Third Five-Year Review Report for the Hudson River PCBs Superfund Site

APPENDIX 2

EVALUATION OF SURFACE SEDIMENT CONCENTRATIONS

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EXECUTIVE SUMMARY

Background

The purpose of this appendix is to assess the 0 to 2-inch surface sediment Polychlorinated Biphenyl (PCB) concentrations in the Upper Hudson River (UHR) for the Hudson River PCBs Superfund Site (Site) measured during the post-dredging or natural recovery phase of the remedy, from 2016 to 2021. Per the requirements of the Consent Decree, as amended by the 2010 Phase 2 Operations, Maintenance, and Monitoring (OM&M) Scope (EPA, 2010), the sediment monitoring program consists of collecting surface sediment samples (from the 0 to 2-inch depth interval) every five years to examine the post-dredging PCB levels and to track changes in sediment PCB concentrations over time.

Analyses

This appendix provides a summary of findings on the measured PCB concentrations in 0 to 2-inch surface sediment samples collected from the main stem of UHR during two monitoring periods: 2016/2017 and 2021. Both datasets were generated from unbiased sampling designs. Analyses presented in this appendix include (1) estimating the average PCB concentrations in recoverable areas (i.e*.,* areas that can be sampled) and the entire river bottom areas (i.e., recoverable, non-recoverable [i.e*.,* areas that could not be sampled such as gravel or cobble], bedrock [i.e., un-sampleable areas with a solid rock surface]) by river section and reach, (2) comparing the sediment PCB concentrations in 2016/2017 and 2021, and (3) assessing Tri+ PCB concentrations near the three areas of interest.

Technical Assessment

Characterize post-dredging surface sediment PCB concentrations by river section and reach

Overall concentration level: Data collected during the post-dredging period show that about 99 percent of sediment samples contained Tri+ PCB concentrations (the sum of all measured PCB congeners with three or more chlorine atoms per molecule) that were lower than the most stringent ROD-specified surface sediment remediation criterion of 10 milligrams per kilogram (mg/kg), and 70 percent of samples contained less than 1 mg/kg Tri+ PCB. The median Tri+ PCB concentration was around 0.5 mg/kg in both the 2016/2017 and 2021 datasets. According to the latest data in 2021, the River-Wide-Area- (RWA-)weighted average Tri+ PCB concentrations were 0.99, 1.5, and 0.44 mg/kg in River Section (RS) 1, RS 2, and RS 3, respectively. The RWA-weighted average

Total PCB Homologue Equivalent ($TPCB_{HE}$) concentrations were 3.0, 3.4, and 0.96 mg/kg in RS 1, RS 2, and RS 3, respectively.

Dredged and non-dredged area comparison: In RS 1 and RS 2, where about 55 percent and 18 percent of the river bottom was dredged, respectively, the median Tri+ PCB concentrations in samples collected from dredged areas (0.29 mg/kg and 0.69 mg/kg in RS 1 and RS 2, respectively) in 2021 were much lower than those from non-dredged areas by a factor of 2.5 to 3.4 (0.99 mg/kg and 1.7 mg/kg in RS 1 and RS 2, respectively). In RS 3, where less than 5 percent of the river bottom was dredged, the median Tri+ PCB concentration in dredged areas (0.33 mg/kg) in 2021 was at the same level as that in non-dredged areas (0.33 mg/kg). The concentration difference between the two areas decreased over time from 2016/2017 to 2021 across all three river sections. Similar results were also observed for $TPCB_{HE}$, where the median concentration in dredged areas were a factor of 3.8 and 2.0 lower than in non-dredged areas for RS 1 and RS 2, but comparable in RS 3.

Comparison of PCB concentrations in the silt and non-silt areas: PCB concentrations from the silt areas were found to be lower or comparable to those in non-silt areas.

Spatial pattern: In non-dredged areas, Tri+ PCB and $TPCB_{HE}$ concentrations were the highest in RS 2, followed by RS 1, and lowest in RS 3. In dredged areas, RS 2 was the area with the highest PCB concentrations, and concentrations from RS 1 and RS 3 were similar. Reaches 7, 4, and 3, where the three areas of interest were located, continued to show elevated concentrations in non-dredged areas. Changes in PCB concentrations in these three reaches over time will be carefully examined in the next Five-Year-Review (FYR).

Examine changes in surface sediment PCB concentrations during the post-dredging period (2016/2017 to 2021) as a result of Monitored Natural Recovery (MNR)

Evaluating the recovery rate of PCB concentrations in surface sediment was not performed, as the sediment OM&M program requires 10 years of data (year 0, year 5, and year 10) to detect a 5-percent annual rate of decline with 80-percent power and 95-percent confidence. Rather, temporal change in surface sediment PCB concentrations was explored by comparing the geometric mean concentrations in recoverable sediments sampled in 2016/2017 and 2021, as well as the RWA-weighted average concentrations.

Recoverable dredged areas: In dredged areas, measured sediment PCB concentrations increased from 2016/2017 to 2021 in all three river sections, and the increase was the largest in RS 2 (by about 70 percent). The increased concentrations in dredged areas over time are expected likely due to the resuspension of sediment from the non-dredged areas, followed by deposition of these sediment in the dredged areas. This redistribution is expected as dredged areas are typically located within depositional areas of the river and the majority of the areas were not backfilled to the pre-dredged elevations. Therefore, creating an ideal environment for sediment deposition. Since the

PCB concentrations in the dredged areas that were backfilled are low right after the completion of dredging, concentrations in these areas will increase over time and go toward the concentrations in non-dredged areas as they continue to accumulate depositing solids.

Recoverable non-dredged areas: In non-dredged areas, measured sediment PCB concentrations remained unchanged in RS 1 and RS 2, but declined from 2016/2017 to 2021 in RS 3, primarily due to the decrease in Reach 5. At least 10 years of post-dredging data are needed to estimate the Tri+ PCB recovery rates with 95-percent confidence and 80-percent power.

RWA-weighted average concentrations: In RS 1 and RS 2, the RWA-weighted average PCB concentrations measured in 2021 remained unchanged from those measured in 2016/2017. In RS 3, the RWA-weighted average Tri+ PCB concentration decreased from 0.57 mg/kg in 2016/2017 to 0.44 mg/kg in 2021; and the RWA-weighted average $TPCB_{HE}$ concentration decreased from 1.2 mg/kg in 2016/2017 to 0.96 mg/kg in 2021.

Evaluate the Tri+ PCB concentrations near previously identified areas of interest.

In the United States Environmental Protection Agency's (EPA's) *Technical Memorandum Evaluation of 2016 EPA/GE and 2017 NYSDEC Surface Sediment Data* (EPA, 2019b), three areas of interest were identified as zones of comparatively elevated surface sediment Tri+ PCB concentrations, based on sample data collected during 2016 and 2017:

(1) Near Galusha Island between River Mile (RM) 188 and 187 in RS 2/Reach 7

(2) Near the Upper Mechanicville Dam, north of RM 166 near Certification Unit (CU) 92 in RS 3/Reach 4

(3) Near the Lower Mechanicville Dam, between RM 164 and 163, near CU-96 in RS 3/Reach 3

The 0 to 2-inch surface sediment data collected in 2021 indicate that the three areas of interest continue to contain sediments with comparatively elevated Tri+ PCB concentrations relative to other areas of the UHR. However, the average Tri+ PCB concentrations in these areas has decreased from 2016/2017 to 2021. Therefore, there does not appear to be an increase in the spatial extent of these three areas. Surface sediment data collected every five years will be used to continue to track the changes of PCB concentrations over time in these areas of interest.

1 INTRODUCTION

1.1 Background and Overview

As stated in the Record of Decision (ROD; EPA, 2002) for the Site, one of the Remedial Action Objectives (RAOs) for OU2 is to reduce the cancer risks and non-cancer health hazards for people eating fish from the Hudson River by reducing the concentration of PCBs in fish. To achieve the fish tissue PCB concentration target levels and remedial goal in the ROD, the selected remedy was intended to reduce the PCB concentrations in sediments[1] through two processes: sediment removal by dredging and backfilling, and monitored natural recovery (MNR).

Dredging was conducted between 2009 and 2015 (with no dredging occurring in 2010) and removed approximately 2.63 million cubic yards of PCB-contaminated sediment from approximately 500 acres of river bottom. The Second Five-Year-Review (FYR) Report considered data collected through December 2016 (EPA, 2019a). In 2016, General Electric Company (GE), under EPA direction, undertook a sediment sampling survey to characterize the PCB concentration in 0 to 2-inch surface sediments in the areas outside the dredged areas (i.e., non-dredged areas). Work to characterize the baseline conditions inside the dredged areas (i.e., the areas inside the certification units, or CUs) was postponed to a later date due to time constraints in 2016. Sampling of sediments in dredged areas by GE was accomplished in fall 2017. However, New York State Department of Environmental Conservation (NYSDEC) undertook a more intensive program in 2017, sampling both dredged and non-dredged areas. Therefore, the samples collected by GE in the fall 2017 were not analyzed for chemistry. Information regarding EPA's analysis of the combined GE 2016 and NYSDEC 2017 surface sediment data can be found in EPA's *Technical Memorandum* (http://www.epa.gov/hudsonriverpcbs; EPA, 2019b).

In response to comments for the second FYR report, EPA evaluated the changes in surface sediment Tri+ PCB[2] concentrations from the pre-dredging period (2002 to 2005) to the first post-dredging monitoring period (2016/2017). The evaluation showed that the dredging and backfilling, along with MNR, resulted in substantial reductions in Tri+ PCB concentrations. Using the combined 2016 and 2017 datasets, the overall percentage reductions on an area-weighted average basis were more than 80 percent[3] for all river sections (EPA, 2019c), which are substantially

[1] PCBs in fish in the UHR are expected to track the changes in surface sediment PCB concentrations (i.e., if PCB concentrations decrease in the surface sediment, then they are also expected to decrease in the overlying water column, and with reductions in sediment and water, the PCB concentrations in fish are expected to decline as well).
[2] Tri+ PCB represents the sum of all measured PCB congeners with three or more chlorine atoms per molecule. PCBs are a group of chemicals consisting of 209 individual compounds known as congeners. The congeners can have from one to 10 chlorine atoms per molecule, each with its own set of chemical properties.
[3] Recently, EPA identified a quantification error for Aroclor 1221 in 2017 samples and subsequently re-quantified all the Aroclor 1221 results for that year (Attachment A). This correction has negligible impact (approximately 1 percent) on the previously reported reductions.

greater than anticipated in the ROD for the active remedy alone—that is, 79 percent, 64 percent, and 4 percent for RS 1, RS 2, and RS 3, respectively (EPA, 2002).

Because the evaluation of dredging effectiveness has been extensively discussed in the second FYR (EPA, 2019a) and in EPA's *Technical Memorandum* (EPA, 2019b), the comparison of concentrations between pre-dredging and post-dredging periods was not duplicated in this appendix. This appendix examines surface sediment PCB concentration data collected during the post-dredging or natural recovery phase of the remedy, 2016 to 2021 (referred to herein as the post-dredging period). Data collected during the first post-dredging monitoring period (2016/2017) are being used as the baseline dataset for the natural recovery phase of the project.

1.2 Purpose and Objectives of the Sediment Sampling Program

The data quality objectives (DQOs) of the overall long-term sediment Operations, Maintenance, and Monitoring (OM&M) program, as outlined in the 2010 Phase 2 OM&M Scope (EPA, 2010), are as follows:

1. Determine post-remediation PCB levels in sediments in non-dredged areas of the Upper Hudson River (UHR).
2. Provide data on Select Areas that exceeded the Mass per Unit Area removal criteria that were not targeted for removal because they were buried by cleaner sediments to assess whether the deposits have experienced erosion.
3. Determine sediment recovery rates in non-dredged areas of the UHR.
4. Examine the changes to surface PCB concentrations in backfill areas.

Of these DQOs, objectives 1, 3, and 4 are being addressed by collecting surface sediment samples (0 to 2-inch depth interval) every five years in the dredged and non-dredged areas using an unbiased, spatially representative sampling design. Objective 2 will be addressed through bathymetry surveys and will be evaluated in a future FYR.

In line with these DQOs, the objectives of this appendix are to utilize samples collected during the post-dredging period to do the following:

- Characterize post-dredging surface sediment PCB concentrations by river section and reach
- Examine changes in surface sediment PCB concentrations during the post-dredging period (2016/2017 to 2021)

1.3 Document Organization

This appendix is organized into the following sections:

- Section 1 (Introduction): Provides the background and objectives for monitoring PCBs in sediments.
- Section 2 (Program Description): Presents an overview of the sediment sampling program, laboratory analytical programs, and data used in this appendix.
- Section 3 (Analysis Methods): Describes various data evaluation methods and the calculation of Tri+ PCB and Total PCBs (TPCB) concentrations from Aroclor concentrations.
- Section 4 (Results and Discussion): Presents the results associated with the objectives listed in Section 1.2.
- Section 5 (Conclusions): Summarizes appendix findings.
- Section 6 (Abbreviations and Acronyms): Defines the abbreviations and acronyms used in this appendix.
- Section 7 (References): Provides the list of references cited in this appendix.

2 PROGRAM DESCRIPTION

The sediment datasets presented in this appendix were collected during the post-dredging period (2016 to 2021) under three different sampling events (Table A2-1). Data collected during the pre-dredging and dredging years were evaluated in the second FYR (EPA, 2019a, 2019b) and will not be discussed in this appendix.

All surface sediment samples were obtained from the 0 to 2-inch depth interval below the sediment water interface. Although EPA considers PCBs in the top 1 foot of sediment to be representative of exposures, the top 2-inch interval provides a more sensitive indicator of how recent perturbations to the river system are impacting surface sediments. Understanding the rate of decline in the top 2 inches can also be used to estimate changes in the top 1 foot of sediment based on relatively simple mixing calculations, so questions of exposure assessment can also be evaluated, albeit less precisely than with direct measurements of contaminant concentrations in the top foot of the sediment bed.

Table A2-2 lists the number of surface sediment samples collected from the main stem of UHR in 2016, 2017 and 2021 by river section and by reach. The sample size and sampling locations for these programs were designed specifically to provide an unbiased estimate of the mean PCB concentration in a given sediment area, as well as a robust dataset to monitor temporal changes. The following subsections summarize the three sediment monitoring programs, as well as any ancillary datasets that are used to support the evaluation in this FYR.

2.1 2016 EPA/GE Surface Sediment Program

The 2016 EPA/GE surface sediment sampling program was the first sampling event conducted during the post-dredging period. The program was designed to provide unbiased estimates of overall river section average Tri+ PCB concentrations in surface sediments, and to account for the anticipated concentration differences between dredged and non-dredged areas. Specifically, the number of samples in dredged and non-dredged areas were selected so that the expected relative error of the estimated mean on a river section scale was no greater than 50 percent in RS 1, 30 percent in RS 2, and 20 percent in RS 3.[4,5] The required target sample size for the non-dredged areas was calculated to be 35, 70, and 121 samples in RS 1, RS 2, and RS 3, respectively; and the corresponding quantities for the dredged areas were 31, 52, and 66 samples, respectively. For each of the two areas (i.e., dredged and non-dredged areas), the required samples were allocated proportionally to the area within each one-mile segment along the north-south direction. For example, if a particular one-mile segment contains 10 percent of the non-dredged area, then 10 percent of the samples for non-dredged areas will be allocated to that segment. The design of the

[4] The sample size was determined based on the variance of Tri+ PCB concentrations from the 2011-2013 samples (DDS studies) for the non-dredged areas, and the post-dredging data from the Fox River for the dredged areas.
[5] These precision targets reflect increasing interest in post-dredging conditions in RS 2 and more so in RS 3 where remedial actions were less laterally extensive than in RS 1.

program is detailed in Attachment A to the 2016 Surface Sediment Sampling Work Plan (GE, 2016).

In 2016, a total of 215 samples were collected from the non-dredged areas (33, 70, and 112 samples in RS 1, RS 2, and RS 3, respectively).[6] However, dredged areas were not sampled until 2017 due to weather-related limitations. In 2017, a total of 30, 51 and 66 samples were collected from dredged areas in RS 1, RS 2, and RS 3, respectively. In addition, EPA's evaluation of the non-dredged area data collected in 2016 indicated that the variance from RS 3 was higher than anticipated and required approximately 100 more samples to be collected from RS 3 to meet the goals of the program (GE, 2017). This led to the collection of additional 83 samples from non-dredged areas of RS 3 in 2017. It was determined after the samples were collected that the analysis of the 2017 samples were not necessary because sufficient data had already been collected under the NYSDEC 2017 program, and the data were determined to be interchangeable.

Prior to collecting a sample, a steel rod was used to probe the sediment bed and to provide inferential information on the sediment type (e.g., rock, fine-grained, coarse-grained). The majority of samples were obtained by using a Van Veen sampler equipped with a landing frame to aid in obtaining reproducible sampling depths. A few samples were collected by a Ponar dredge. Upon retrieving each sediment sample, a visual classification of sediment texture (e.g., clay, silt, sand, gravel) was recorded in the field database.

2.2 2017 NYSDEC Surface Sediment Program

The NYSDEC program targeted 1,678 locations. The program was designed around the eight reaches (or pools) that are found in the UHR project area instead of the three river sections used in EPA/GE's 2016 program. The number of samples was determined with the goal of achieving: (1) the ability to detect an 8 percent annual decline in PCB concentrations within a given reach between two consecutive five-year monitoring periods with a statistical power of 80 percent at the 95 percent confidence level, and (2) the ability to determine the mean PCB concentration for each reach with a relative error no greater than 20 percent (NYSDEC, 2018).[7] Sample locations were selected using a systematic triangular grid with a random start location. Since the sampling design used a grid approach, samples were not allocated by dredged and non-dredged areas. However, due to the unbiased nature of the grid, allocation by dredged and non-dredged areas was not necessary.

A total of 1,162 locations were successfully sampled.[8] Samples were primarily collected using a modified Van Veen Sampler (i.e., with a landing frame), as well as a Ponar dredge sampler and an

[6] Among the 215 samples, one sample (OCU-RS3-6059-286) was collected in landcut area and was excluded in this FYR evaluation (Table A2-1).
[7] The number of samples was determined based on the variance observed in the Sediment Sampling and Analysis Program (SSAP) data (2003–2005), and the 2016 EPA/GE sample data.
[8] Of the 1,162 samples, 1,078 samples from the main stem of the UHR were included in the evaluation. Samples from land cut, backwater, and tributaries areas were excluded (Table A2-1).

unmodified Van Veen sampler. The program utilized the 2016 EPA/GE data and did not target samples from 215 locations that EPA/GE had already identified. Therefore, the 2016 EPA/GE and 2017 NYSDEC datasets were combined to represent PCB concentrations as a single time point (i.e., 2016/2017) in this appendix. The design and outcome of the 2017 program were provided in the data summary report (NYSDEC, 2018). EPA's evaluation on the 2016/2017 data is presented in the EPA's *Technical Memorandum* (EPA, 2019b).

2.3 2021 EPA/GE Surface Sediment Program

The 2021 sediment sampling program was the second round of sampling performed during the post-dredging period. The design objectives of the program were adjusted from the 2016 program to account for changes in EPA's understanding of the system. Specifically, it was determined that the relative error of the mean should be consistent for each river section and the sample size should be sufficient to estimate the mean Tri+ PCB concentrations on a river section scale with a relative error no greater than 25 percent. The other objective for the 2021 program was to detect a 5 percent annual rate of decline in surface sediment Tri+ PCB concentrations over a 10-year period with 80 percent power and 95 percent confidence on a river section scale. To meet both objectives, EPA's power analysis indicated that 180, 165, and 400 samples were required in RS 1, RS 2, and RS 3, respectively, based on the variance observed in the 2016/2017 dataset.

The total number of samples for each river section were allocated to reaches in dredged and non-dredged areas (i.e., strata) within that river section proportionally, according to the area and variance. The sampling locations within each stratum (e.g., Reach 8 dredged area, Reach 8 non-dredged area) were chosen using a stratified, random probability-based, unbiased sampling approach called the Generalized Random Tessellation Sampling (GRTS) algorithm (Stevens and Olsen, 2004).[9,10] This approach allows for the number of locations to be reduced or increased in future years if the need arises while still maintaining the spatial representativeness of the dataset. The design of the 2021 program was documented in Attachment 1 to GE's *Addendum to Surface Sediment Sampling Work Plan* (GE, 2021).

[9] The 2016 EPA/GE program was originally designed to re-occupy the locations that were previously selected. However, since the number of samples was adjusted to account for the refined objectives, a more flexible design approach (*i.e.*, GRTS) was used.

[10] As part of the 2021 program design, the boundary of dredged areas was determined as the intersect of the actual dredged area boundary and CU boundary. This means that dredged areas represent certified dredged areas where residual Tri+ PCB concentrations were less than 1 mg/kg. The access dredged areas, covering around 12 acres of UHR, were included in the non-dredged area strata. This is because the access dredged areas were not certified as dredged areas (*i.e.*, the residual PCB levels were not measured in those areas). In 2021, a total of four locations that were sampled fell in the access dredged areas. Because the access dredged areas were backfilled, it is expected that PCB concentrations in access dredged areas are lower than those in the non-dredged areas. However, including these locations in the non-dredged area will not impact the calculation of area-weighted average concentrations because the target locations were distributed proportionally to the surface areas within a stratum per GRTS.

A total of 178, 165, and 399 surface sediment samples (from 0 to 2-inch depth interval) were collected in 2021 from RS 1, RS 2, and RS 3, respectively (Table A2-2). The samples were collected using the same methods as used in 2016.

In addition to the surface sediment sampling program, the 2010 Phase 2 OM&M Scope (EPA, 2010) also includes the collection of Beryllium-7 (Be-7) bearing samples (from 0 to 2-centimeter depth interval) to track the changes in PCB concentrations in recently deposited sediment. Collection of Be-7 bearing samples was not performed during the initial surface sediment sampling event in 2016 (with EPA concurrence) and was not performed in 2021 because the planned surface sediment sampling event occurred long after the last high-flow event, making the data less useful. In May to June 2022, GE conducted the first sampling event targeting the collection of Be-7 bearing samples in accordance with the *2022 Beryllium-7 Sediment Sampling Memorandum* (GE, 2022). The results will be evaluated in the next FYR.

2.4 Analytical Program

Table A2-3 summarizes the chemical analysis methods and laboratories selected for the post-dredging surface sediment sampling programs.

The 2016 surface sediment samples were analyzed for PCB Aroclors by GE Hudson River (GEHR) Method 8082 (M8082) and total organic carbon (TOC) using the Lloyd Kahn Method at Pace Analytical Services (Schenectady, New York). As part of the oversight program, EPA accepted custody of 23 split samples and had them analyzed for PCB Congeners via EPA Method 1668C (M1668) at SGS AXYS Analytical Services Ltd. (Sidney, British Columbia). However, it should be noted that the EPA split samples were collected after the GE sample jars were filled, rather than in parallel. This sequential sampling procedure contributed to heterogeneity between the parent and split samples, and as such, the two samples cannot be treated as true field split samples and the PCB concentrations are not expected to be comparable. Therefore, these congener-based data are not included in this appendix.

