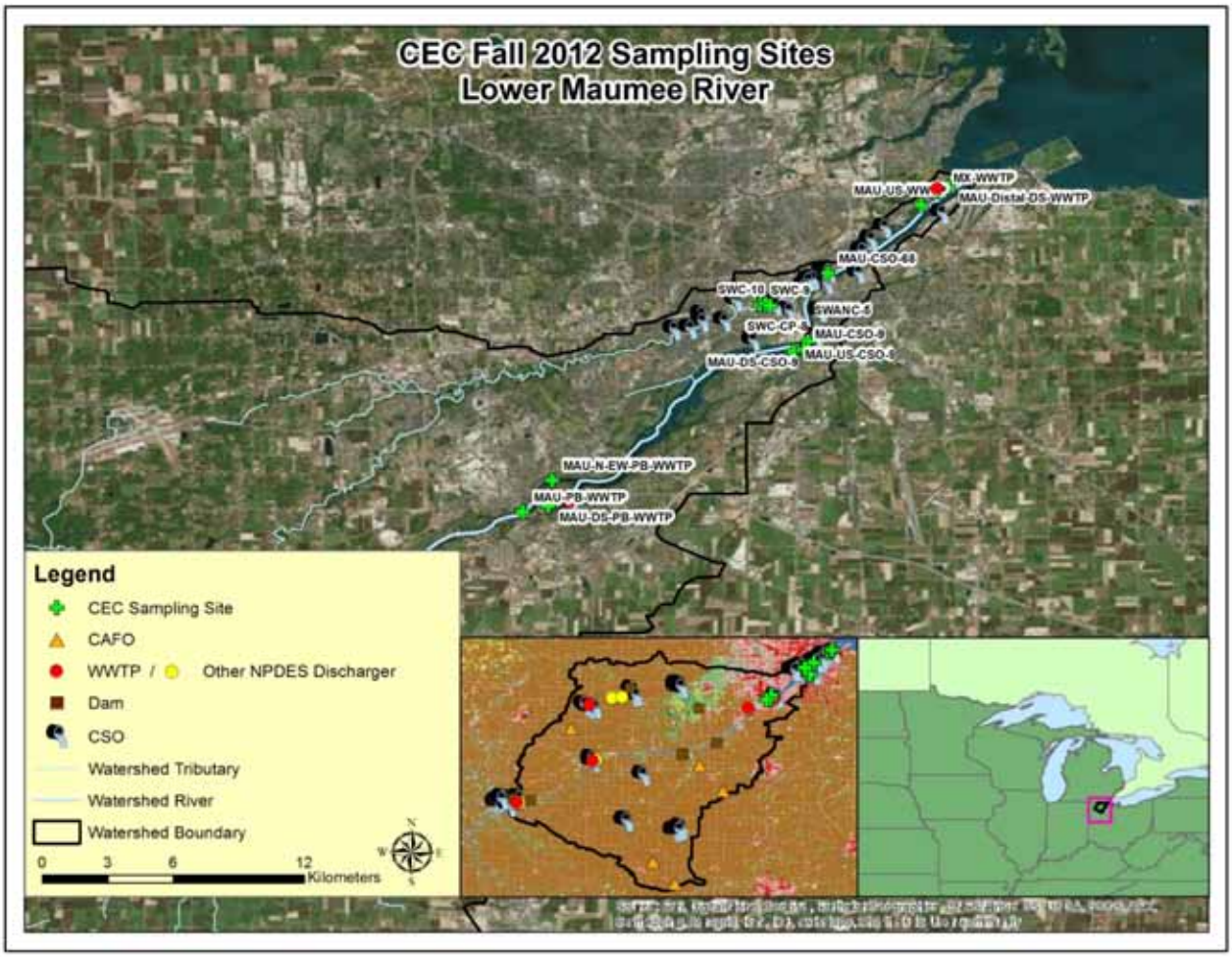
Lower Maumee River Watershed (8-digit HUC)	
Drainage Area (km^2)	2791.62
WTTPs	6
CSOs	93
Land Use Class	**% Cover**
Water	1.36
Developed	14.44
Barren	0.13
Forest	6.68
Shrubland	0
Herbaceous	0.98
Agriculture	75.90
Wetland	0.51

Figure 15. Map of Maumee River sites sampled in spring 2011.



Lower Maumee River Watershed (8-digit HUC)	
Drainage Area (km^2)	2791.62
WTTPs	6
CSOs	93
Land Use Class	**% Cover**
Water	1.36
Developed	14.44
Barren	0.13
Forest	6.68
Shrubland	0
Herbaceous	0.98
Agriculture	75.90
Wetland	0.51

Figure 16. Map of Maumee River sites sampled in spring 2012.