The 2017 surface sediment samples were analyzed for PCB Aroclors and TOC using the same analytical methods as those used in 2016. To maintain comparability between the 2017 NYSDEC and the 2016 EPA/GE analytical results, NYSDEC contracted with the same analytical firm (Pace Analytical Services) used by GE, although at a different location (Minneapolis, Minnesota). In addition, 131 samples (approximately 10 percent) were randomly selected for PCB congener analysis via EPA Method 1668A at Pace Analytical Services (Minneapolis, Minnesota). A data quality assessment for the 2017 PCB results was provided in EPA's *Technical Memorandum* (EPA, 2019b).

During the data evaluation in 2021, EPA revisited the high surrogate 2,4,5,6-Tetrachloro-Meta-Xylene (TCMX) recoveries issue which was initially identified in 2019. This new review identified that Aroclor 1221 was being underreported (overall biasing the results low) due to co-elution of

the Aroclor 1221 peak 2 and the surrogate TCMX. The co-elution exists due to the inconsistency in the Aroclor-based method M8082 used to quantify Aroclor 1221 in the 2017 NYSDEC samples. To address this, EPA re-quantified Aroclor 1221 in all 2017 samples (except samples where Aroclor 1221 was not detected). Attachment A provides details on the inconsistency and the procedures used to re-quantify Aroclor 1221. The PCB results for 2017 in this appendix are based on adjusted/corrected Aroclor 1221 data.

The 2021 surface sediment samples were analyzed for PCB Aroclors and TOC using the same analytical methods as those used in 2016. The analysis was performed at Pace Analytical Services (Green Bay, Wisconsin). In addition, a subset of the sediment samples (60 samples or approximately 8 percent) was analyzed for PCB congeners by Method 1668C at Vista Analytical Laboratory (El Dorado Hills, California). Attachment B evaluates the quality of 2021 PCB data by examining the National Institute of Standards and Technology Standard Reference Material test results.

2.5 Ancillary Datasets

Side-Scan Sonar Survey

A side-scan sonar survey was conducted in 2002 and 2003 (GE, 2004) and the resultant data were used to classify surficial sediment types into five textures: silt, silt and sand, gravel, transitional, and bedrock. These five types of sediment texture were shown in Figure A2-1. Results from the survey were used to support the delineation of five sediment category areas that were used in the area-weighted average calculations (see Section 3.2.1).

3 ANALYSIS METHODS

3.1 Data Handling

The primary analytical method for PCB analysis in sediment since 2002 has been the Aroclor-based method M8082, thus PCB concentrations reported in this appendix are Aroclor-based results. TPCB concentrations were calculated as sum of detected Aroclors (including results with "J" qualifiers). Tri+ PCB concentrations were estimated from Aroclor data using the following equation developed by GE in 2011.[11]

$$\text{Tri+ PCB} = 0.13 \times \text{Aroclor 1221} + 0.89 \times (\text{Aroclor 1242} + \text{Aroclor 1254}) \qquad \text{(Eq. 1)}$$

Details of the development of this equation (hereafter referred to as GE's equation) can be found in Appendix 5 of the second FYR (EPA, 2019d). This equation has been applied to estimate Tri+ PCB concentrations in samples collected since 2002.

To confirm the equation developed for the Site is still applicable, a subset of samples from each sampling event was also analyzed for PCB congeners by EPA Method 1668. Estimated Aroclor-based Tri+ PCB concentrations from GE's equation were then compared to congener-based Tri+ PCB measurements to confirm the equation is still properly estimating the Tri+ PCB concentration with Aroclor data. Similarly, Aroclor-based TPCB concentrations ($TPCB_{Aroclor}$) were compared to congener-based TPCB concentrations ($TPCB_{congener}$) to ensure the consistency in Aroclor-based TPCB measurements over time. Details on the comparison between Aroclor-based and congener-based PCB concentrations can be found in Attachment B to this appendix. The comparison indicates that Aroclor-based Tri+ PCB and TPCB results were biased low (approximately 20 percent) compared to congener-based results. However, the magnitudes of bias were similar between the two monitoring periods (2017 and 2021). Therefore, the bias in Aroclor-based measurements will not impact the assessment of changes in PCB concentrations over time. However, in this FYR, Aroclor-based TPCB results were adjusted by a factor of 1.2, which is the geometric mean of the $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratios, to standardize these results to a homologue equivalent value ($TPCB_{HE}$).

Parent and field duplicate sample results were combined based on the following criteria:

- If the concentrations in both the parent and field duplicate samples were detected, then the values were averaged.
- If the concentration in one sample was reported as detected and the other was reported as non-detect, only the detected value was used. This was done to avoid uncertainty introduced by assigning a specific value for the non-detectable result.

[11] This equation was developed by regressing Tri+ PCB concentrations derived from congener data (reported via modified Green Bay method [mGBM]) against Aroclor concentrations (reported via M8082 method) using 445 sediment samples collected from 2004 to 2011.

- If the concentrations for both samples were reported as non-detect, the maximum of the two reporting-limit values was used. For Aroclor results, reporting limits are sample-specific quantitation limits. For congener results, reporting limits are sample-specific reporting detection limits.

3.2 Data Evaluation Approaches

3.2.1 Methods for Evaluating Concentrations and Spatial Distribution of PCB Concentrations

The surface sediment PCB results are presented in this appendix as individual sample results and as area-weighted average concentrations with 95 percent confidence limits. Individual sample results are presented on a map and shown in various figures, including concentration *versus* river mile plots and cumulative probability distribution plots.

Concentration *versus* river mile plots were used to display the spatial distribution of PCB concentration along the river. These plots show individual sample PCB concentration (y-axis) plotted against their corresponding river mile locations (x-axis). Lines representing the geometric mean concentrations for each river section or reach were added to aid the visualization of spatial distribution. Furthermore, the Tri+ PCB plots also included the ROD-specified surface sediment dredging criterion[12] for each river section (i.e., 10 mg/kg in RS 1, 30 mg/kg in RS 2 and RS 3, to assess whether elevated concentrations remained). The results and observations for spatial distribution of PCB concentrations are presented in Sections 4.1.2 and 4.1.3 for dredged and non-dredged areas, respectively.

The cumulative probability distribution plots were used to 1) assess the distribution of the PCB concentrations and 2) compare the distribution of concentrations between two or more datasets. On such plots, the x-axis represents individual sample results and the y-axis represents the percentage of samples with concentrations less than or equal to a given value on the x-axis. If the cumulative probability distribution curves for two datasets overlap closely on the plot, this suggests that their concentration profiles are similar. On the other hand, if the curves for two datasets are widely separated on these plots, this suggests that their concentration profiles are different. In addition, if the curve for one dataset is located to the right of the curve of another dataset at a given percentile, this indicates that it has a higher concentration at that percentile compared to the other dataset. The results and observations for the distribution of Tri+ PCB and $TPCB_{HE}$ concentration levels are shown in Sections 4.1.1 and their comparison for dredged and non-dredged areas are presented in Section 4.1.5.

[12] The ROD indicated the 0 to 12-inch depth as surface sediment. The 0 to 2-inch depth was selected for long-term monitoring since it will respond more rapidly to changes in PCB conditions in the river. A larger sample (box apparatus) could be collected from the 0 to 2-inch depth, providing a more consistent and representative sample collection at the same locations in each event compared to a 12-inch-deep core.

Area-weighted average concentrations were estimated for each river section and reach using two calculation methods. The first calculation method is based solely on recoverable sediments. The results are shown as Recoverable-Sediment-Area- (RSA-) weighted average concentrations. The second calculation method considers all types of river bottom features (i.e., recoverable, non-recoverable and bedrock areas). The results are shown as River-Wide-Area (RWA)-weighted average concentrations.

RSA-weighted average concentrations are discussed in Sections 4.1.2 through 4.1.4, and RWA-weighted average concentrations are discussed in Section 4.1.6. The two weighted average methods are based on arithmetic means and are discussed in detail below.

RSA-Weighted Average Concentrations in Dredged and Non-Dredged Areas

The RSA-weighted average concentrations were calculated for dredged and non-dredged areas separately, and for combined dredged and non-dredged areas together. For dredged areas, the RSA-weighted average concentration for each reach was calculated by directly averaging (i.e., arithmetic mean) sample results collected from the dredged areas, since each location has the same weight per sampling design.[13] These reach averages were then weighted by their respective areas to derive the RSA-weighted average concentration in the corresponding river section. This same procedure was applied to obtain the RSA-weighted average concentrations in non-dredged areas. The RSA-weighted average for combined dredged and non-dredged areas was derived by weighting the RSA-weighted average concentrations in dredged and non-dredged areas by their respective surface areas. This calculation method is the same as that used to calculate the average concentrations in recoverable sediments for the 2016/2017 data presented in EPA's *Technical Memorandum* (EPA, 2019b).

RWA-Weighted Average Concentrations

RWA-weighted average concentrations were calculated for each river section and reach to better characterize the fish exposure conditions. For this calculation, the river bottom was divided into five sediment categories, as follows:

- Category 1: Bedrock
- Category 2: Dredged areas with sampleable and inaccessible locations
- Category 3: Dredged areas with non-recoverable locations
- Category 4: Non-dredged areas with sampleable and inaccessible locations
- Category 5: Non-dredged areas with non-recoverable locations

[13] The combined 2016/2017 locations were designed on a reach scale, and locations within each reach follow a triangular systematic grid and have the same weight. The 2021 locations were generated by stratifying the UHR by reaches, and further by dredged and non-dredged areas. Locations within each reach-area stratum were generated by GRTS and have the same weight.

For each reach, the RWA-weighted average concentration, $\bar{C}$, was calculated according to Equation 2:

$$\bar{C} = \frac{\sum_{i=1}^{n} A_i \bar{C}_i}{\sum_{i=1}^{n} A_i} \qquad \text{(Eq. 2)}$$

Where:

- A_i is the area for a specific sediment category i;
- $\bar{C}_i$ is the average concentration (i.e., arithmetic mean) for a specific sediment category i; and
- n represents total number of sediment categories.

Table A2-4 describes the methods and procedures used to estimate the values for the variables needed for Equation 2. These values were either derived from direct measured data or estimated based on professional judgement as follows:

- The area (or boundary) for each sediment category was determined using the information from GE's 2002–2003 side-scan sonar classifications, and polygons associated with corresponding location types (i.e., sampleable, inaccessible, or non-recoverable) from the spatially extensive 2016/2017 datasets. Figure A2-2 provides the total areas for each reach and the percentage of area for each sediment category. For the RWA-weighted average calculation, the areas and boundaries of these categories are deemed as fixed, until a further delineation study is necessary and completed. Detailed information on how areas were delineated for the five sediment categories are presented in Attachment 1 to the *Addendum to Surface Sediment Sampling Work Plan* (GE, 2021).
- Average concentration for each sediment category was determined based on either Tri+ PCB and $TPCB_{HE}$ concentrations or assumed concentrations based on professional judgement. Specifically, for sampleable and inaccessible locations in a dredged area (Category 2) or non-dredged area (Category 4), average measured concentrations from sampleable locations were used. Sediments from inaccessible locations were assumed to have concentrations equivalent to those found in successfully sampled sediments. The concentrations in bedrock areas (Category 1) and non-recoverable sediments areas (Categories 3 and 5) were assumed to be very low due to the absence of recoverable sediments in these areas. A concentration of one-half of the median reporting limit from all non-detect results in the post-dredging dataset (0.03 mg/kg) was assigned as the concentration for these three categories (1, 3, and 5).

After the areas and concentrations were estimated for Categories 1 through 5, they were combined to generate the RWA-weighted average for each reach using Equation 2. To calculate the RWA-weighted average for each river section, the river bottom was stratified by both reach and sediment category. Using RS 2 as an example, a total of 10 strata (n=10), representing two reaches and five sediment categories per reach, were used in Equation 2 to calculate the RWA-weighted average.

Note that this method of calculating the *RWA*-weighted average concentrations is consistent with that used in *EPA's Technical Memorandum* (EPA, 2019b).[14]

Uncertainty in the area-weighted (both RSA and RWA) average concentration was estimated by bootstrapping the data to yield 95 percent confidence limits, which are the 2.5th and 97.5th percentile values from 10,000 bootstrapping runs. The 2.5th and 97.5th percentile values were computed using the bias corrected and accelerated (BCa) bootstrap interval method,[15] which was implemented through the use of the "BCa" command in the "coxed" package in R (Kropko and Harden, 2020).

Because the 2021 sampling program was designed to provide an estimate of mean within 25 percent error, the relative error (%error) on the RWA-weighted average concentration was calculated using Equation 3 below:

$$\%error = \frac{C_{UCL} - \bar{C}}{\bar{C}} \times 100 \qquad \text{(Eq. 3)}$$

Where:

- $\bar{C}$ is the RWA-weighted average concentration; and
- C_{UCL} is the 95-percent upper confidence limit (UCL) on the RWA-weighted average.

Statistical Comparison of PCB Concentrations between Dredged and Non-Dredged Areas

Tri+ PCB and $TPCB_{HE}$ concentrations between dredged and non-dredged areas (i.e., sample groups) were compared using the non-parametric Wilcoxon rank sum test. Data groups with a p-value less than 0.05 are statistically different at the 95 percent confidence level. The Wilcoxon rank sum test was conducted using the wilcox.test() function in R (R Core Team, 2022). The results are presented in Section 4.1.5.

Comparison of PCB Concentrations between Silt and Non-Silt Areas

The sediment texture significantly influences the accumulation and persistence of pollutants in aquatic systems. In particular, fine sediment particles, such as silt, have been shown to have a higher capacity for retaining PCBs than coarser sediment particles, such as sand or gravel. Because fish are more likely to reside in fine-grained sediments, PCB concentrations in silt and non-silt

[14] During the design of 2021 sediment program, the areas for the five sediment categories have been refined to exclude areas that are outside the main stem of UHR, including tributaries, areas above Rogers Island, and a small section south of the Troy dam. This adjustment has resulted in a minor change in the areas used in the RWA- weighted average calculation.

[15] This method of estimating uncertainty is different from that used in the second FYR. The bootstrapping method does not make assumptions about the distribution of the data. Conversely, the method used in the second FYR assumes that data follows a normal distribution, which can yield negative values for the lower confidence limits. As such, the bootstrapping method is used in this FYR.

areas were evaluated to understand the potential influence of sediment texture on the PCB distribution.

Historically the PCB concentrations in the sediments were evaluated separately for the finer-grained (cohesive) and coarser-grained (non-cohesive) based on the side-scan sonar survey conducted in 1992 for RS 1 and RS 2. GE conducted a second side-scan sonar survey in 2002-2003, which covered RS 1 to RS 3. GE classified the sediment texture as Silt, Silt and Sand, Gravel, Transitional and Bedrock. To continue the evaluation of the PCB concentrations in the finer-grained and coarser-grained sediments, in this FYR, the sediment texture is classified as silt and non-silt. The classification of silt and non-silt areas was based on GE's side-scan sonar survey conducted in 2002-2003. The non-silt areas include those classified as Silt and Sand, Gravel, Transitional and Bedrock areas. As the sediment texture in dredged areas has significantly altered since the survey, the 2002-2003 data cannot accurately represent the current texture inside these areas. Therefore, only surface sediment data collected in the non-dredged areas were used in this evaluation. Furthermore, since GE's survey did not cover the entire river bottom bank to bank, only a subset of the surface sediment data was included.

Comparison of Tri+ PCB and $TPCB_{HE}$ concentrations between silt and non-silt areas was pursued by comparing average concentrations and associated 95-percent confidence limits. The calculation method is similar to the RSA-weighted average calculation, except that the areas used in the calculation are silt or non-silt areas rather than recoverable areas. The results are presented in Section 4.1.3.

3.2.2 Methods for Evaluating Temporal Changes of PCB Concentrations

Temporal changes in sediment PCB concentrations were explored by comparing concentrations between the two monitoring periods (2016/2017 and 2021) at both the river section and reach scales. The comparison was performed by comparing the geometric mean concentrations in recoverable sediment areas, and the RWA-weighted average concentrations.

The geometric mean concentrations of PCBs in sediment samples collected in 2016/2017 and 2021 were compared using the ratio of the geometric means from the 2021 data to that of the 2016/2017 data, along with the 95-percent confidence interval on the ratio. A ratio of one means the geometric mean stays the same between 2016/2017 and 2021, while a ratio of less than one means a lower geometric mean in 2021 compared to 2016/2017, and a ratio of greater than one means a higher geometric mean in 2021. The 95-percent confidence interval on the ratio, derived from bootstrapping analysis, provides a range of plausible values for the ratio, and is used to evaluate the statistical significance of the change in PCB concentrations. If the interval includes the value of 1, there is no statistically significant difference in PCB concentrations between the two time periods. If the 95-percent lower confidence limit (LCL) is above 1, it indicates a statistically significant increase in geometric mean concentration from 2016/2017 to 2021. If the 95-percent UCL is below 1, it indicates a statistically significant decrease in geometric mean concentration

from 2016/2017 to 2021. The results are presented in Section 4.2.1 for recoverable sediments in dredged areas and Section 4.2.2 for recoverable sediments in non-dredged areas.

The ratio of geometric means is a statistical measure that is commonly used to compare the levels of contaminants in two sample groups. This measure is appropriate because it accounts for the fact that contaminant concentrations are typically not normally distributed, but rather follow a log-normal distribution. Moreover, the temporal trend of contaminant concentrations usually follows a first-order rate of decline model, which requires transforming the concentration data into log-space to obtain a constant rate.

To assess the change in river-wide exposure, RWA-weighted average concentrations (derived from arithmetic mean) are also used. The results are discussed in Section 4.2.3.

Temporal trends in PCB concentrations were not evaluated using a first-order rate of decline or other regression models, due to the limited availability of data (only two sampling events over five years) and the program design requiring at least 10 years of data to detect a 5-percent annual rate of decline with 80-percent power and 95-percent confidence. This is further supported by the moving window analysis presented in Appendix 1 (Evaluation of Water Column PCB Concentrations and Loads) and Appendix 3 (Evaluation of Fish Tissue PCB Concentrations).

3.2.3 Method for Evaluating Areas of Interest

Three areas of interest were identified based on EPA's assessment of surface sediment Tri+ PCB concentrations measured during 2016 and 2017 (EPA, 2019b). An area of interest comprises a cluster of locations where the average Tri+ PCB concentration within a 250-foot[16] radius of those locations is statistically significantly greater than the average Tri+ PCB concentration across the entire UHR at a 95-percent confidence level. An area of interest often contains sediments with Tri+ PCB concentrations greater than the ROD-specified surface sediment dredging criterion for each river section—that is, 10 mg/kg in RS 1 and 30 mg/kg in RS 2 and RS 3 (EPA, 2002). This appendix compares the 2021 data collected from within or near the three areas of interest, with the 2016/2017 data, to evaluate the Tri+ PCB concentrations near the three areas of interest, and to examine any changes in the spatial extent of each of the previously identified areas of interest. Observations of the 2021 data in the three areas of interest are presented in Section 4.3.

[16] The search radius of 250 ft was specified in EPA's *Technical Memorandum* (EPA, 2019b).

4 RESULTS AND DISCUSSION

As discussed in Section 2, both the 2016/2017 and 2021 programs yielded unbiased and spatially representative data that support rigorous, unbiased estimates of average sediment PCB concentrations and associated uncertainty bounds in RS 1, RS 2, and RS 3. The results and discussions presented in the upcoming sections are organized to present the results associated with the methods listed under Section 3.2. Specifically, Section 4.1 describes the concentrations and spatial distribution; Section 4.2 discusses the changes in concentrations between 2016/2017 and 2021; and Section 4.3 evaluates the current status of the three areas of interest using the most recent 2021 data.

4.1 Concentrations and Spatial Distribution of PCB Concentrations in Surface Sediments

The spatial distribution of sediment PCB concentrations were explored by evaluating individual sample results as well as area-weighted average concentrations. Individual sample results from 2016/2017 and 2021 are presented in Figure A2-1 (concentration map), Figure A2-3 (cumulative probability distribution of PCB concentrations), Figure A2-4 (dredged area concentrations by river section and by reach *versus* river mile plot), Figure A2-5 (non-dredged area concentrations by river section and by reach *versus* river mile plot), and Figure A2-8 (cumulative probability distribution by dredged/non-dredged area plot). Table A2-5 compares the area-weighted average PCB concentrations and 95-percent confidence limits across river sections and reaches for the three different evaluation points-—that is, recoverable dredged areas, recoverable non-dredged areas, and river-wide areas (recoverable, non-recoverable, bedrock). Data presented in Table A2-5 are plotted as the area-weighted average with error bars on Figures A2-6 (recoverable areas) and A2-9 (river-wide areas).

4.1.1 Tri+ PCB and $TPCB_{HE}$ Concentration Levels

The Tri+ PCB concentrations observed in surface sediment samples generally ranged from 0.01 mg/kg to 10 mg/kg (Figures A2-3 to A2-5). Around 70 percent of samples contained Tri+ PCB concentrations less than 1 mg/kg, and about 30 percent in the range of 1 mg/kg to 10 mg/kg (Figure A2-3). Twelve samples from 2016/2017 and four samples from 2021 (out of a total of 2,034 samples) contained Tri+ PCB concentrations greater than the RS 1 dredging criterion of 10 mg/kg. Three samples from 2016/2017 and one sample from 2021 (out of a total of 2,034 samples) contained Tri+ PCB concentrations greater than the RS 2 and RS 3 dredging criterion of 30 mg/kg.

Similarly, the $TPCB_{HE}$ concentrations in the sediment samples generally ranged from 0.1 mg/kg to 10 mg/kg, as shown in Figures A2-3 to A2-5. About 50 percent of the samples had $TPCB_{HE}$ concentrations less than 1 mg/kg and approximately 45 percent in the range of 1 mg/kg to 10 mg/kg.

The Tri+ PCB and $TPCB_{HE}$ concentrations in the sediments varied substantially across the sampling locations even within a small spatial scale, as demonstrated on the concentration map

(Figure A2-1) and concentrations *versus* river mile plot (Figures A2-4 and A2-5). At any given river mile, Tri+ PCB and $TPCB_{HE}$ concentrations generally varied by more than one order of magnitude, and these local variations appeared to be larger in the 2016/2017 samples than in the 2021 samples, especially in non-dredged areas (Figures A2-4 and A2-5).

4.1.2 Spatial Distribution of PCB Concentrations in Recoverable Sediments for Dredged Areas

The spatial distribution of sediment PCB concentrations in dredged areas is provided in Figure A2-4, Figure A2-6a, and Table A2-5.

Sediment Tri+ PCB and $TPCB_{HE}$ concentrations in dredged areas generally increased from RS 1 to RS 2, and then gradually decreased through RS 3, as shown on the concentration *vs.* river mile plot (Figure A2-4). The Tri+ PCB concentrations in dredged areas remained low, with only one sample collected in 2017 exceeding the ROD-specified surface sediment dredging criteria. Approximately 80 percent of samples in RS 1 and RS 3 had Tri+ PCB concentrations below 1 mg/kg in 2021, as shown in the cumulative probability distribution plot (Figure A2-8a). About 60 percent of samples collected in RS 2 in 2021 had Tri+ PCB concentrations below 1 mg/kg (Figure A2-8a). The RSA-weighted average concentrations of Tri+ PCB in RS 1, RS 2, and RS 3 were 0.59 mg/kg, 1.7 mg/kg, and 0.72 mg/kg, respectively, in 2021 (Table A2-5a and Figure A2-6a). $TPCB_{HE}$ showed a similar spatial pattern, with RSA-weighted average concentrations of 1.4 mg/kg, 4.0 mg/kg, and 1.5 mg/kg in RS 1, RS 2, and RS 3, respectively (Table A2-5b and Figure A2-6a).

At the reach level (Figure A2-4b and Figure A2-6a), Reaches 6 and 7 in RS 2 had similar concentrations, which were either greater than or comparable to the concentrations found in Reach 8 (RS 1) and Reaches 5 through 1 (RS 3). Within RS 3, the upper reaches (Reaches 5 to 3) had higher concentrations than the lower reaches (Reaches 2 and 1), a consistent pattern observed in both monitoring periods. Notably, sediments from Reach 4 in 2016/2017 had relatively high RSA-weighted average concentrations of 4.2 mg/kg Tri+ PCB and 18 mg/kg $TPCB_{HE}$ (Figure A2-6a). However, these averages were greatly influenced by one sample, HR17-OU2-R4-060, which showed elevated concentrations of 33 mg/kg Tri+ PCB and 160 mg/kg $TPCB_{HE}$ (Figure A2-4b). This sample was not consistent with the other values detected in dredged areas. If this sample is excluded, the RSA-weighted average concentrations in Reach 4 would be 1.3 mg/kg Tri+ PCB and 4.0 mg/kg $TPCB_{HE}$, which is comparable to the results in Reach 3.

Overall, PCB concentrations in the dredged areas remained low, but RS 2 had slightly higher concentrations than RS 1 and RS 3.

4.1.3 Spatial Distribution of PCB Concentrations in Recoverable Sediments for Non-Dredged Areas

The spatial distribution of sediment PCB concentrations in non-dredged areas is provided in Figure A2-5, Figure A2-6b, and Table A2-5.

In the non-dredged areas, sediment Tri+ PCB concentrations remained below the ROD-specified surface sediment dredging criteria, with only six samples (four in RS1, two in RS 2) out of a total of 1,647 samples exceeding the criteria (Figure A2-5). RS 2 had the highest Tri+ PCB and $TPCB_{HE}$ concentrations, followed by RS 1, and while RS 3 had the lowest (Figure A2-5a). When examining the 2021 RSA-weighted average concentrations provided in Table A2-5 and Figure A2-6b, the non-dredged areas in RS 1, RS 2 and RS 3 had RSA-weighted average Tri+ PCB concentrations of 1.9 mg/kg, 2.0 mg/kg, and 0.63 mg/kg, respectively; the RSA-weighted average $TPCB_{HE}$ concentrations were 6.4 mg/kg, 4.6 mg/kg and 1.4 mg/kg in RS 1, RS 2, and RS 3, respectively. The higher average PCB concentrations in RS 1 in 2021 were due to one sample with high PCB concentrations (43 mg/kg Tri+ PCB and 316 mg/kg $TPCB_{HE}$ [17]) that, if excluded, would bring the 2021 RSA-weighted average to 1.5 mg/kg Tri+ PCB and 3.5 mg/kg $TPCB_{HE}$.

At the reach scale, the concentrations of Tri+ PCB and $TPCB_{HE}$ increased from Reach 8 to Reach 7, then decreased from Reach 7 to Reach 5. Downstream of Reach 5, the concentrations in Reaches 4 and 3 were comparable to Reach 5, while the concentrations Reaches 2 and 1 were lower (Figure A2-5b). When examining the RSA-weighted average concentrations in Table A2-5 and Figure A2-6b, Reaches 7, 4, and 3 had comparatively higher average concentrations than their adjacent reaches. This is likely due to a few elevated concentrations reported in these reaches. These elevated concentrations in Reaches 7, 4, and 3, where the three areas of interest are located, were previously discussed in EPA's *Technical Memorandum* (EPA, 2019b). The PCB concentrations in the 2021 samples from these reaches were similar to those in the 2016/2017 samples (Figure A2-5b). Ongoing monitoring will track changes in PCB concentrations in these three reaches and areas of interest over time.

Overall, sediment Tri+ PCB concentrations in non-dredged areas were mostly below the ROD-specified surface sediment dredging criteria, with slightly higher concentrations observed in RS 2.

Comparison of PCB Concentrations between Silt and Non-Silt Areas

Figure A2-7 compares the Tri+ PCB and $TPCB_{HE}$ concentrations between silt and non-silt areas in the non-dredged areas. This comparison was performed by river section and monitoring period. The analysis shows that the silt area average PCB concentrations (represented by blue points) were either lower or comparable to the non-silt area data (represented by red points), with overlapping 95-percent confidence intervals, except for Tri+ PCB in RS 2 in 2021. These findings suggest that

[17] This sample result is substantially higher than the next highest concentration, *i.e.,* 5.3 mg/kg Tri+ PCB and 18 mg/kg TPCB, reported in non-dredged areas of RS 1 in 2021.

there is no significant difference in Tri+ PCB and $TPCB_{HE}$ concentrations between the silt and non-silt areas, except for the higher Tri+ PCB concentration in non-silt areas of RS 2 in 2021 (i.e., 95-percent confidence intervals do not overlap).

4.1.4 Spatial Distribution of PCB Concentrations in Recoverable Sediments for Combined Dredged and Non-Dredged Areas

Similar to the discussion of recoverable sediments in dredged and non-dredged areas, Figure A2-6c and Table A2-5 show the RSA-weighted average Tri+ PCB and $TPCB_{HE}$ concentrations by river section and by reach for the combined dredged and non-dredged areas. These data show similar spatial patterns as those observed in the non-dredged areas. At the river section scale, RS 2 had the highest concentrations, followed by RS 1 and then RS 3. The 2021 RSA-weighted average Tri+ PCB concentrations were 1.1 mg/kg, 1.9 mg/kg, and 0.64 mg/kg in RS 1, RS 2, and RS 3, respectively; the 2021 RSA-weighted average $TPCB_{HE}$ concentrations were 3.4 mg/kg, 4.5 mg/kg and 1.4 mg/kg in RS 1, RS 2, and RS 3, respectively. At the reach scale, concentrations increased from Reach 8 to Reach 7, then generally decreased from Reach 7 to Reach 1 (i.e., from upstream to downstream). Reaches 7, 4, and 3 had comparatively higher average concentrations than their adjacent reaches.

4.1.5 Comparison of PCB Concentrations between Dredged and Non-Dredged Areas

Figure A2-8 compares the distribution of Tri+ PCB and $TPCB_{HE}$ concentrations between dredged and non-dredged areas. In RS 1 and RS 2, the cumulative distribution curves of non-dredged area data (blue dots) were well separated from and located to the right of the curve representing dredged area data (orange dots), indicating that concentrations in non-dredged areas were higher than in dredged areas. These differences were statistically significant with p-values less than 0.05, as suggested by the two-sample Wilcoxon rank sum test.

In RS 3, the cumulative distribution curves of non-dredged area data were close to the curve representing dredged area data, indicating that concentrations in non-dredged areas were comparable to those in dredged areas. This similarity of concentrations between the two areas in RS 3 was further supported by the two-sample Wilcoxon rank sum test, where no statistically significant difference was observed for $TPCB_{HE}$ in both years and for Tri+ PCB in 2021 (p-values greater than 0.05). Tri+ PCB in 2016/2017 was the only dataset where non-dredged areas concentrations were statistically higher than dredged area concentrations in RS 3 (p-value< 0.05).

The spacing between the two cumulative distribution curves on the plots indicates that the difference in PCB concentrations between the two areas was largest in RS 1, followed by RS 2, and the smallest in RS 3. In 2016/2017, median Tri+ PCB concentrations in non-dredged areas were about a factor of 5.3, 3.8, and 1.5 of those in dredged areas in RS 1, RS 2, and RS 3, respectively (Figure A2-8a). Over time, the difference decreased. In 2021, median Tri+ PCB concentrations in non-dredged areas were about a factor of 3.4, 2.5, and 1.0 of those in dredged

areas in RS 1, RS 2, and RS 3, respectively (Figure A2-8a). This temporal change suggests the redistribution of remaining contamination from non-dredged areas to dredged areas.

4.1.6 Spatial Distribution of RWA-Weighted Average PCB Concentrations Across UHR

RWA-weighted average concentrations were calculated to account for bedrock and non-recoverable areas, providing a more representative measure of fish exposure conditions than RSA-weighted averages.

The RWA-weighted average Tri+ PCB and $TPCB_{HE}$ concentrations by river section and by reach for the two monitoring periods are presented in Table A2-5 and Figure A2-9. The results show similar spatial patterns for Tri+ PCB and $TPCB_{HE}$, which were also consistent between the two monitoring periods. At the river section scale, RS 2 had the highest concentrations, followed by RS 1 and then RS 3. In 2021, RWA-weighted average concentrations for Tri+ PCB were 0.99 mg/kg, 1.5 mg/kg, and 0.44 mg/kg in RS 1, RS 2, and RS 3, respectively (Table A2-5a). The relative errors on these averages, derived from Equation 3, were 39 percent, 19 percent, and 19 percent in RS 1, RS 2 and RS 3, respectively. The high relative error in RS 1 was due to one non-dredged area sample containing 43 mg/kg Tri+ PCB, as discussed in Section 4.1.3. Excluding this sample reduced the relative error in RS 1 to 16 percent. Overall, the results suggest that the relative errors on the RWA-weighted averages meet the design criterion of 25 percent.

At the reach scale, the RWA-weighted average Tri+ PCB concentrations in 2021 increased from Reach 8 (about 0.99 mg/kg) to Reach 7 (about 1.6 mg/kg), followed by a general decrease from Reach 7 to Reach 1. Reach 2 and Reach 1 had the lowest RWA-weighted average concentrations, at about 0.1 mg/kg and 0.2 mg/kg, respectively.

Overall, RWA-weighted average concentrations varied by a factor of three across the three river sections and by an order of magnitude across the eight reaches. Tri+ PCB and $TPCB_{HE}$ exhibited a similar spatial pattern, and the highest Tri+ PCB and $TPCB_{HE}$ concentrations were found in Reach 7.

4.2 Temporal Change of PCB Concentrations in Surface Sediments between 2016/2017 and 2021

The temporal change of sediment PCB concentrations were explored by evaluating the ratio of geometric mean from 2021 to 2016/2017 data and RWA-weighted average concentrations. Figures A2-10a and A2-10b display the ratio of geometric means from 2021 to 2016/2017 in dredged and non-dredged areas, respectively. Table A2-5 and Figure A2-9 provide a comparison of RWA-weighted average concentrations and 95-percent confidence limits between the two monitoring events.

4.2.1 Temporal Change of PCB Concentrations in Recoverable Sediments in Dredged Areas

Sediment PCB concentrations in dredged areas increased from 2016/2017 to 2021 across all three river sections (Figure A2-10a, left panel). On the geometric mean basis, Tri+ PCB concentrations increased by approximately 30 percent in RS 1, 60 percent in RS 2, and 30 percent in RS 3. $TPCB_{HE}$ concentrations increased by approximately 70 percent in RS 1, 70 percent in RS 2, and 30 percent in RS 3. The Tri+ PCB in RS 2, and $TPCB_{HE}$ in RS 1 and RS 2 showed statistically significant increases with a 95-percent LCL on the ratio above 1. However, changes in Tri+ PCB in RS 1 and RS 3, as well as $TPCB_{HE}$ in RS 3, were not statistically significant, as the 95-percent confidence interval on the ratio included 1.

At the reach scale (Figure A2-10a, right panel), the largest increase in Tri+ PCB and $TPCB_{HE}$ concentrations occurred in Reaches 7 and 3, and these increases were statistically significant with a 95-percent LCL on the ratio above 1. However, there were also high uncertainties in these reaches as shown by the large 95-percent confidence intervals. Although Tri+ PCB and $TPCB_{HE}$ concentrations in Reaches 8, 6 and 5 also increased, the increases were not statistically significant, except for $TPCB_{HE}$ at Reach 8, as the 95-percent confidence interval on the ratio included 1. At Reach 4, the geometric mean Tri+ PCB and $TPCB_{HE}$ concentrations decreased from 2016/2017 to 2021, although the decrease was not statistically significant as the 95-percent confidence interval on the ratio included 1. This decrease was primarily due to the two unusually high values detected in 2016/2017 in this area (Figure A2-4b). Data for Reaches 2 and 1 were too limited to draw any meaningful conclusions, but the available data suggested similar concentrations between 2016/2017 and 2021 (Figure A2-4b and Figure A2-10a, right panel). Overall, the concentrations of PCBs were found to be increasing in the dredged areas of Reaches 8 to 5, whereas Reaches 4, 2, and 1 did not demonstrate similar increases. Reach 3 was an exception, as the concentrations increased significantly despite being a downstream reach. However, it also had the largest 95-percent confidence intervals.

The observation that the increases in PCB concentrations in dredged areas occurred mainly in the upstream reaches aligns with the fact that these reaches also exhibited elevated PCB concentrations in non-dredged areas, as discussed in Section 4.1.3. This suggests that the increasing concentrations of PCBs in dredged areas over time may be due to the resuspension of sediments from non-dredged areas and their subsequent deposition in the dredged areas. This conclusion is further supported by the narrowing of differences in sediment PCB concentrations between dredged and non-dredged areas from 2016/2017 to 2021 for all three river sections, as discussed in Section 4.1.5 and illustrated in Figure A2-8. This phenomenon is expected as dredged areas are typically located in depositional areas of the river, and over time, their concentrations would converge towards the concentrations in non-dredged areas due to continued accumulation of depositing solids.

4.2.2 Temporal Change of PCB Concentrations in Recoverable Sediments in Non-Dredged Areas

At the river section scale (Figure A2-10b, left panel), the ratios of geometric mean concentrations from 2021 to 2016/2017 show that there was no statistically significant reduction in Tri+ PCB and $TPCB_{HE}$ concentrations in non-dredged areas of RS 1 and RS 2 (i.e., 95-percent confidence intervals of the ratio covering a value of 1). On the other hand, a statistically significant decrease was observed in RS 3 (i.e., 95-percent UCL of the ratio was only slightly above 1).

At the reach scale (Figure A2-10b, right panel), the data show that the decrease in PCB concentrations in RS 3 was due to the reduction in Reach 5. However, there were no statistically significant changes in PCB concentrations observed in any other reaches (i.e., 95-percent confidence intervals of the ratio covering a value of 1).

The lack of a statistically significant reduction in sediment concentrations in RS 1 and RS 2 is expected, given that the number of samples was not designed to detect the small changes in concentrations over the five-year period. Assuming a 5-percent annual rate of decline, the expected change in concentrations over a five-year period would be 22 percent, and over a 10-year period, it would be 39 percent. Based on a power analysis using the sample sizes and standard deviation from the existing 2016/2017 and 2021 Tri+ PCB data, the smallest change that can be detected is 40 percent in RS 1, 26 percent in RS 2, and 18 percent in RS 3, respectively, with 95-percent confidence and 80-percent power. At RS 3, because the expected change of 22 percent over the five-year period is larger than the smallest change that can be detected with the current data (18 percent), the sample size in RS 3 is adequate as of five years. However, at RS 2, the current data is only able to detect a change that is 26 percent or greater. Because this change is greater than the expected change of 22 percent in five years, but lower than the expected change of 39 percent in 10 years, RS 2 data are not sufficient to detect the changes in five years, but would be able to in 10 years. Similarly, at RS 1, the current data is only able to detect a change that is 40 percent or greater. As this change is greater than the expected change of 22 percent in five years, but comparable to the expected change of 39 percent in 10 years, it is expected that RS 1 data would be adequate at the end of 10 years to detect the expected change of 39 percent. These results indicate that 10 years of sediment monitoring data would be required to detect the expected change of 39 percent with the number of samples collected in RS 1 and RS 2.

4.2.3 Temporal Change of RWA-weighted Average PCB Concentrations

The RWA-weighted average concentration is a measure of the exposure condition for the entire area. Because all post-dredging sampling programs are designed to provide an unbiased estimate of average concentration, by comparing changes in RWA-weighted average concentrations between 2016/2017 and 2021, the progress of natural recovery can be assessed. As summarized in Table A2-5 and Figure A2-9, the RWA-weighted average PCB concentrations in RS 1 and RS 2 in 2021 were similar to those in 2016/2017, with overlapping 95-percent confidence intervals.

However, in RS 3, the RWA-weighted average Tri+ PCB concentration decreased from 0.57 mg/kg in 2016/2017 to 0.44 mg/kg in 2021; and the RWA-weighted average $TPCB_{HE}$ concentration decreased from 1.2 mg/kg in 2016/2017 to 0.96 mg/kg in 2021.

At the reach scale, it was observed that Reach 5 exhibited a significant decrease in RWA-weighted average Tri+ PCB and $TPCB_{HE}$ concentrations from 2016/2017 to 2021, as indicated by the non-overlapping 95-percent confidence intervals. However, for other reaches, there were no statistically significant changes in terms of RWA-weighted average concentrations as their 95-percent confidence intervals overlapped. This finding aligns with the one observed in non-dredged areas where a statistically significant reduction was only evident in Reach 5 (Figure A2-10b).

Overall, the largest reduction in sediment PCB concentrations from 2016/2017 to 2021 was measured in non-dredged areas in RS 3, particularly in Reach 5. As dredged areas only represent approximately 3 percent of the total area in RS 3 and 4 percent in Reach 5, the reduction in non-dredged areas led to an overall decrease in terms of RWA-weighted average concentration in RS 3 and Reach 5. For this evaluation, data from dredged areas were analyzed separately from those in non-dredged areas to understand the differences in temporal changes of PCB concentrations between the two areas. However, the sediment program was not designed to detect the temporal changes at such a granular level, but rather on an entire river section basis. When additional data become available, a regression model can be developed to calculate the PCB trend on a river section scale, while accounting for the spatial differences in recovery rates within that river section.

4.3 Areas of Interest

In EPA's *Technical Memorandum* (EPA, 2019b), three areas of interest were identified based on the surface sediment Tri+ PCB concentrations collected during 2016 and 2017:

(1) Near Galusha Island between RM 188 and 187 in RS 2/Reach 7

(2) Near Upper Mechanicville Dam, north of RM 166 near CU-92 in RS 3/Reach 4

(3) Near Lower Mechanicville Dam, between RM 164 and 163, near CU-96 in RS 3/Reach 3

The purpose of this section is to evaluate the Tri+ PCB concentrations in the 2021 samples collected near the three areas of interest and to determine if there have been any changes in the spatial extent of these areas. Figures A2-11a through A2-11c show the three areas of interest, derived from the 2016/2017 Tri+ PCB data, along with the individual sample results collected in 2016/2017 and 2021. On these plots, the areas of interest were identified by locations that had comparatively elevated concentrations (tagged with purple check marks) and their spatial extents were represented by the purple polygons. Each of these three areas of interest is described below in terms of the range of Tri+ PCB concentrations and their comparison to the ROD-specified surface sediment dredging criteria for Tri+ PCB—that is, 10 mg/kg in RS 1, and 30 mg/kg in RS 2 and RS 3 (EPA, 2002).

In the first area of interest near Galusha Island, a cluster of 20 locations were identified as comparatively elevated locations based on the 2016/2017 Tri+ PCB data (Figure A2-11a). Out of these 20 locations, two locations had Tri+ PCB concentrations above 30 mg/kg (at 42 and 43 mg/kg), while the rest had Tri+ PCB concentrations below 10 mg/kg. The two locations with concentrations above 30 mg/kg are in non-dredged areas and are close to the island's shoreline, which could have presented access challenges during dredging. In 2021, 15 samples were collected within 50 feet of the area of interest boundary. Out of the 15 samples, 10 (or 67 percent) had Tri+ PCB concentrations greater than 3 mg/kg (shown as large yellow triangles on the map), with a maximum concentration of 8 mg/kg. The average Tri+ PCB concentrations in these 15 samples was 3.5 mg/kg, which is lower than the average of 8.1 mg/kg observed in 2016/2017, but higher than the overall average of 1.2 mg/kg across the UHR in 2021 (Figure A2-3). This comparison indicates that this area still contains relatively higher concentrations than other areas of the UHR, but the recent data from 2021 were all below the RS 1 dredging criterion of 10 mg/kg and exhibited a decrease in Tri+ PCB concentrations.

In the second area of interest near the Upper Mechanicville Dam, the geostatistical tool identified a cluster of six locations with comparatively elevated Tri+ PCB concentrations based on the 2016/2017 dataset (Figure A2-11b). However, upon closer examination, it was found that the cluster was influenced by only one sample in the dredged area (CU-92), which had a Tri+ PCB concentration of 33 mg/kg. The other five samples in this cluster had concentrations below 3 mg/kg. In 2021, five samples were collected within 50 feet of the area of interest boundary (Figure A2-11b), with Tri+ PCB concentrations ranging from 0.44 mg/kg to 3.7 mg/kg. The average Tri+ PCB concentration from these five samples in 2021 was 1.7 mg/kg, which is lower than the average of 6.4 mg/kg reported in the 2016/2017 samples in this area. It should be noted that one sample from 2021—OCU-RCH4-6766-P039, located about 300 feet north of the area of interest boundary— contained 30 mg/kg Tri+ PCB, which was similar to the maximum concentration of 33 mg/kg in the 2016/2017 samples. However, both were isolated locations surrounded by low concentrations. The data revealed that this area of interest is driven by one isolated location with high Tri+ PCB concentration and the average Tri+ PCB concentration within this area has declined recently.

In the third area of interest, which is situated about 600 feet north of the Lower Mechanicville Dam, a cluster of seven locations with comparatively elevated Tri+ PCB concentrations was identified by the geostatistical tool using data from the 2016/2017 dataset (Figure A2-11c). This cluster was driven by two non-dredged area samples with high Tri+ PCB concentrations (18 and 22 mg/kg). In this cluster, one other location had a Tri+ PCB concentration of 9.9 mg/kg, while the remaining four locations had Tri+ PCB concentrations below 1 mg/kg. In 2021, four samples were collected within 50 feet of the area of interest boundary (Figure A2-11c). One sample had a Tri+ PCB concentration of 13 mg/kg, and the other three had concentrations below 3 mg/kg. The 2021 location with the highest Tri+ PCB concentration (13 mg/kg) was adjacent to the two 2016/2017 locations with high Tri+ PCB concentrations (18 mg/kg and 22 mg/kg). The average

Tri+ PCB concentration in the four 2021 samples was 4.0 mg/kg, which is lower than the average of 7.3 mg/kg from the seven 2016/2017 samples in this area. Although this area of interest still has elevated PCB concentrations, the average Tri+ PCB concentration has decreased recently. The spatial extent of this area appears to be relatively small, approximately 3 acres (located between the southern end of Quack Island [RM 163.6] and the Lower Mechanicville Dam [RM 163.4]).