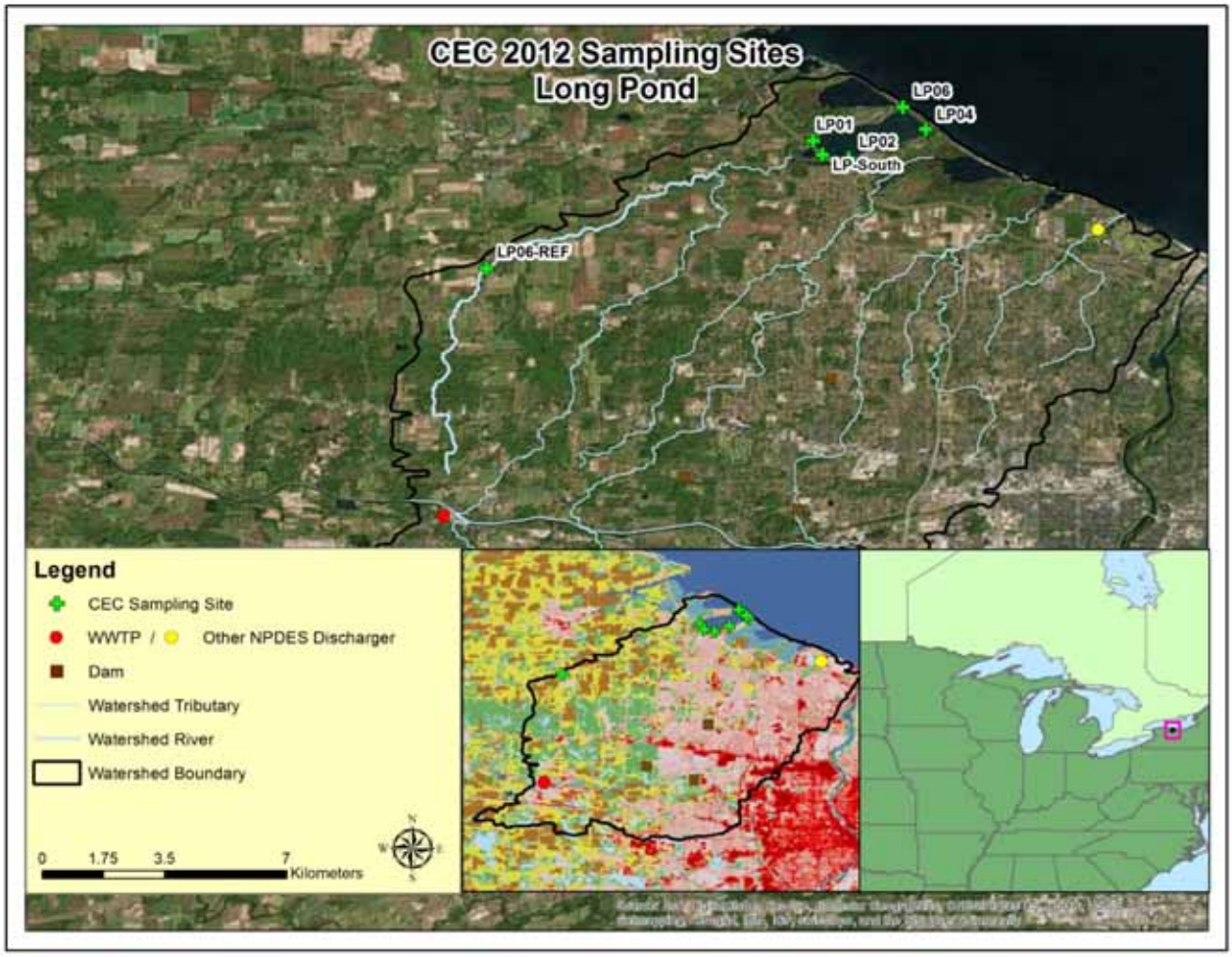


Lower Maumee River Watershed (8-digit HUC)	
Drainage Area (km^2)	2791.62
WTTPs	6
CSOs	93
Land Use Class	**% Cover**
Water	1.36
Developed	14.44
Barren	0.13
Forest	6.68
Shrubland	0
Herbaceous	0.98
Agriculture	75.90
Wetland	0.51

Figure 17. Map of Maumee River sites sampled in fall 2012.