To summarize, the 2021 results verified the comparatively elevated Tri+ PCB concentrations in the three areas of interest, but their spatial extents did not appear to increase between 2016/2017 and 2021. None of the 2021 samples taken within these areas had Tri+ PCB concentrations exceeding the RS 2 and RS 3 dredging criterion of 30 mg/kg. The average Tri+ PCB concentrations in all three areas have decreased based on the 2021 data. The first area of interest has moderately high concentrations (3 mg/kg to 10 mg/kg Tri+ PCB) over a relatively larger area (approximately 21 acres) compared to the other two areas of interest. The second area of interest only exhibits localized contamination, while the third area of interest contains the highest level of contamination (greater than 10 mg/kg Tri+ PCB) over a small area (<3 acres).

5 CONCLUSIONS

Surface sediments (from the 0 to 2-inch interval) in the main stem of UHR are monitored every five years to track the decline of PCB concentrations over time. This appendix presented the results of statistical and comparative evaluations of PCB concentrations in surface sediment samples collected during the 2016/2017 and 2021 sampling events. A total of 1,292 and 742 sediment samples were collected from both the dredged and non-dredged areas in 2016/2017 and 2021, respectively. All samples were analyzed for PCB Aroclors using M8082, and a subset sample was analyzed for PCB congeners using M1668. In this FYR, Tri+ PCB concentrations were estimated from Aroclor data using Equation 1 developed by GE in 2011.

$$\text{Tri+ PCB} = 0.13 \times \text{Aroclor 1221} + 0.89 \times (\text{Aroclor 1242} + \text{Aroclor 1254}) \qquad \text{(Eq. 1)}$$

TPCB concentrations were reported on a homologue equivalent basis ($TPCB_{HE}$), which were calculated by multiplying the Aroclor-based TPCB results with a factor of 1.2.

In 2016/2017, the Tri+ PCB concentrations in sediments ranged from non-detected to 43 mg/kg, and in 2021, they ranged from 0.01 mg/kg to 43 mg/kg. About 99 percent of sediment samples contained Tri+ PCB levels below the most stringent ROD-specified surface sediment dredging criterion of 10 mg/kg, and 70 percent contained less than 1 mg/kg Tri+ PCB (the target post-dredging residual sediment PCB concentration). The RWA-weighted average Tri+ PCB concentrations were found to be between 0.44 mg/kg to 1.5 mg/kg across the three river sections. The RWA-weighted average $TPCB_{HE}$ concentrations ranged from 0.96 mg/kg to 4.1 mg/kg across the three river sections.

In the dredged areas, Tri+ PCB concentrations remained low. In 2021, the RSA-weighted average concentrations of Tri+ PCB in RS 1, RS 2, and RS 3 were 0.59 mg/kg, 1.7 mg/kg, and 0.72 mg/kg, respectively. The concentrations of PCB generally increased from RS 1 to RS 2 and then gradually decreased through RS 3. Reaches 8 through 3 had relatively higher PCB concentrations compared to Reaches 2 and 1.

In the non-dredged areas, sediment Tri+ PCB concentrations remained below the ROD-specified surface sediment dredging criteria. Out of a total of 1,646 samples, only six samples (four in RS1, two in RS 2) exceeded the criteria. In 2021, the RSA-weighted average concentrations of Tri+ PCB in RS 1, RS 2, and RS 3 were 1.9 mg/kg, 2.0 mg/kg, and 0.63 mg/kg, respectively. RS 2 had the highest PCB concentrations, followed by RS 1, with the lowest in RS 3. Reaches 7, 4, and 3 had comparatively higher average concentrations than their adjacent reaches. PCB concentrations from the silt areas were found to be lower or comparable to those in non-silt areas.

As expected, temporal trend analysis of sediment PCB concentrations could not be performed in this FYR due to the amount of long-term data available and the program design. Instead, sediment PCB concentrations in 2021 were compared to those in 2016/2017 using the ratio of geometric means. The results showed that sediment PCB concentrations had slightly increased as expected

from 2016/2017 to 2021 in all three river sections in dredged areas, with the largest increase observed in RS 2. The increase in dredged areas are likely due to the redistribution of remaining contamination from non-dredged areas to dredged areas. In non-dredged areas, sediment PCB concentrations appear to remain unchanged in RS 1 and RS 2, but decreased from 2016/2017 to 2021 in RS 3, mainly due to the decrease in Reach 5. This decrease in concentrations in non-dredged areas of RS 3 was also reflected in the RWA-weighted average concentration data in RS 3, where Tri+ PCB concentration decreased from 0.57 mg/kg in 2016/2017 to 0.44 mg/kg in 2021; and $TPCB_{HE}$ concentration decreased from 1.2 mg/kg in 2016/2017 to 0.96 mg/kg in 2021.

The three areas of interest identified in the second FYR based on the 2016/2017 data were confirmed by the detection of comparably somewhat elevated concentrations in samples collected from these areas in 2021. However, the average Tri+ PCB concentrations in these areas has decreased from 2016/2017 to 2021. Additionally, there does not appear to be an increase in the spatial extent of these areas.

6 ABBREVIATIONS AND ACRONYMS

BCa	Bias Corrected and Accelerated
Be-7	Beryllium-7
CU	Certification Unit
DQO	Data Quality Objective
EPA	United States Environmental Protection Agency
FYR	Five-Year-Review
GE	General Electric Company
GEHR	GE Hudson River
GRTS	Generalized Random Tessellation Sampling
LCL	Lower Confidence Limit
mGBM	Modified Green Bay Method
mg/kg	milligram per kilogram
MNR	Monitored Natural Recovery
NYSDEC	New York State Department of Environmental Conservation
OM&M	Operations, Maintenance, and Monitoring
PCB	Polychlorinated Biphenyl
RAO	Remedial Action Objectives
RM	River Mile
RS	River Section
RSA	Recoverable-Sediment-Area
ROD	Record of Decision
RWA	River-Wide-Area
TCMX	2,4,5,6-Tetrachloro-Meta-Xylene
TOC	Total Organic Carbon
TPCB	Total PCBs
$TPCB_{Aroclor}$	TPCB calculated as sum of measured Aroclors
$TPCB_{congener}$	TPCB calculated as sum of measured 209 congeners
$TPCB_{HE}$	TPCB estimated as homologue equivalents by applying a conversion factor to $TPCB_{Aroclor}$

Tri+ PCB	Sum of all measured PCB congeners with three or more chlorine atoms per molecule
UCL	Upper Confidence Limit
UHR	Upper Hudson River

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APPENDIX 2
EVALUATION OF SURFACE SEDIMENT CONCENTRATIONS
Tables and Figures

Tables

Table A2-1
Sediment Sampling Programs Since the Completion of Dredging

Year	Sampled by	Sample Type	Design Basis	Sample Size		
				Dredged Area	Non-Dredged Area	Total
2016	EPA / GE	0-2 inch Surface Sediment	Simple Random Sampling (SRS)	0	214	214
2017	NYSDEC	0-2 inch Surface Sediment	Systematic Triangular Grid	241	837	1,078
2021	EPA / GE	0-2 inch Surface Sediment	Generalized Random Tessellation Sampling (GRTS) Algorithm	146	596	742

Note:
Sample counts only include locations in the main stem of Upper Hudson River; samples from land cut, backwater, and tributaries areas were excluded.

Table A2-2
Comparison of Number of Samples Collected in 2016, 2017 and 2021

Reach/ River Section		Dredged Area		Non-Dredged Area		Total	
		2017	2021	2016/2017	2021	2016/2017	2021
River Section	1	137	70	88	108	225	178
	2	57	30	170	135	227	165
	3	47	46	793	353	840	399
Reach	8	137	70	88	108	225	178
	7	28	15	89	80	117	95
	6	29	15	81	55	110	70
	5	18	12	266	88	284	100
	4	11	12	218	82	229	94
	3	12	12	103	68	115	80
	2	3	5	76	60	79	65
	1	3	5	130	55	133	60
UHR		241	146	1,051	596	1,292	742

Notes:

- Sample counts only include locations in the main stem of Upper Hudson River; samples from land cut, backwater, and tributaries areas were excluded.
- In 2021, three samples intended for dredged areas were actually collected from non-dredged areas; and nine samples intended for non-dredged areas were collected from dredged areas. Because these samples are generally located within a proximity of 10 feet from the dredged boundary, these samples were assigned the strata they were originally designed for.

Table A2-3
Analytical Program Summary

Sample Program	PCB Aroclor		PCB Congener		Total Organic Carbon	
	Analytical Method	**Laboratory**	**Analytical Method**	**Laboratory**	**Analytical Method**	**Laboratory**
2016 GE Surface Sediment Program	GEHR8082	Pace Analytical Services (Schenectady, NY)	1668C	SGS AXYS Analytical Services Ltd. (Sidney, British Columbia)	Lloyd Kahn Method	Pace Analytical Services (Schenectady, NY)
2017 NYSDEC Surface Sediment Program	GEHR8082	Pace Analytical Services (Minneapolis, MN)	1668A	Pace Analytical Services (Minneapolis, MN)	Lloyd Kahn Method	Pace Analytical Services (Minneapolis, MN)
2021 GE Surface Sediment Program	GEHR8082	Pace Analytical Services (Green Bay, WI)	1668C	Vista Analytical Laboratory (El Doraod Hills, CA)	Lloyd Kahn Method	Pace Analytical Services (Green Bay, WI)

Notes:
GEHR: GE Hudson River
Analysis of PCB congeners in 2016 was performed by EPA

Table A2-4
RWA-Weighted Average Calculation

Sediment category, i.e., area represented by:	Source of information used for the development of sediment areas	PCB concentration
1. Bedrock	GE's 2002-2003 side-scan sonar	Assigned 0.03 mg/kg, one-half the median reported limit for non-detect samples from 2016/2017[1]
2. Dredged areas with sampleable and inaccessible locations	Polygons associated with 2016/2017 sampleable and inaccessible locations in dredged area; inaccessible areas further refined considering available data (e.g., side-scan sonar results, previous accessibility, proximity to dams, and adjoining sediment types)	Average from sampled sediments in dredged area
3. Dredged areas with non-recoverable locations	Polygons associated with 2016/2017 non-recoverable locations in dredged area	Assigned 0.03 mg/kg, one-half the median reported limit for non-detect samples from 2016/2017[1]
4. Non-dredged sediment areas with sampleable and inaccessible locations	Polygons associated with 2016/2017 sampleable and inaccessible locations in non-dredged area; inaccessible areas further refined considering available data (e.g., side-scan sonar results, previous accessibility, proximity to dams, and adjoining sediment types)	Average from sampled sediments in non-dredged area
5. Non-dredged sediment areas with non-recoverable locations	Polygons associated with 2016/2017 non-recoverable locations in non-dredged area	Assigned 0.03 mg/kg, one-half the median reported limit for non-detect samples from 2016/2017[1]

Notes:
RWA: River-Wide-Area
1. One-half the median reporting limit for non-detect results is 0.03 mg/kg for Tri+ PCB and TPCB in 2016/2017 samples; there are no non-detect results in 2021 samples.

Table A2-5a

Tri+ PCB Area-Weighted Average Concentrations

River Section / Reach		Recoverable Sediments Dredged Areas				Recoverable Sediments Non-Dredged Areas				Recoverable Sediments Dredged and Non-dredged Areas Combined				River-Wide			
		2016/2017		2021		2016/2017		2021		2016/2017		2021		2016/2017		2021	
		RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RWA-Weighted Average	95% Confidence Limits	RWA-Weighted Average	95% Confidence Limits
River Section	1	0.62	0.46-0.82	0.59	0.44-0.78	1.9	1.4-2.5	1.9	1.3-3.0	1.1	0.89-1.4	1.1	0.85-1.5	1.0	0.80-1.2	0.99	0.77-1.4
	2	0.77	0.59-1.0	1.7	0.9-3.0	2.3	1.9-3.0	2.0	1.7-2.3	2.0	1.6-2.5	1.9	1.6-2.3	1.5	1.2-1.9	1.5	1.2-1.7
	3	1.1	0.46-2.1	0.72	0.43-1.3	0.81	0.7-0.97	0.63	0.54-0.76	0.82	0.71-0.98	0.64	0.55-0.76	0.57	0.50-0.68	0.44	0.38-0.53
Reach	8	0.62	0.46-0.82	0.59	0.44-0.78	1.9	1.4-2.5	1.9	1.3-3.0	1.1	0.89-1.4	1.1	0.85-1.5	1.0	0.80-1.2	0.99	0.77-1.4
	7	0.76	0.36-1.4	1.3	0.66-2.0	3.7	2.7-5.4	2.8	2.4-3.3	3.1	2.3-4.4	2.5	2.1-2.9	2.0	1.5-2.9	1.6	1.4-1.9
	6	0.78	0.60-0.98	1.9	0.73-3.8	1.5	1.1-2.0	1.5	1.1-1.9	1.3	1.1-1.7	1.6	1.2-2.1	1.1	0.89-1.4	1.3	0.99-1.8
	5	0.49	0.32-0.69	0.79	0.33-1.7	0.92	0.76-1.2	0.58	0.49-0.69	0.90	0.75-1.1	0.59	0.49-0.70	0.81	0.68-1.0	0.53	0.45-0.63
	4	4.2	0.44-12	0.75	0.51-1.0	0.72	0.62-0.86	1.1	0.65-2.2	0.92	0.67-1.4	1.1	0.66-2.1	0.65	0.48-0.96	0.80	0.47-1.5
	3	0.99	0.11-2.7	0.84	0.37-1.5	1.3	0.83-2.0	1.3	0.87-1.8	1.3	0.83-1.9	1.2	0.85-1.7	0.66	0.43-0.99	0.63	0.45-0.88
	2	0.17	0.065-0.35	0.11	0.052-0.19	0.33	0.25-0.41	0.32	0.19-0.62	0.32	0.25-0.4	0.32	0.19-0.60	0.12	0.096-0.14	0.12	0.078-0.20
	1	0.23	0.049-0.34	0.11	0.069-0.15	0.49	0.37-0.73	0.33	0.28-0.39	0.49	0.37-0.72	0.33	0.27-0.39	0.30	0.23-0.44	0.21	0.18-0.24

Notes:

- RSA: Recoverable-Sediments-Area
- RWA: River-Wide-Area
- Section 3.2.1 provides calculation procedures for area-weighted average concentrations and 95% confidence limits on the average.

Table A2-5b
$TPCB_{HE}$ Area-Weighted Average Concentrations

River Section / Reach		Recoverable Sediments Dredged Areas				Recoverable Sediments Non-Dredged Areas				Recoverable Sediments Dredged and Non-dredged Areas Combined				River-Wide			
		2016/2017		2021		2016/2017		2021		2016/2017		2021		2016/2017		2021	
		RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	RSA-Weighted Average	RSA-Weighted Average	95% Confidence Limits	RSA-Weighted Average	95% Confidence Limits	RWA-Weighted Average	95% Confidence Limits	RWA-Weighted Average	95% Confidence Limits
River Section/	1	1.2	0.95-1.6	1.4	1.0-1.8	4.4	3.2-5.9	6.4	3.1-15	2.5	2.0-3.1	3.4	2.0-6.7	2.2	1.8-2.8	3.0	1.8-6.0
	2	1.8	1.4-2.3	4.0	2.2-6.9	6.4	4.3-9.8	4.6	4.0-5.4	5.4	3.8-8.0	4.5	3.8-5.3	4.1	2.9-6.1	3.4	2.9-4.0
	3	3.6	1.1-8.7	1.5	0.94-2.6	1.7	1.4-2.1	1.4	1.1-1.8	1.8	1.5-2.2	1.4	1.2-1.8	1.2	1.0-1.5	0.96	0.80-1.2
Reach	8	1.2	0.95-1.6	1.4	1.0-1.8	4.4	3.2-5.9	6.4	3.1-15	2.5	2.0-3.1	3.4	2.0-6.7	2.2	1.8-2.8	3.0	1.8-6.0
	7	1.6	0.82-2.9	2.9	1.6-4.5	11	5.8-19	6.5	5.5-7.7	8.7	4.9-16	5.8	4.9-6.7	5.7	3.2-10	3.8	3.2-4.4
	6	1.9	1.5-2.3	4.6	1.9-8.9	3.8	2.7-5.6	3.4	2.6-4.4	3.4	2.5-4.8	3.7	2.8-4.9	2.8	2.1-4.0	3.1	2.3-4.1
	5	1.2	0.75-1.6	1.6	0.76-3.3	1.9	1.6-2.7	1.2	1.0-1.4	1.9	1.5-2.6	1.2	1.0-1.4	1.7	1.4-2.3	1.1	0.92-1.3
	4	18	1.1-59	1.7	1.2-2.3	1.6	1.3-2.1	3.0	1.5-6.9	2.5	1.5-4.7	2.9	1.5-6.6	1.8	1.1-3.3	2.1	1.0-4.6
	3	1.8	0.26-4.9	1.8	0.80-3.2	2.8	1.7-4.5	2.8	1.8-4.4	2.7	1.7-4.3	2.7	1.8-4.1	1.4	0.86-2.2	1.4	0.93-2.1
	2	0.30	0.11-0.62	0.21	0.098-0.37	0.57	0.45-0.70	0.68	0.38-1.4	0.56	0.44-0.69	0.67	0.38-1.4	0.19	0.15-0.23	0.22	0.13-0.43
	1	0.45	0.063-0.72	0.25	0.17-0.33	0.91	0.70-1.3	0.63	0.54-0.74	0.90	0.69-1.3	0.63	0.53-0.73	0.55	0.42-0.80	0.39	0.33-0.45

Notes:

• $TPCB_{HE}$: Represents homologue-equivalent TPCB concentrations, and calculated as 1.157*$TPCB_{Aroclor}$; Conversion factor of 1.157 is the geometric mean of the $TPCB_{Congener}$ to $TPCB_{Aroclor}$ ratios from matched pair samples analyzed in 2017 and 2021. See Section 3.1 and Attachment B for detail.
• RSA: Recoverable-Sediments-Area
• RWA: River-Wide-Area
• Section 3.2.1 provides calculation procedures for area-weighted average concentrations and 95% confidence limits on the average.

Figures

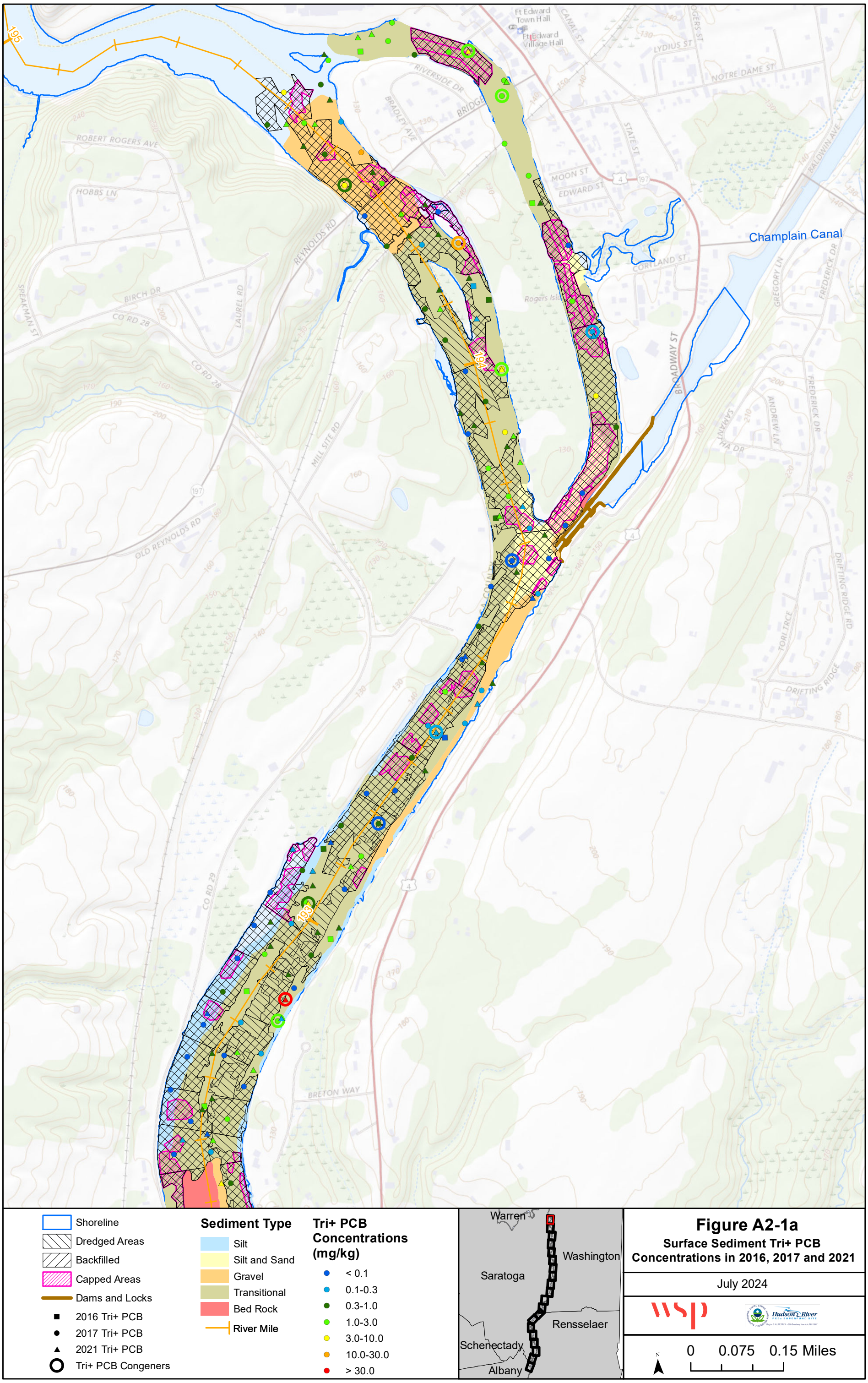

Figure A2-1a
Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021

July 2024

0 0.075 0.15 Miles

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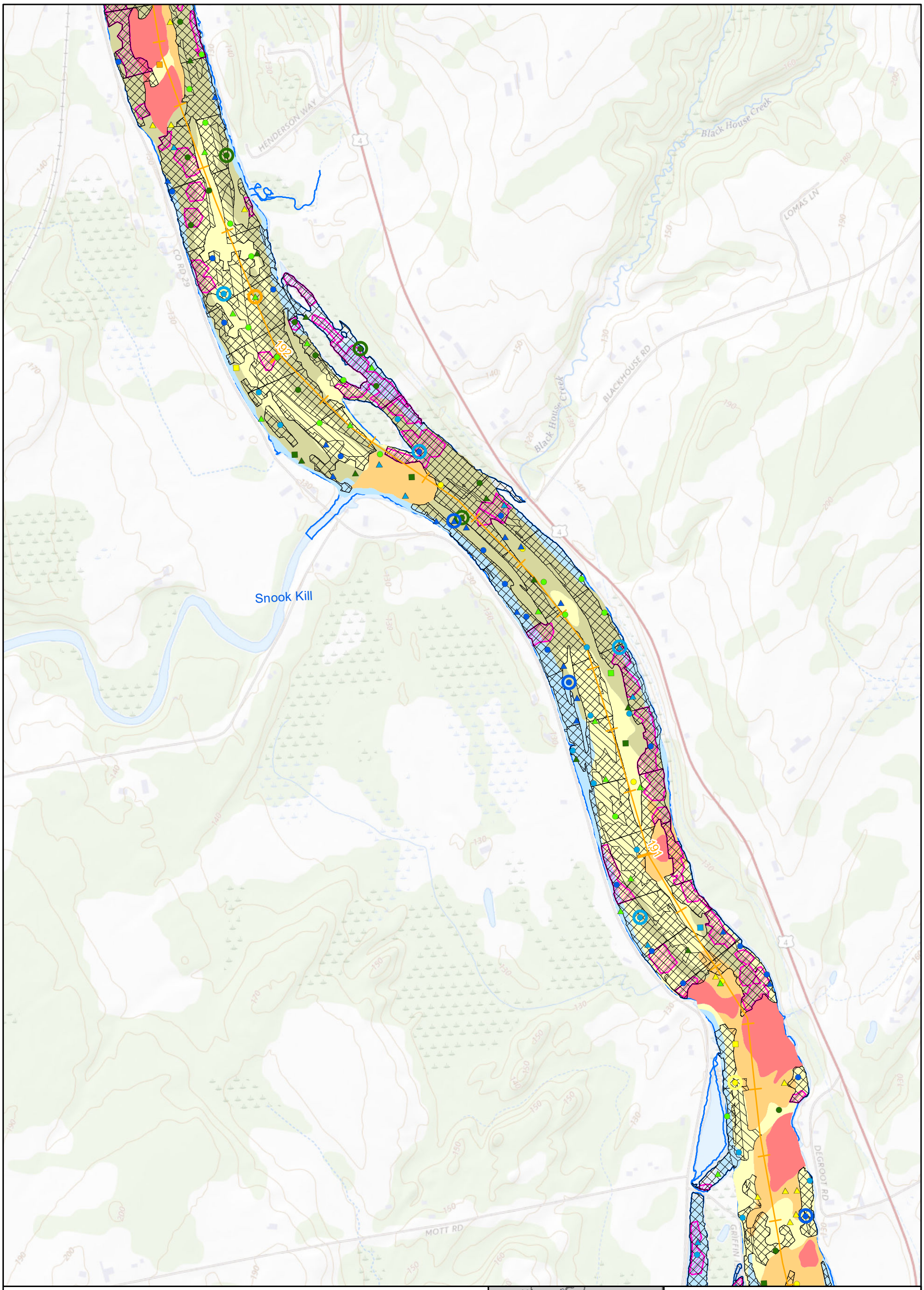

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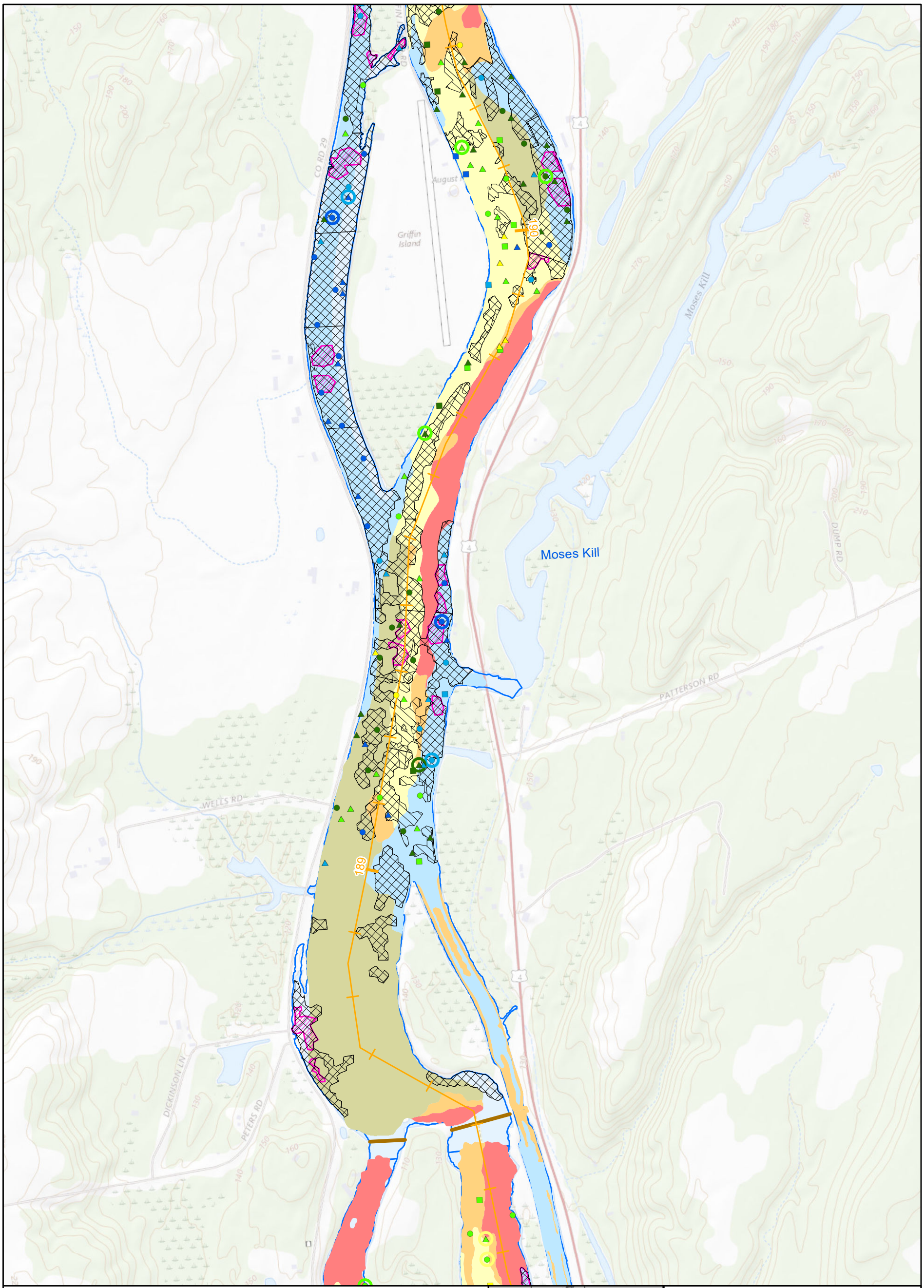

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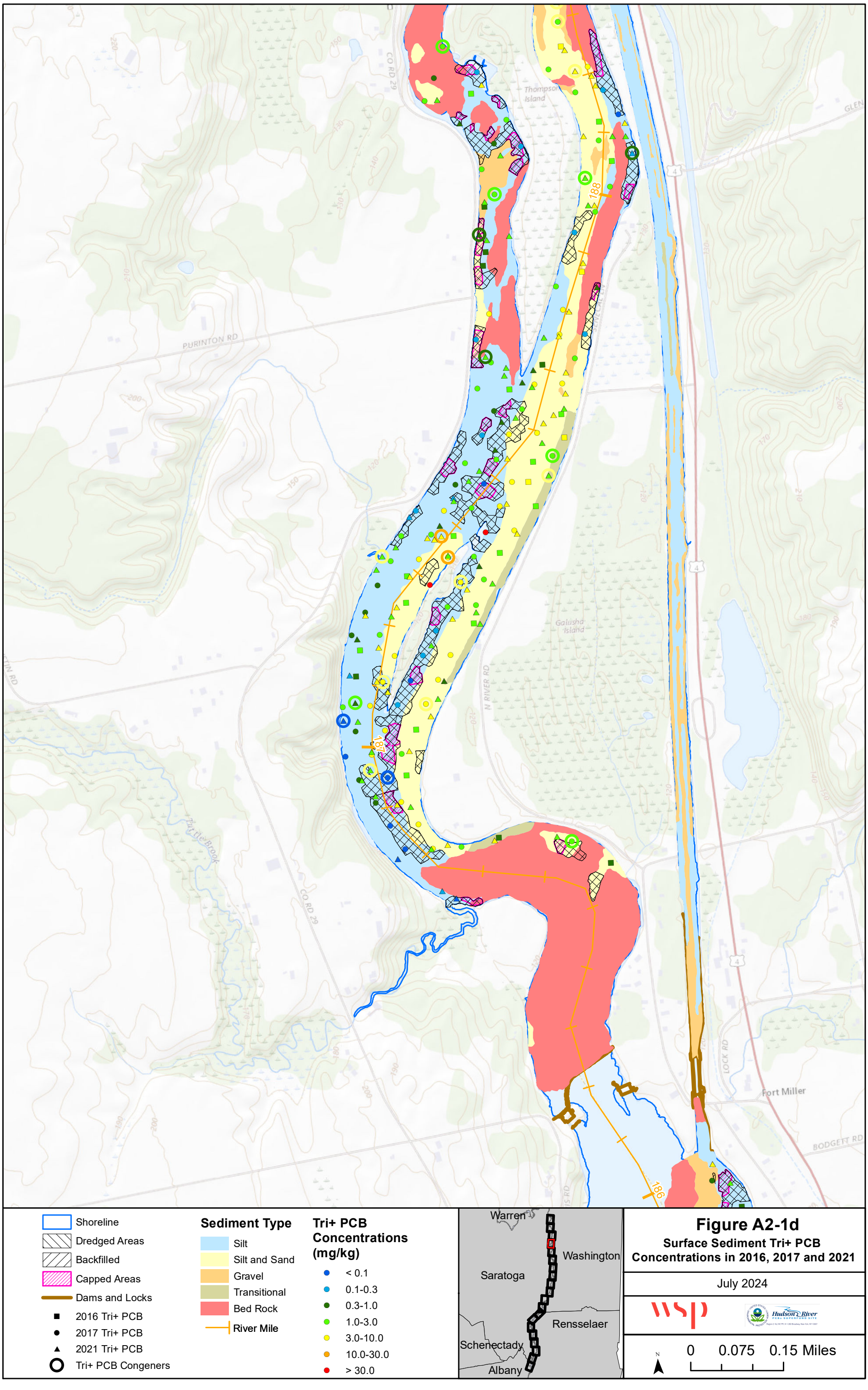
CO RD 29
Thompson Island
188
PURINTON RD
Galusha Island
N RIVER RD
187
Turtle Brook
LOCK RD
Fort Miller
BODGETT RD
186
Shoreline
Dredged Areas
Backfilled
Capped Areas
Dams and Locks
2016 Tri+ PCB
2017 Tri+ PCB
2021 Tri+ PCB
Tri+ PCB Congeners
Sediment Type
Silt
Silt and Sand
Gravel
Transitional
Bed Rock
River Mile
Tri+ PCB Concentrations (mg/kg)
< 0.1
0.1-0.3
0.3-1.0
1.0-3.0
3.0-10.0
10.0-30.0
> 30.0
Warren
Washington
Saratoga
Rensselaer
Schenectady
Albany
Figure A2-1d
Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021
July 2024
0 0.075 0.15 Miles
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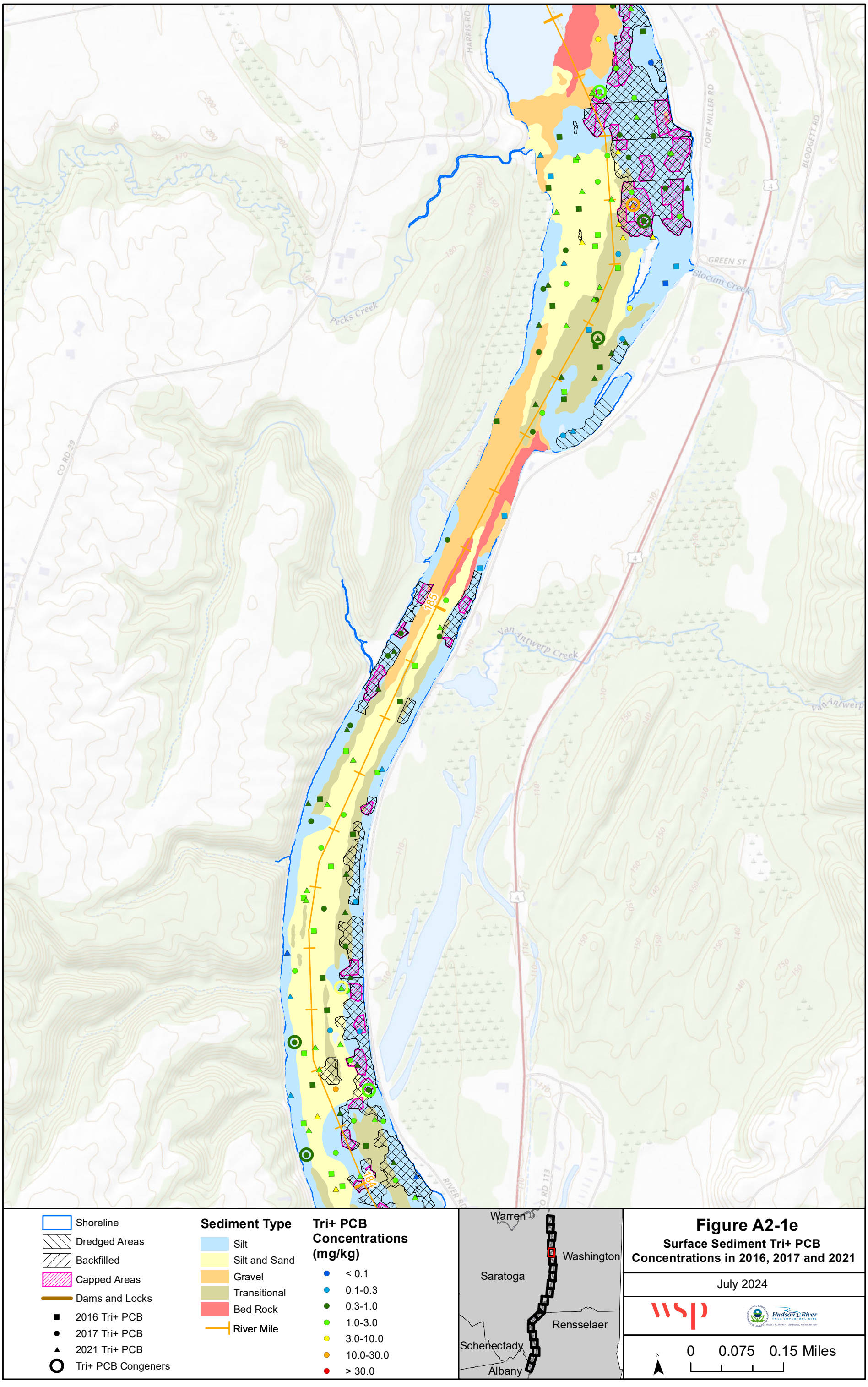
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FORT MILLER RD
BLODGETT RD
GREEN ST
Sloctum Creek
Pecks Creek
CO RD 29
185
Van Antwerp Creek
Van Antwerp
RIVER RD
CO RD 113
Shoreline
Dredged Areas
Backfilled
Capped Areas
Dams and Locks
2016 Tri+ PCB
2017 Tri+ PCB
2021 Tri+ PCB
Tri+ PCB Congeners
Sediment Type
Silt
Silt and Sand
Gravel
Transitional
Bed Rock
River Mile
Tri+ PCB Concentrations (mg/kg)
< 0.1
0.1-0.3
0.3-1.0
1.0-3.0
3.0-10.0
10.0-30.0
> 30.0
Warren
Washington
Saratoga
Rensselaer
Schenectady
Albany
Figure A2-1e
Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021
July 2024
0 0.075 0.15 Miles
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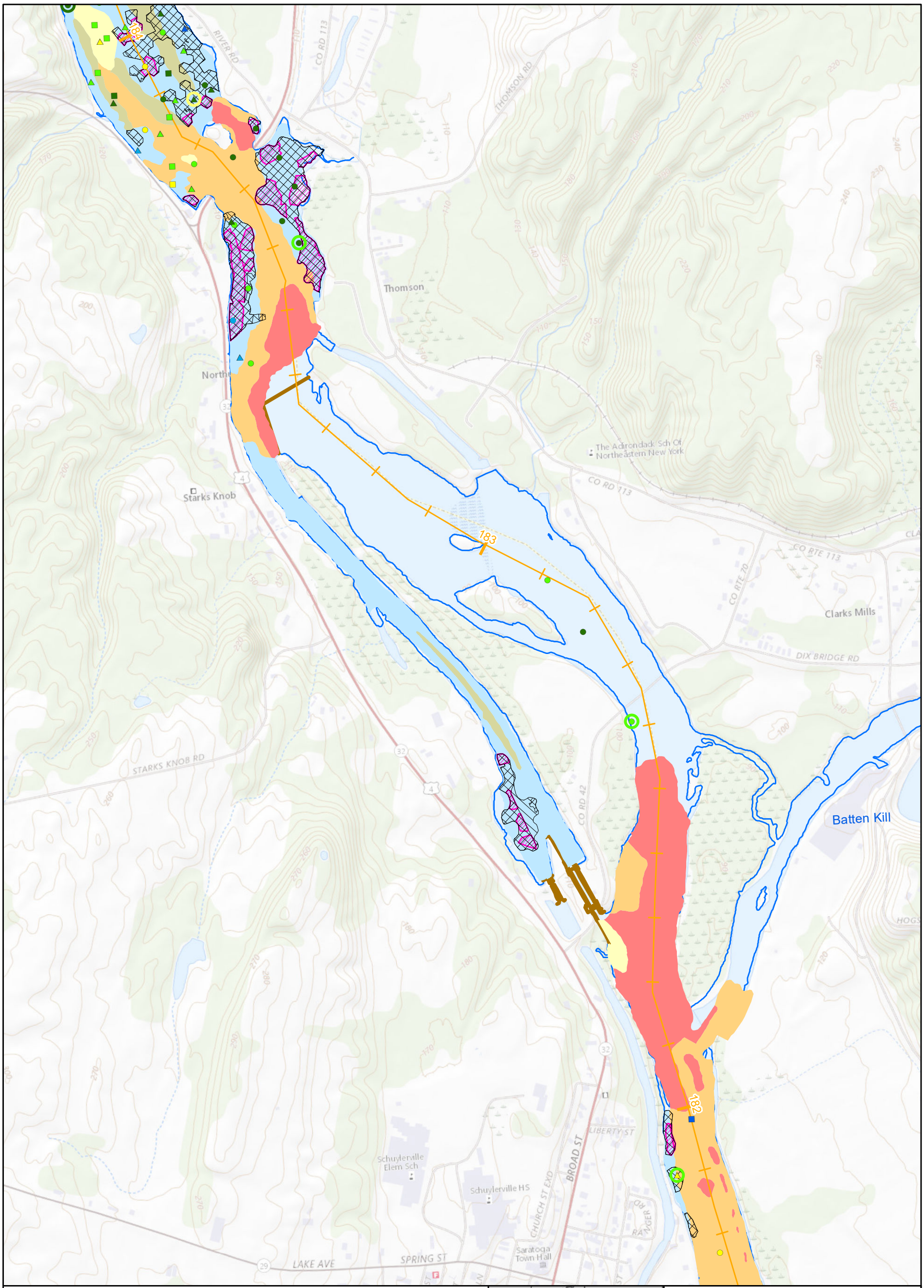

Figure A2-1f
Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021

July 2024

0 0.075 0.15 Miles

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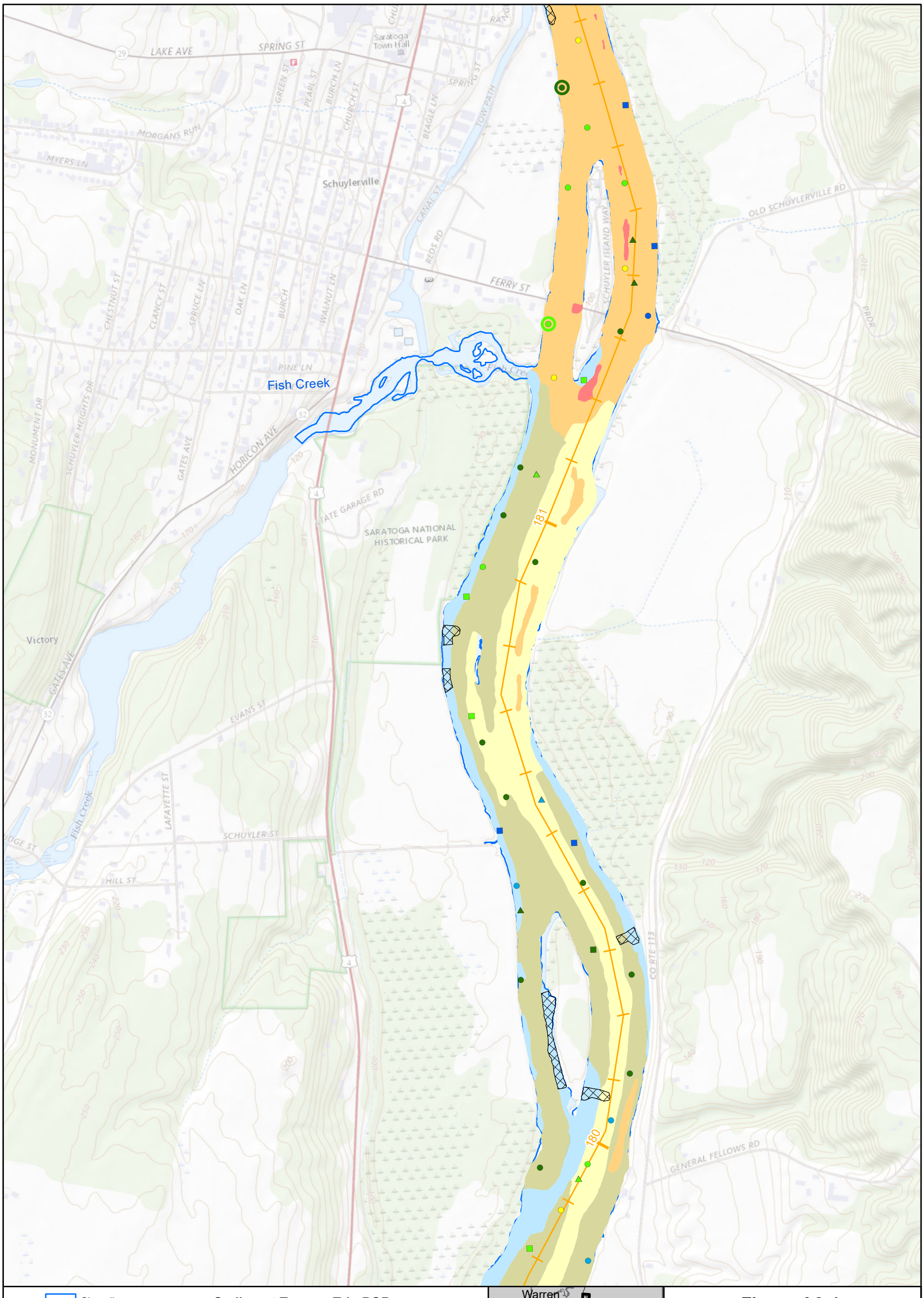