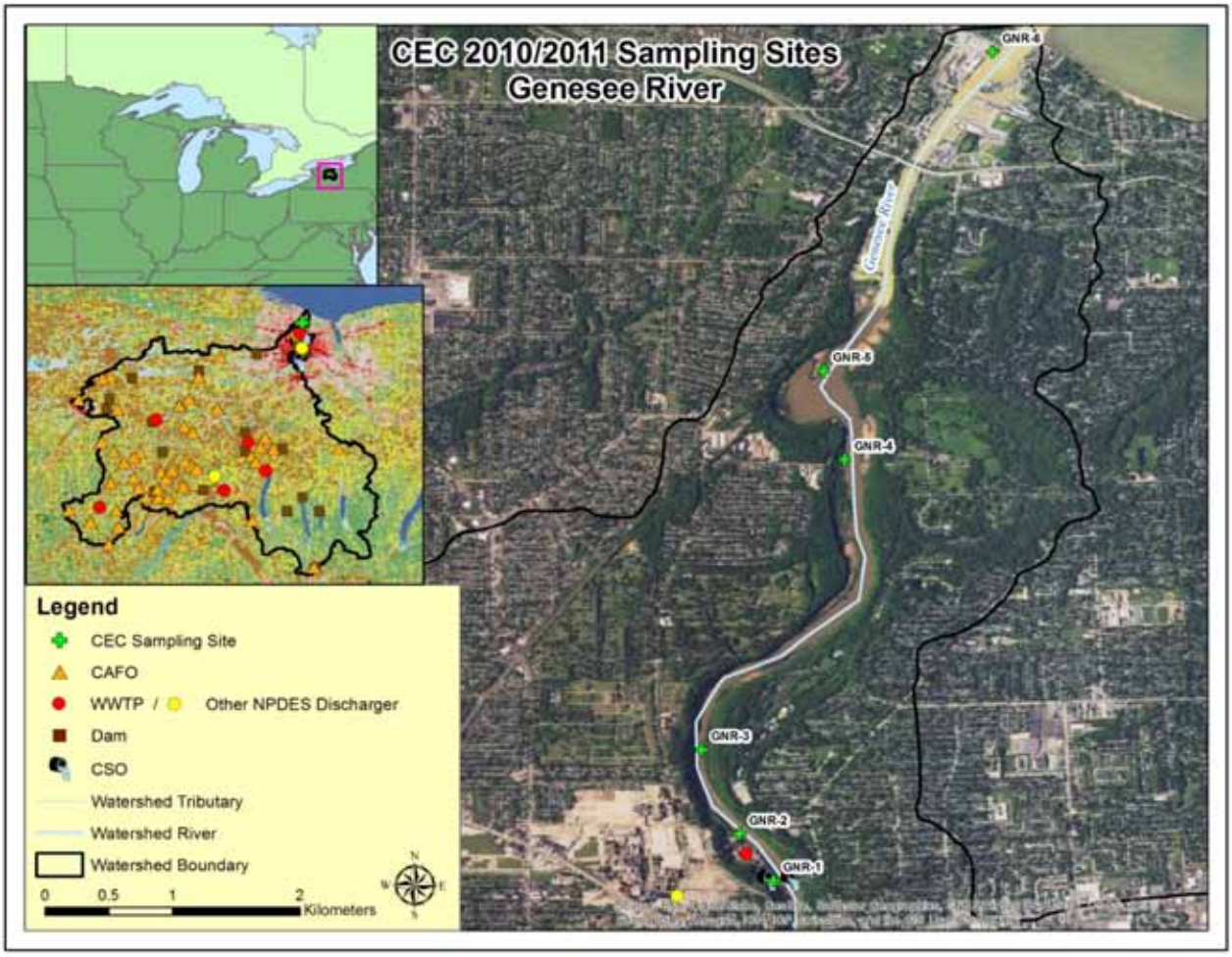
Ashtabula-Chagrin Watershed (10-digit HUC)	
Drainage Area (km^2)	353.97
WTTPs	1
CSOs	0
Land Use Class	**% Cover**
Water	0.83
Developed	12.21
Barren	0.05
Forest	41.88
Shrubland	2.23
Herbaceous	3.23
Agriculture	35.19
Wetland	4.39

Figure 18. Map of Ashtabula River sites sampled in spring 2011.