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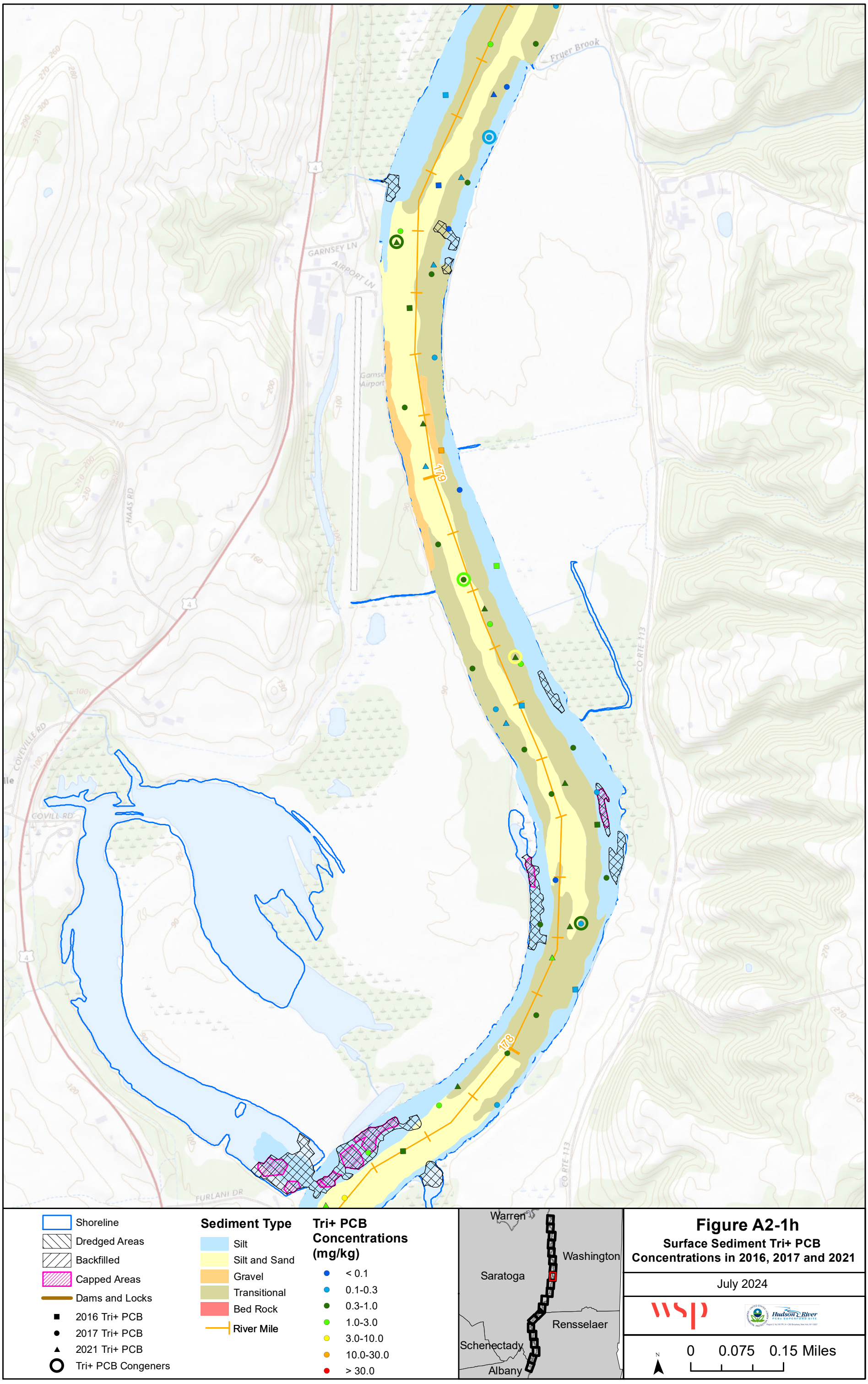

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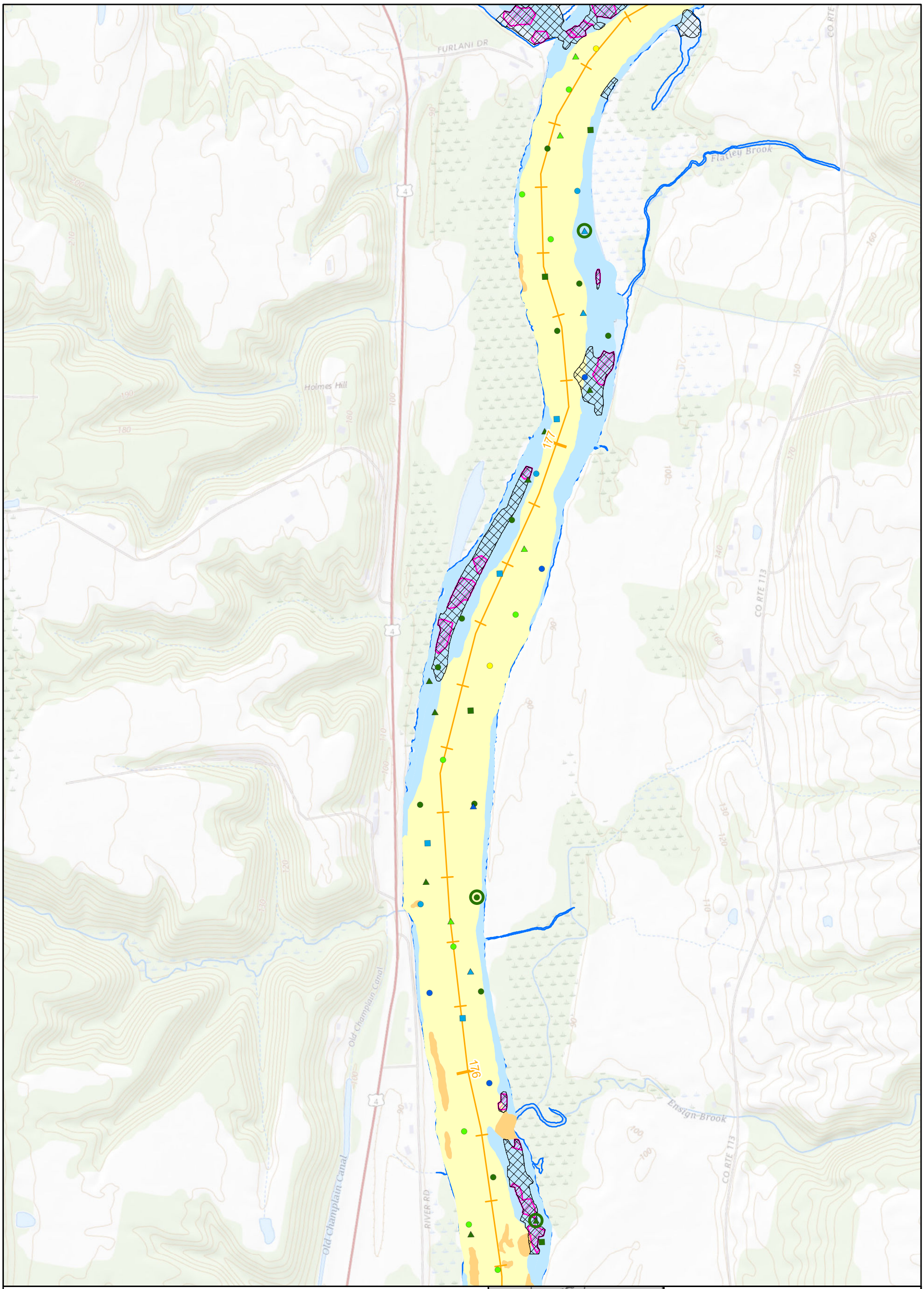

Figure A2-1i
Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021

July 2024

0 0.075 0.15 Miles

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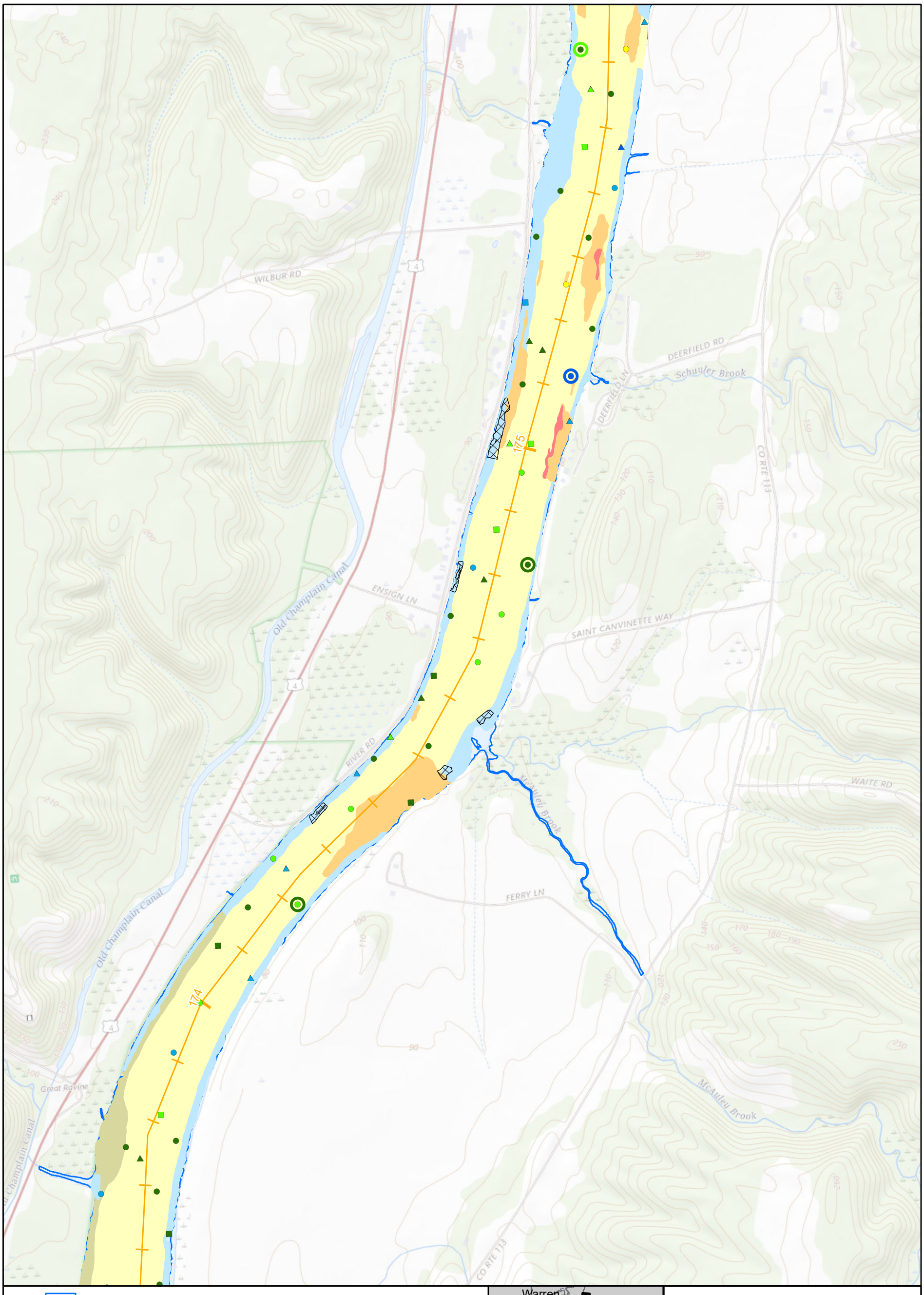

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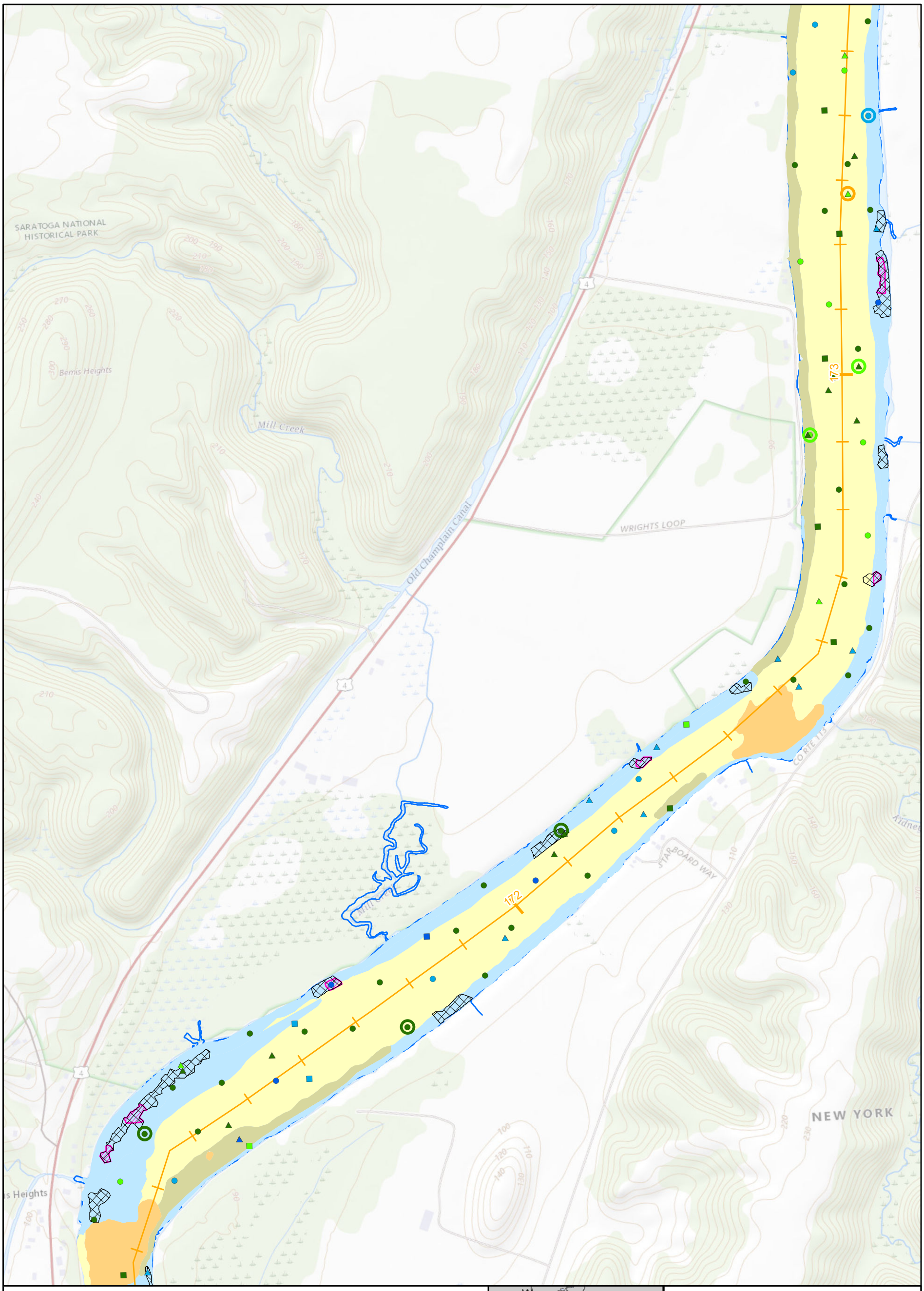

Figure A2-1k
Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021

July 2024

0 0.075 0.15 Miles

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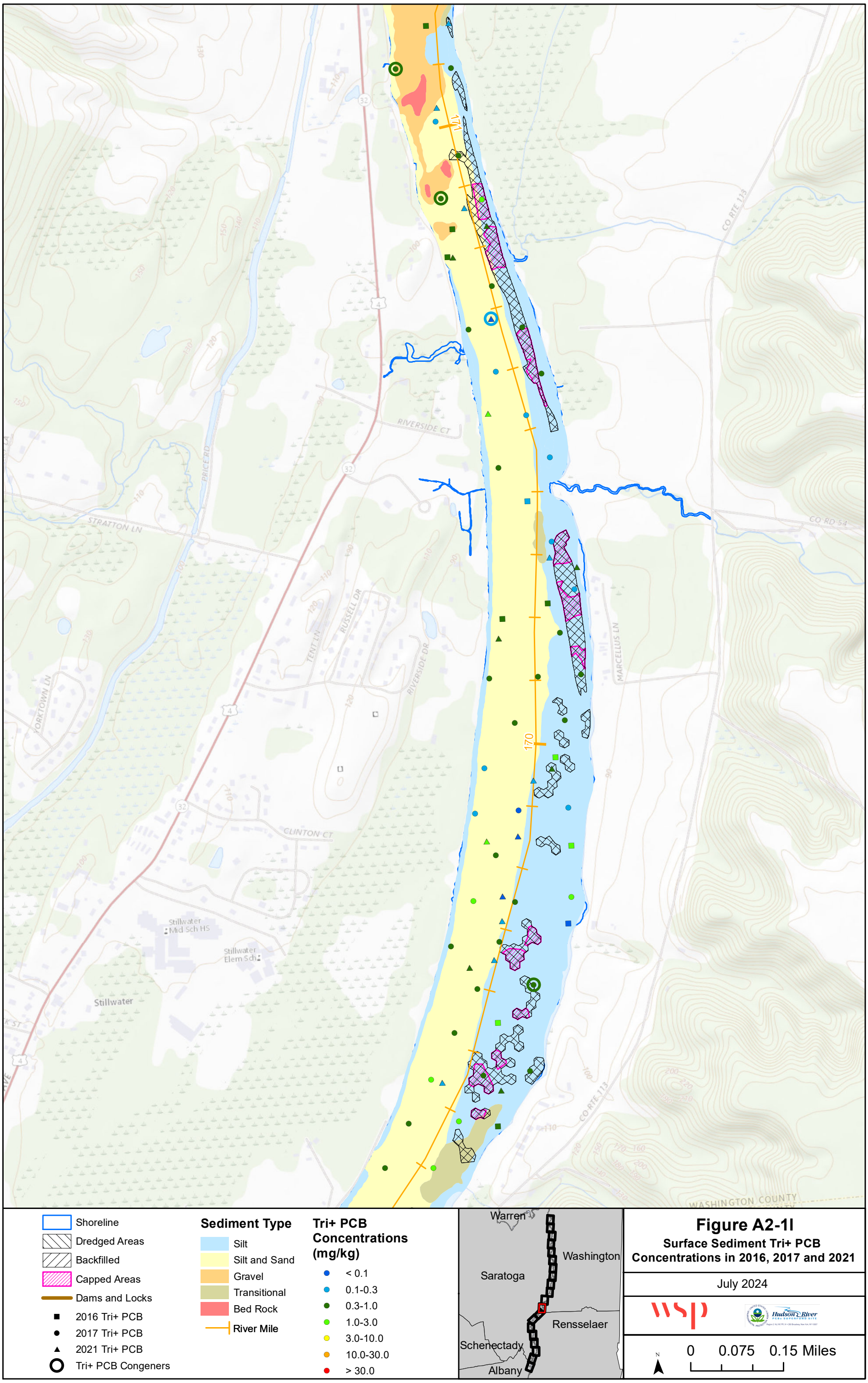

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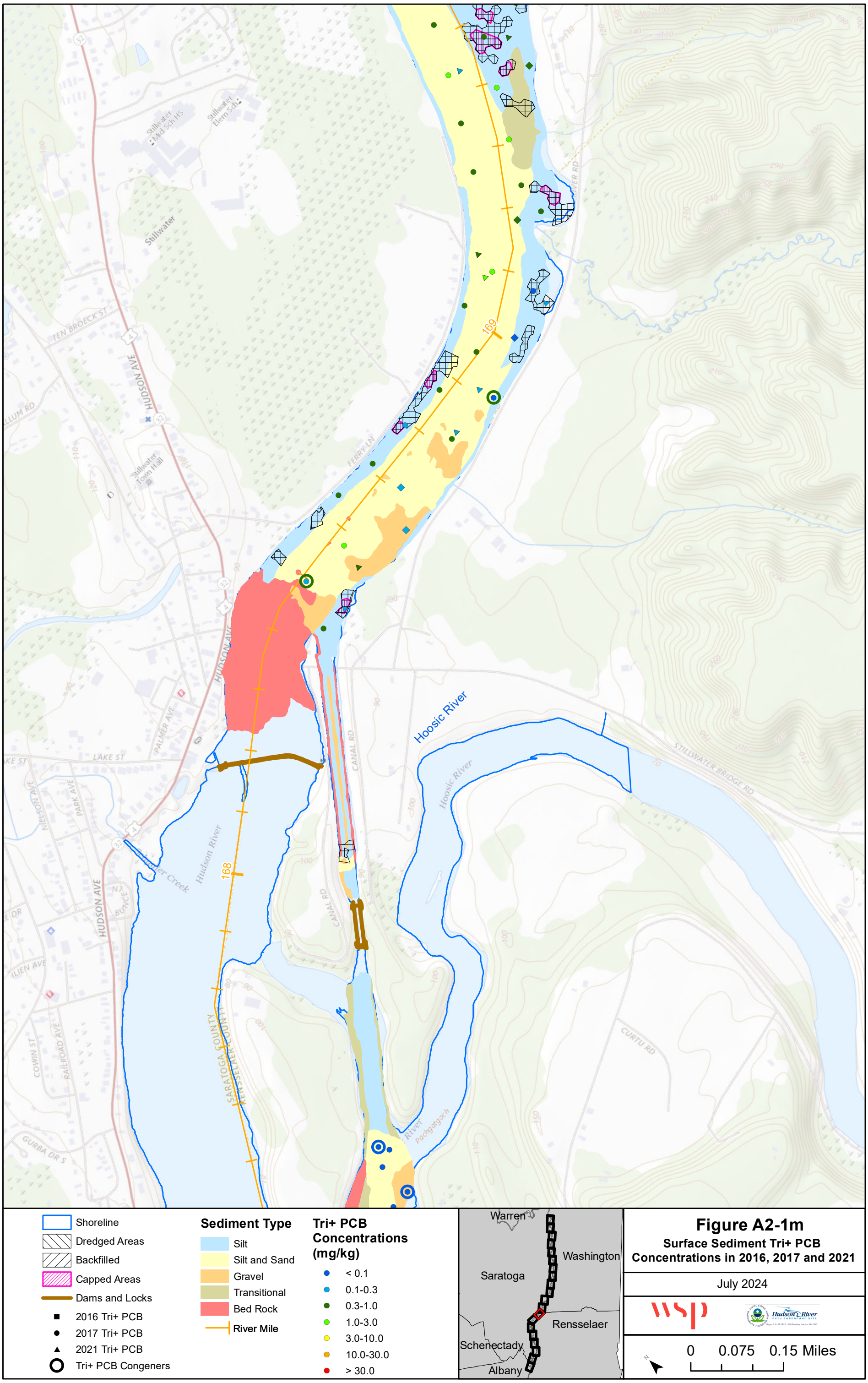

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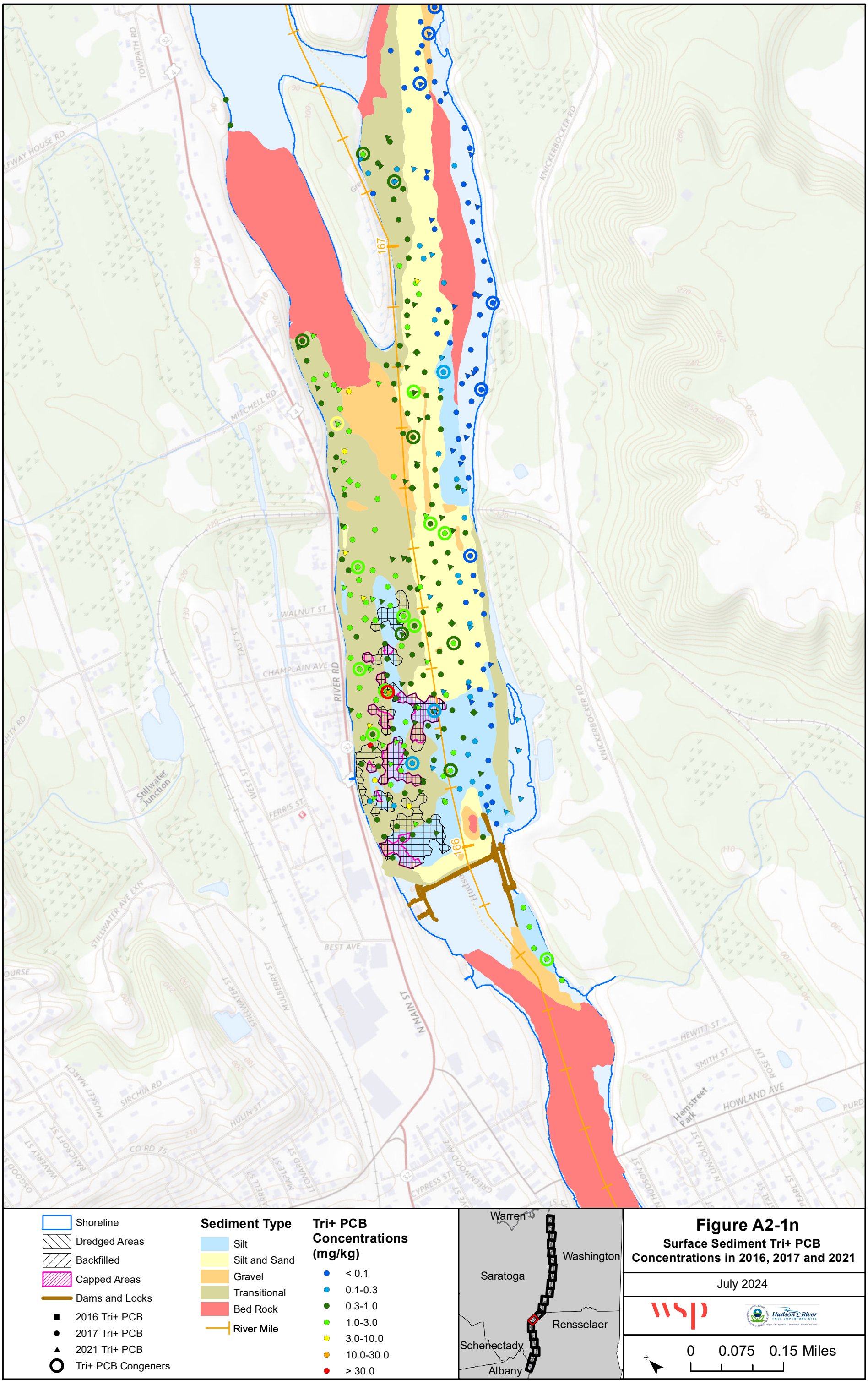

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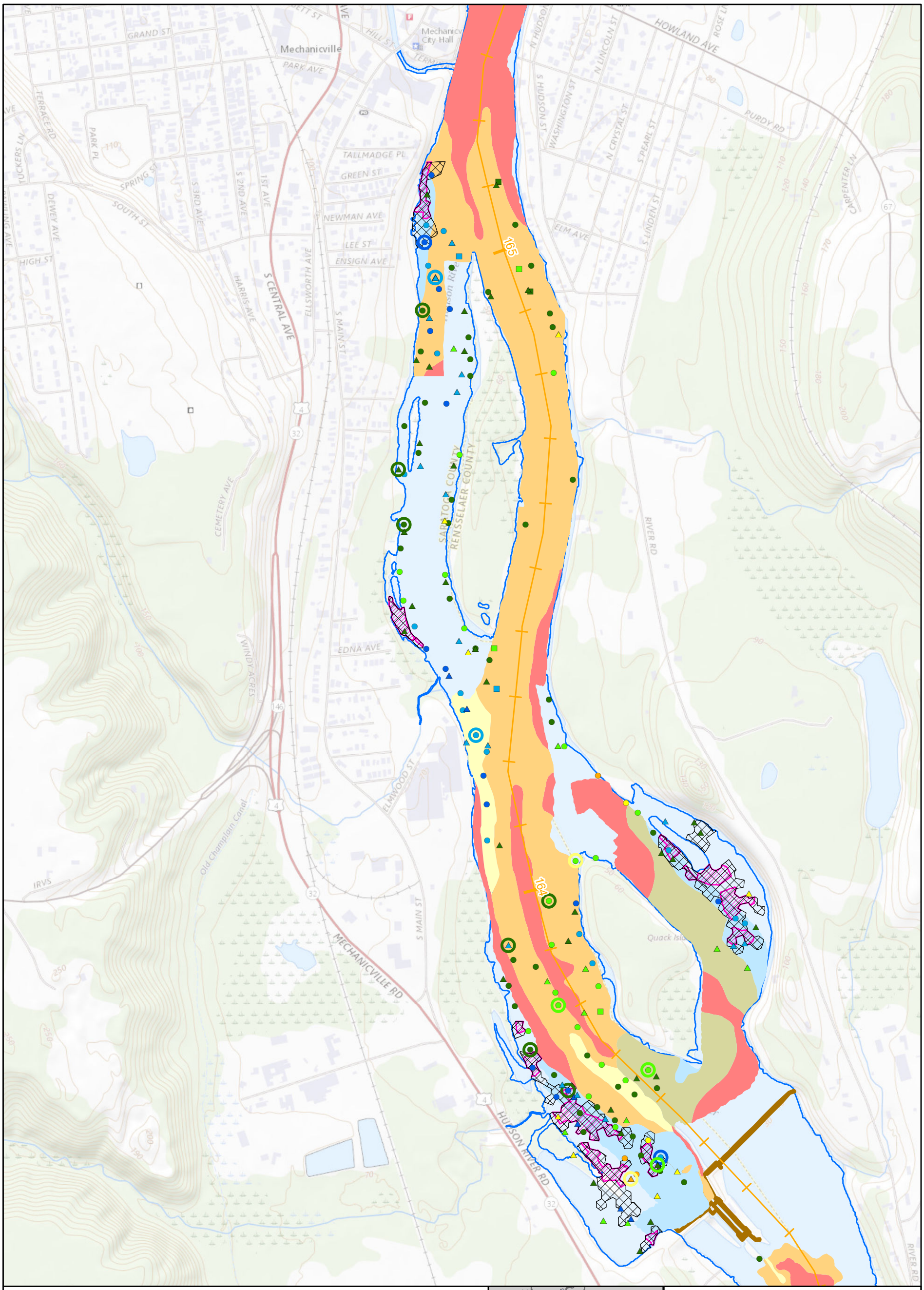

Figure A2-1o
Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021

July 2024

0 0.075 0.15 Miles

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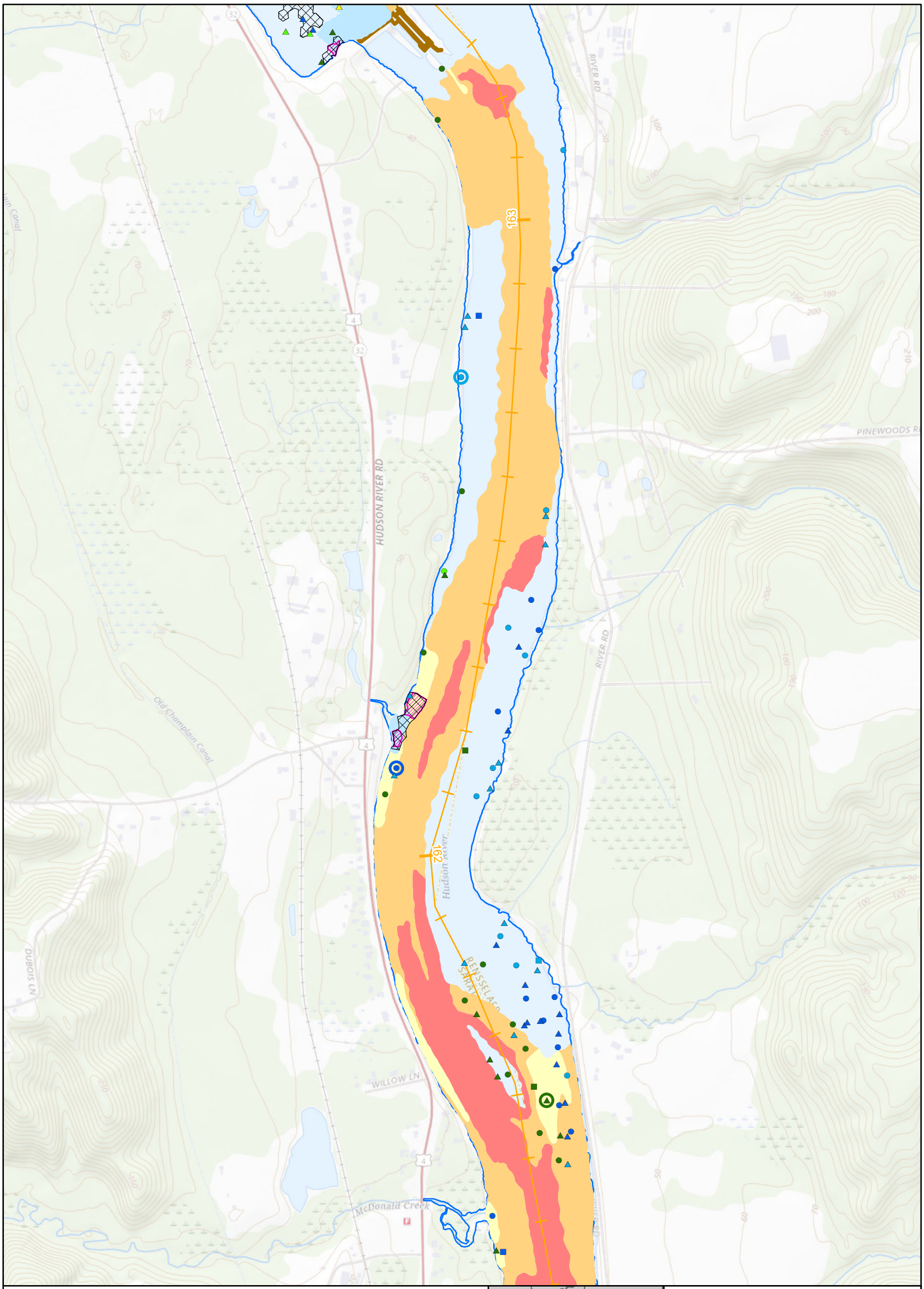

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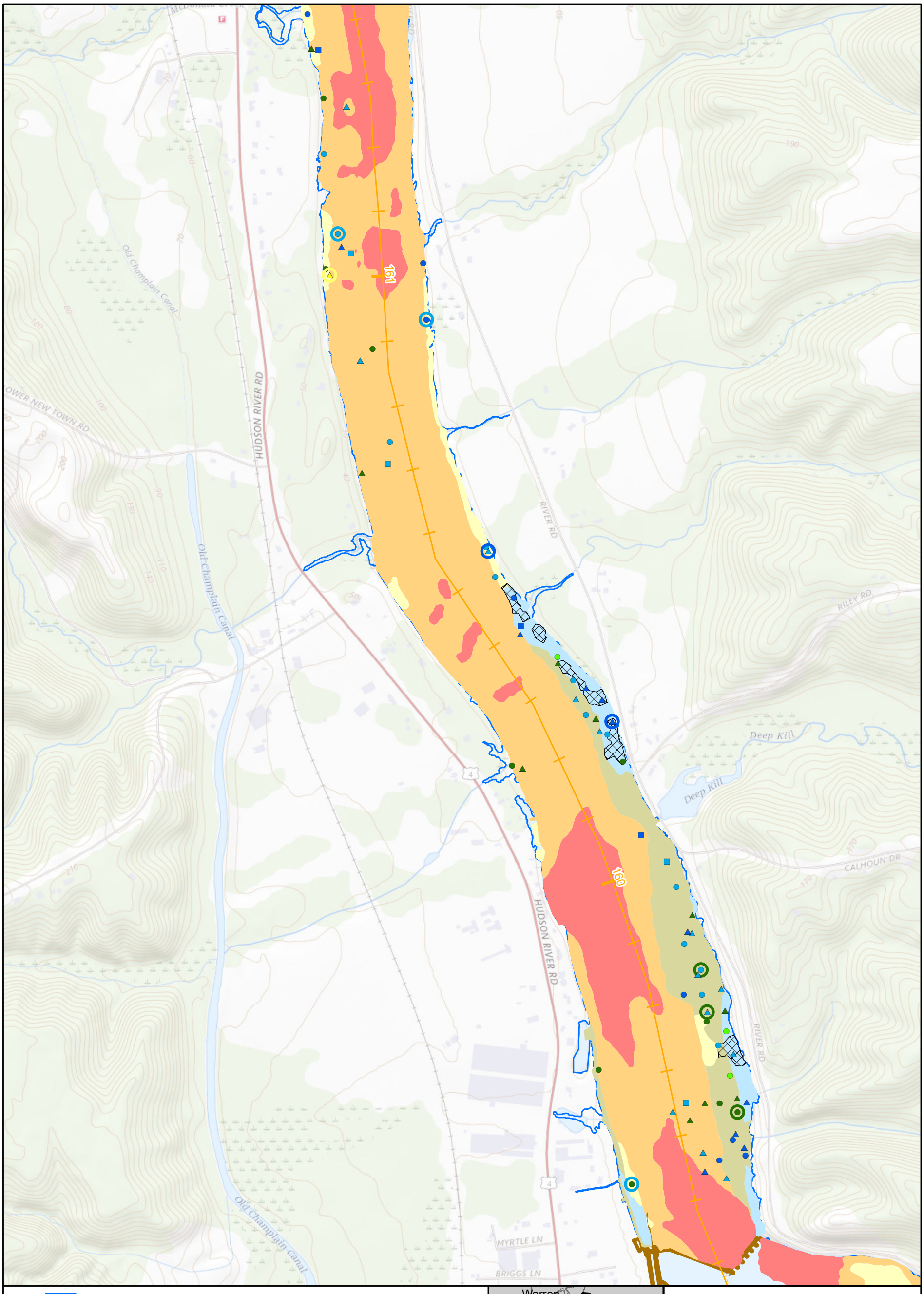

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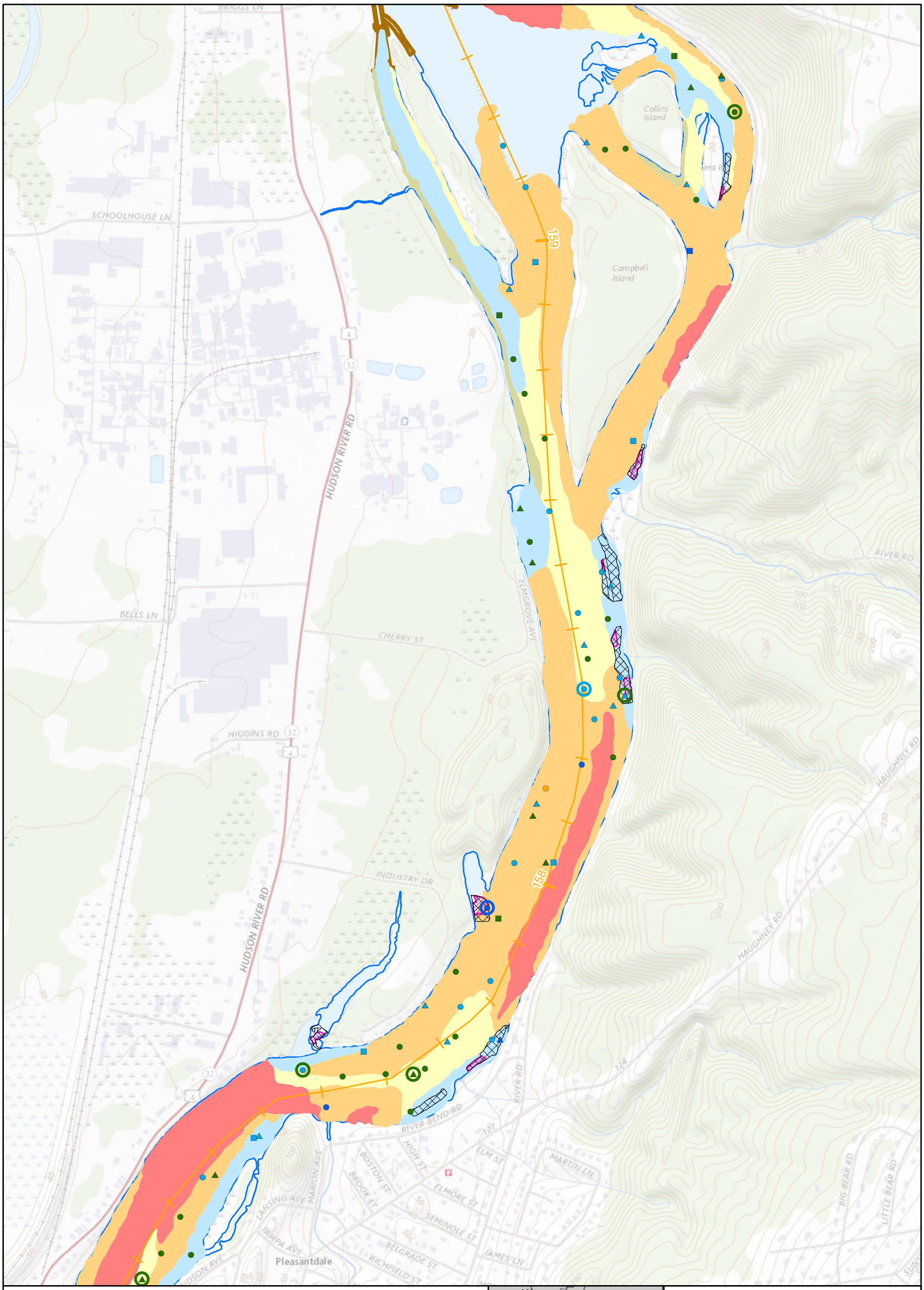

Figure A2-1r

Surface Sediment Tri+ PCB Concentrations in 2016, 2017 and 2021

July 2024

0 0.075 0.15 Miles

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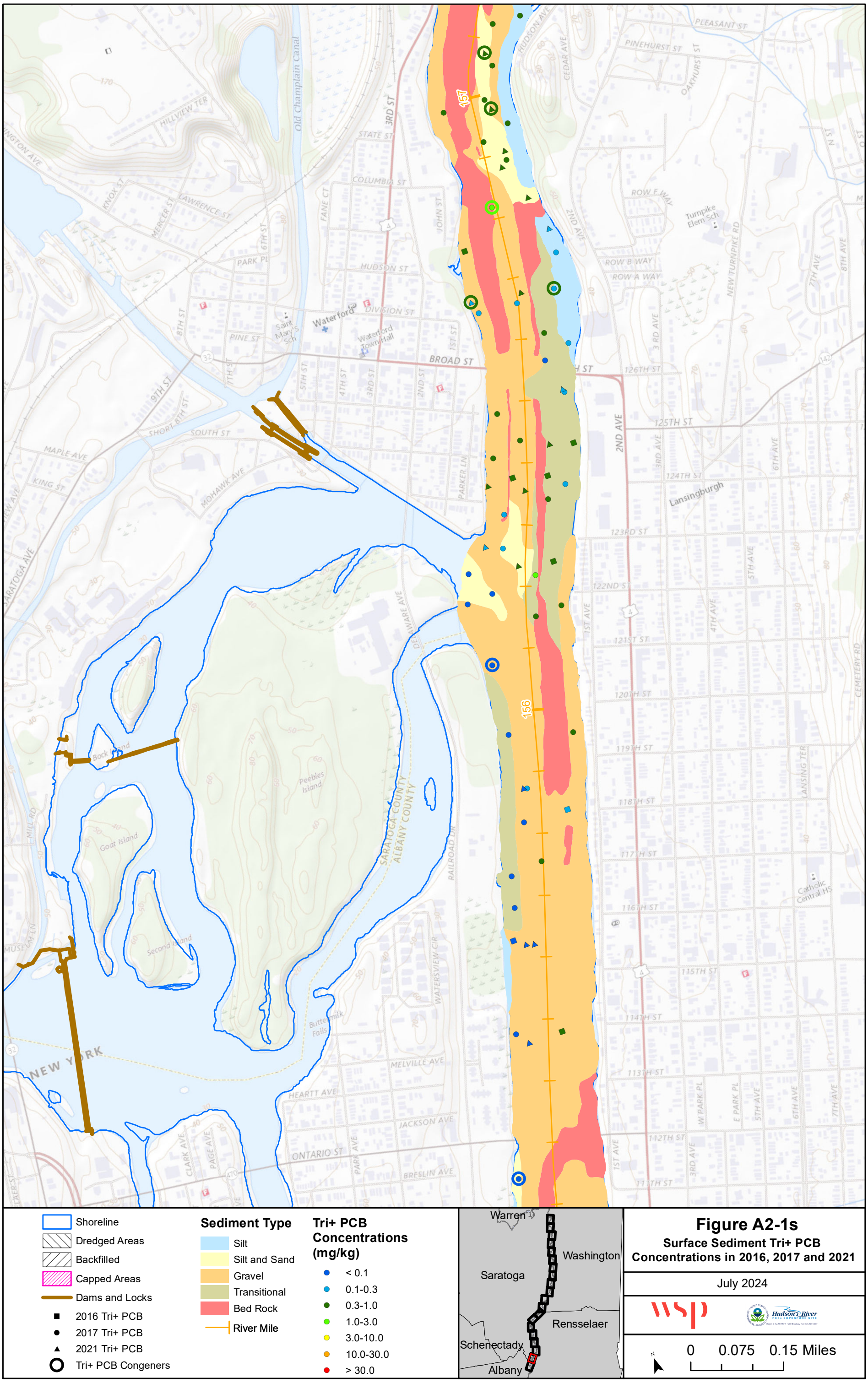