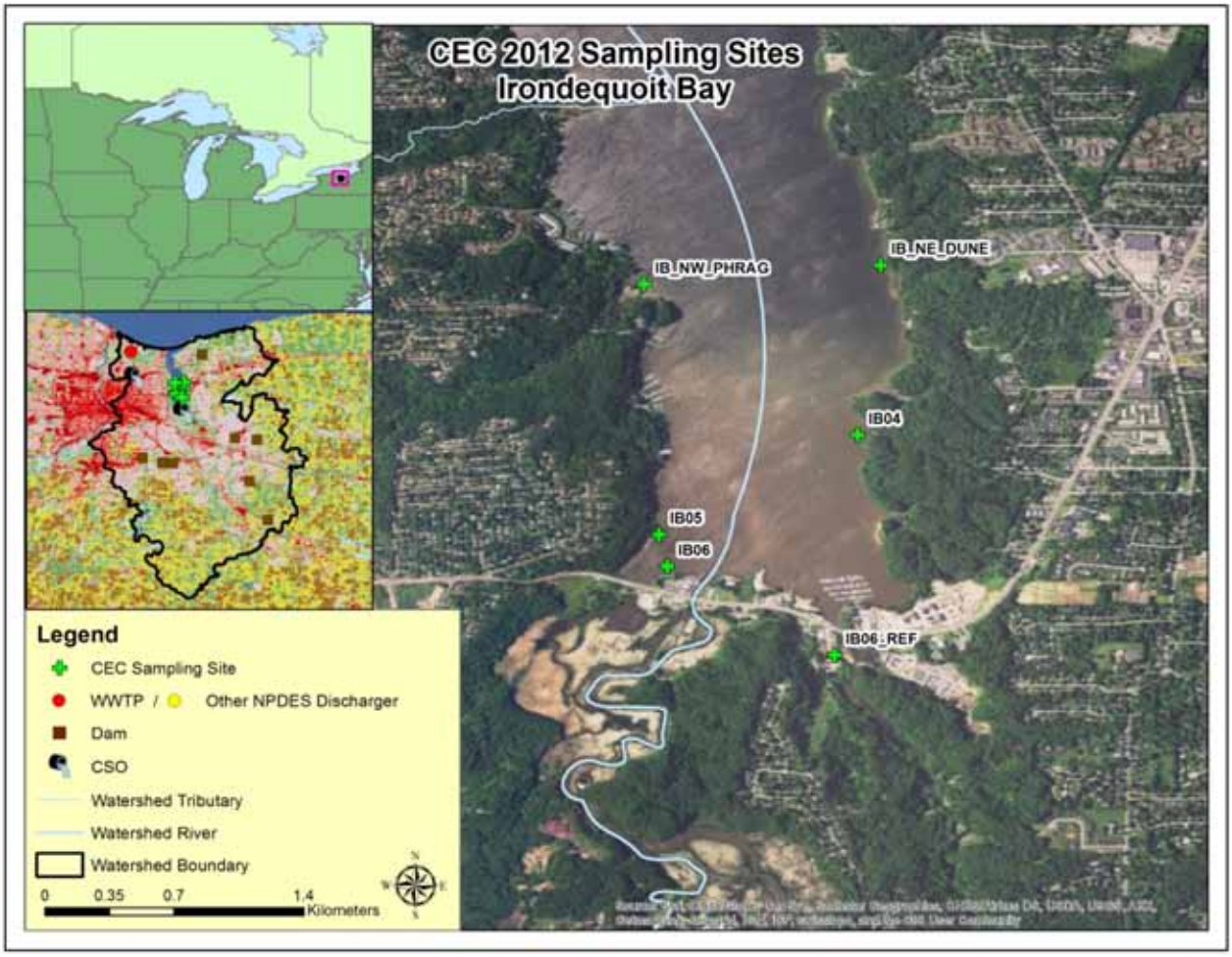
Black Creek-Frontal Lake Ontario (10-digit HUC)	
Drainage Area (km^2)	182.75
WTTPs	1
CSOs	0
Land Use Class	**% Cover**
Water	2.17
Developed	46.04
Barren	0.24
Forest	20.61
Shrubland	1.67
Herbaceous	0.50
Agriculture	22.44
Wetland	6.32

Figure 19. Map of Long Pond sites sampled in spring 2012.



Lower Genesee River Watershed (8-digit HUC)	
Drainage Area (km^2)	2763.59
WTTPs	6
CSOs	4
Land Use Class	**% Cover**
Water	1.50
Developed	11.14
Barren	0.25
Forest	21.60
Shrubland	3.78
Herbaceous	0.38
Agriculture	55.17
Wetland	6.18

Figure 20. Map of Genesee River sites sampled in fall 2010 and spring 2011.



Irondequoit Creek-Frontal Lake Ontario Watershed (10-digit HUC)	
Drainage Area (km^2)	513.36
WTTPs	1
CSOs	2
Land Use Class	**% Cover**
Water	1.78
Developed	45.29
Barren	0.55
Forest	20.36
Shrubland	2.56
Herbaceous	0.89
Agriculture	24.22
Wetland	4.36

Figure 21. Map of Irondequoit Bay sites sampled in spring 2012.

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