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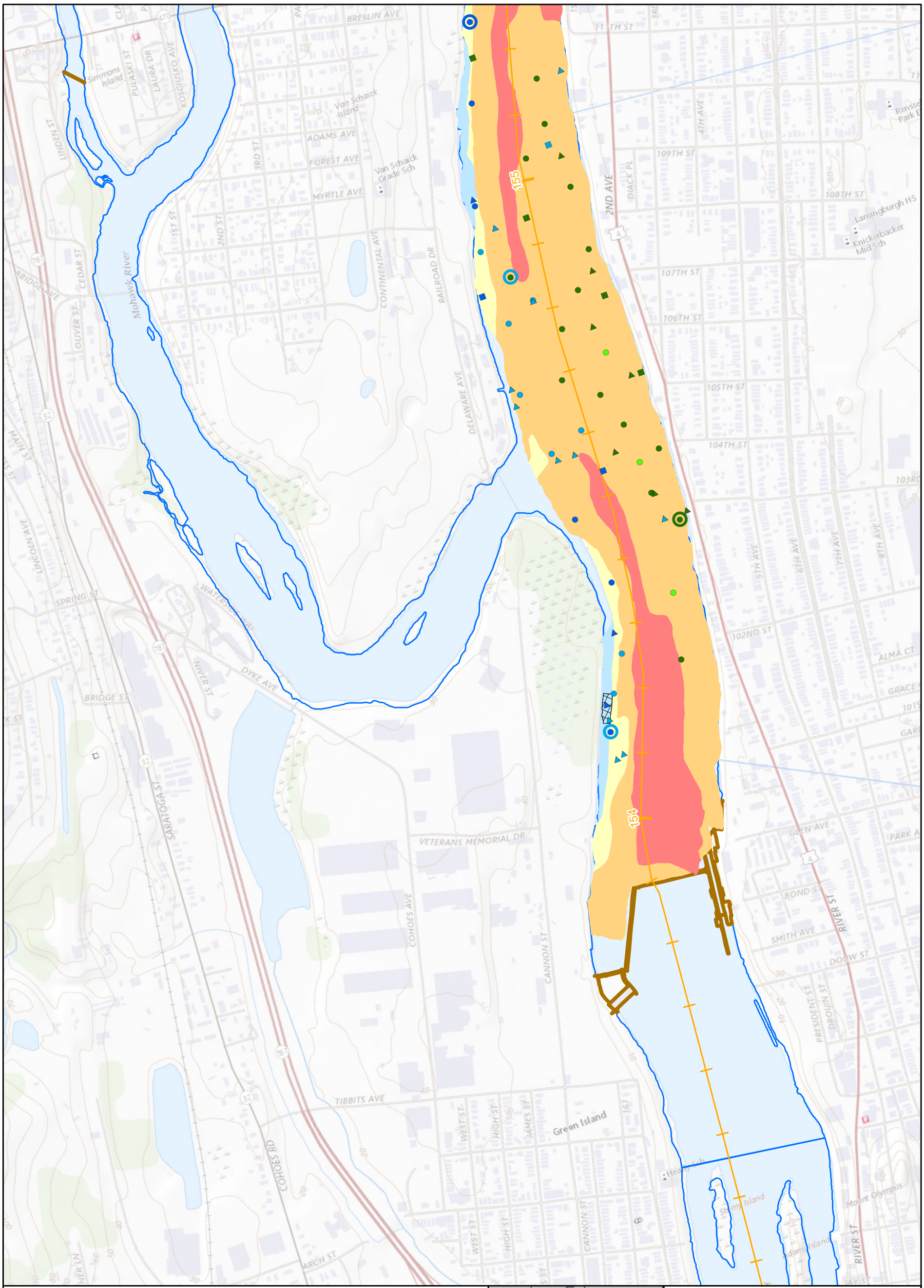

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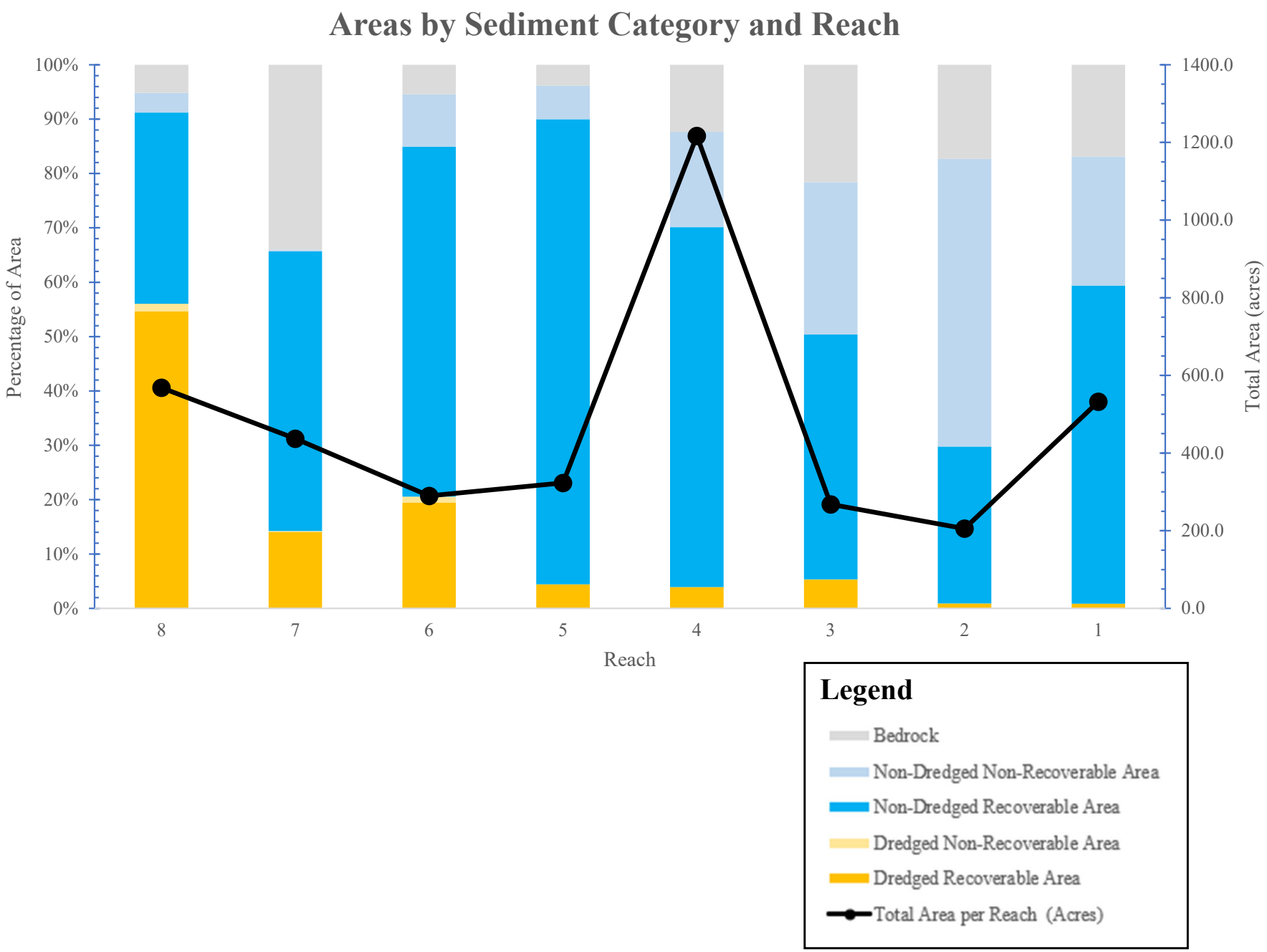
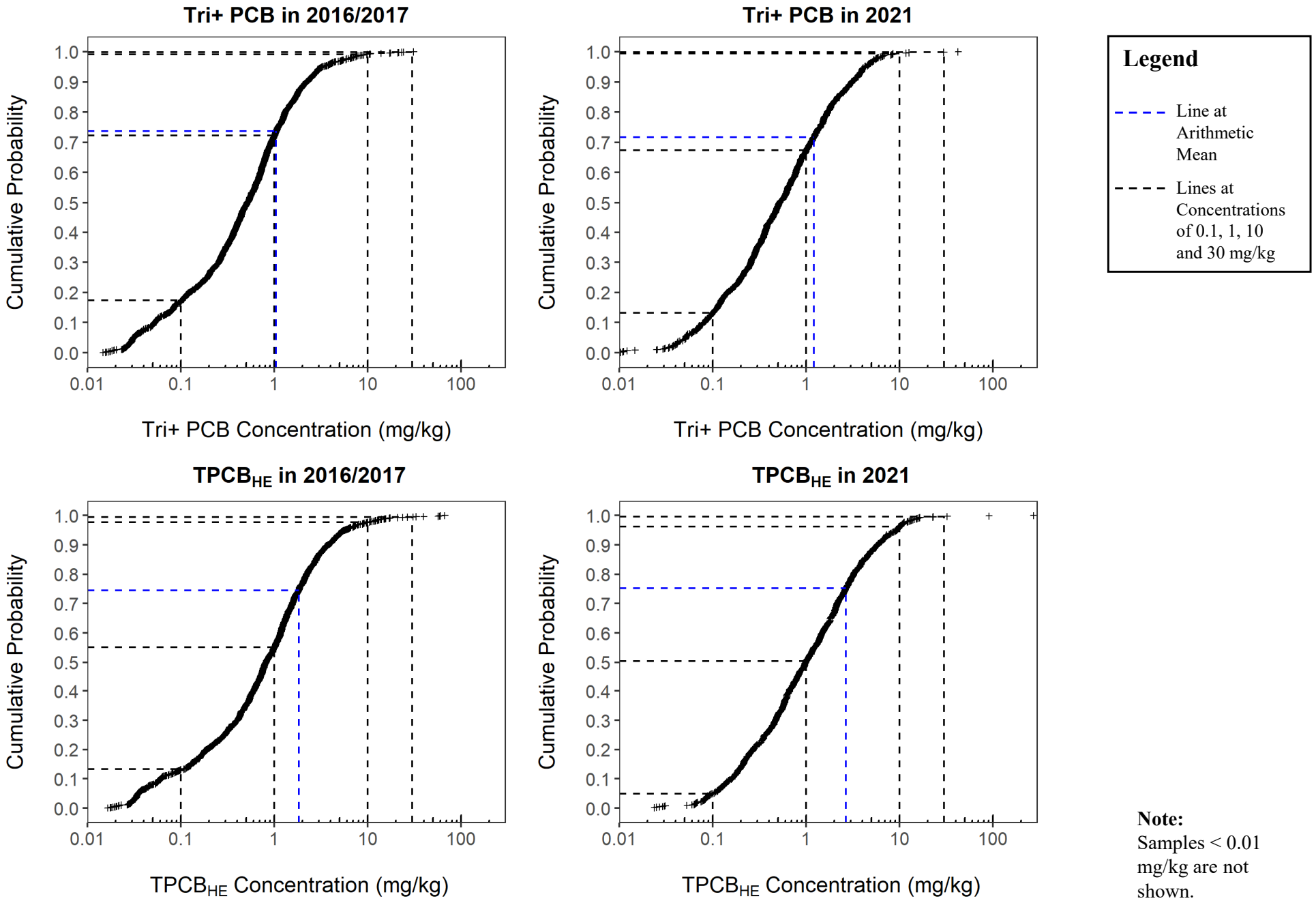


Areas Used in Area-Weighted Average Calculation

Figure A2-2

July 2024

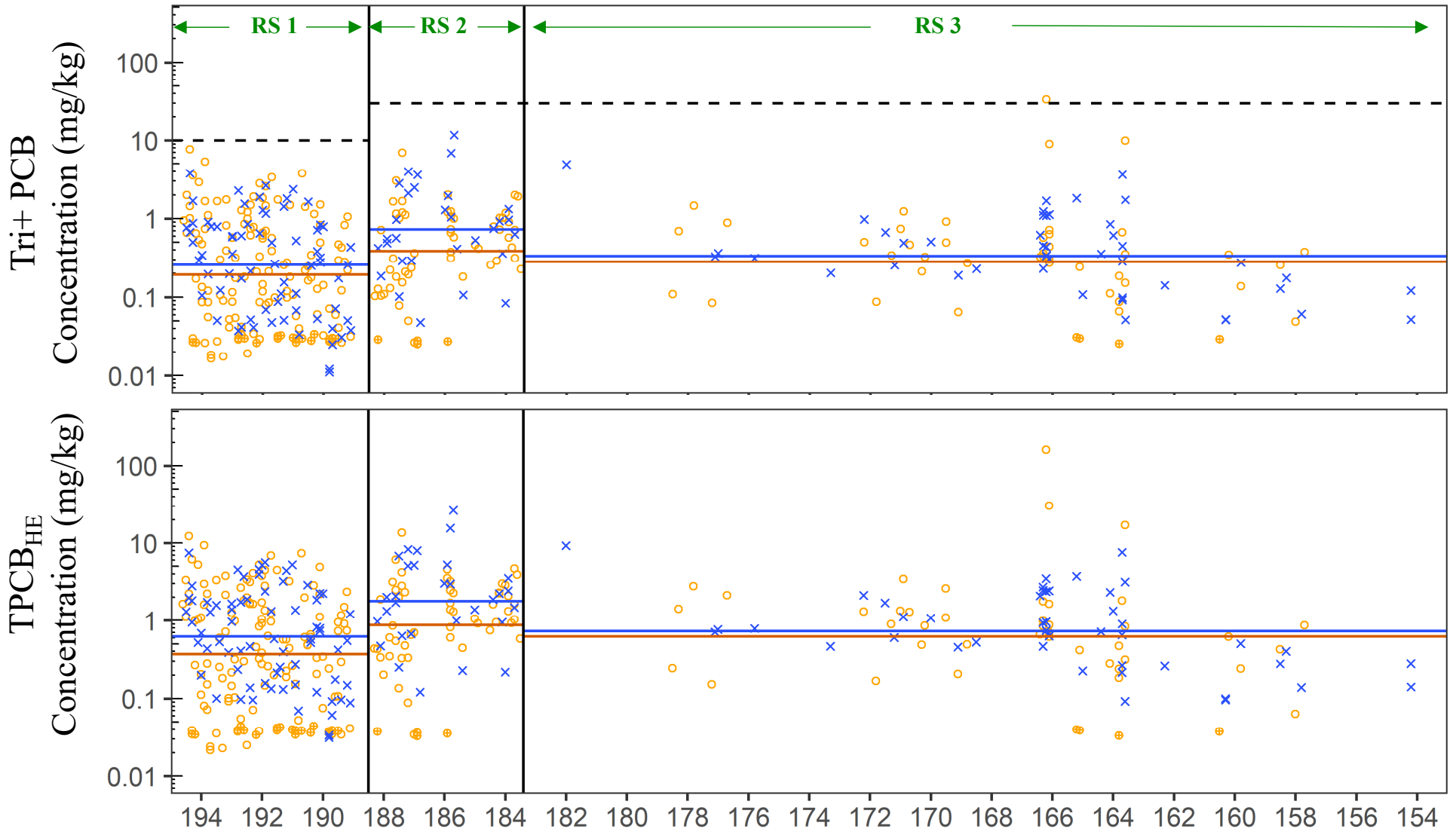


Note:
Samples < 0.01 mg/kg are not shown.

Cumulative Probability Distribution of PCB Concentrations in Surface Sediments

Figure A2-3

July 2024



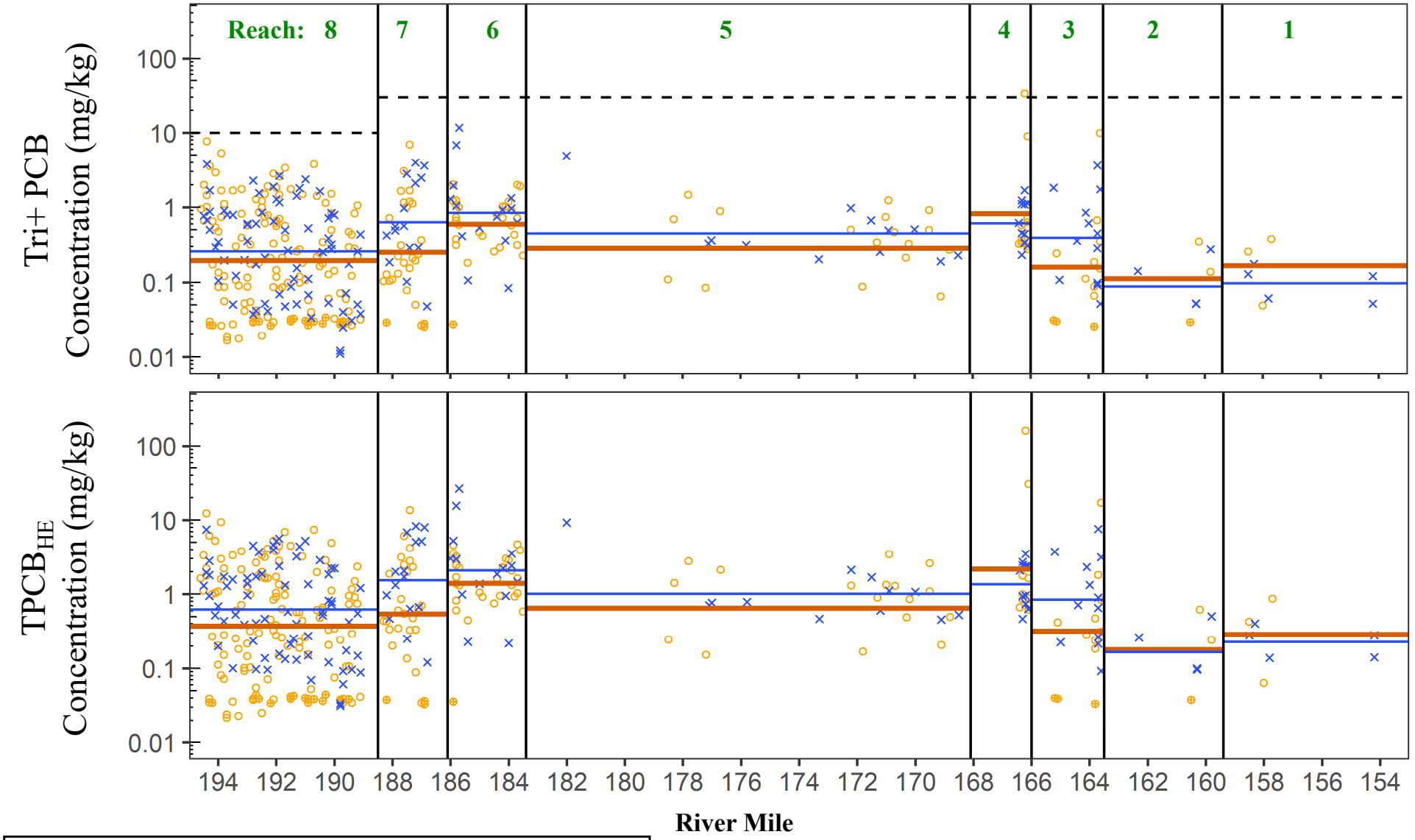
Notes:

- All 2021 results were detected.
- Samples < 0.01 mg/kg are not shown.

PCB Concentrations in Recoverable Sediments *versus* River Mile: Dredged Areas by River Section

Figure A2-4a

July 2024



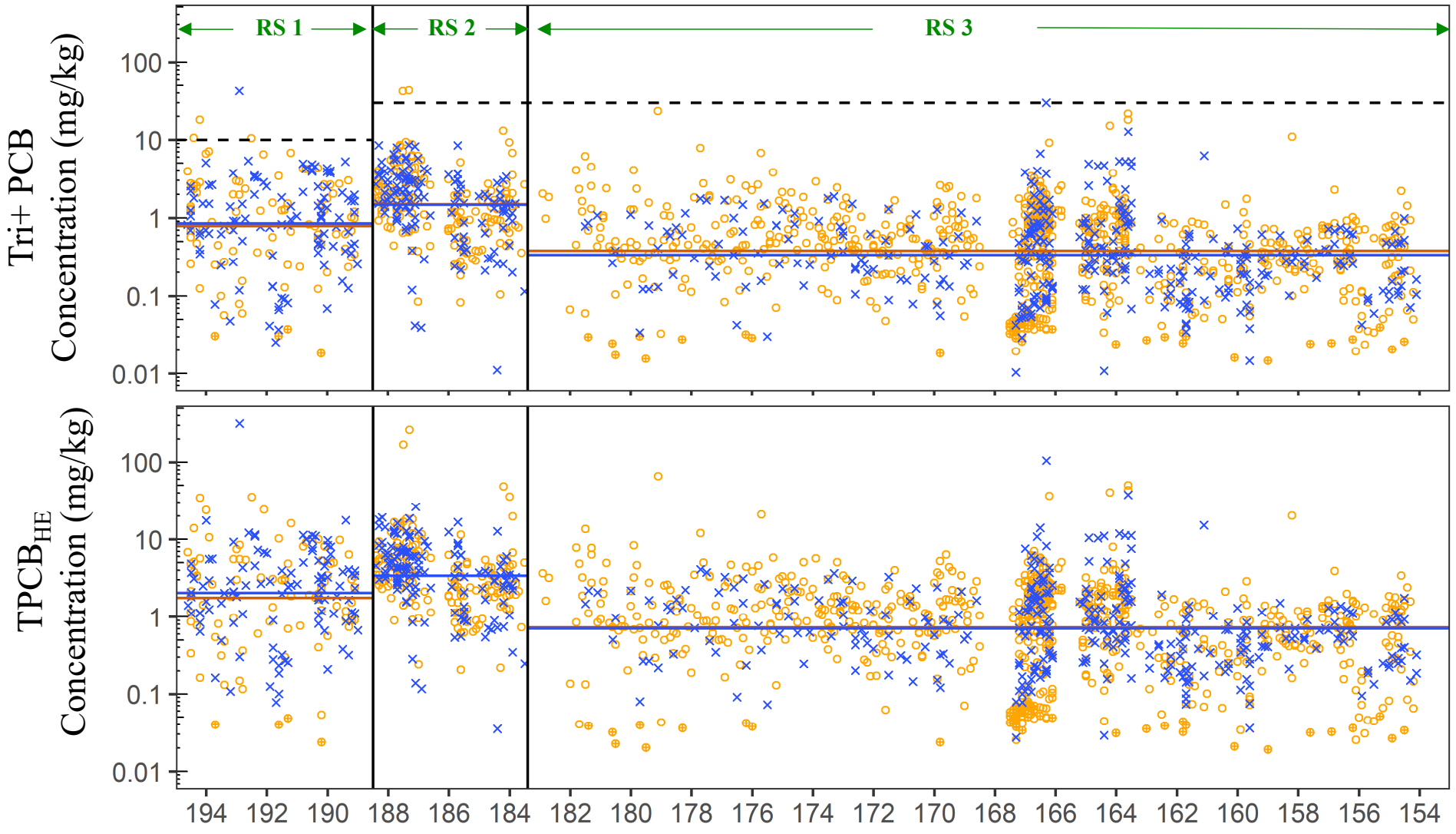
Notes:

- All 2021 results were detected.
- Samples <0.01 mg/kg are not shown.

PCB Concentrations in Recoverable Sediments *versus* River Mile: Dredged Areas by Reach

Figure A2-4b

July 2024



Legend

- 2016/2017 Detect
- 2016/2017 Non-Detect
- 2021 Detect
- Tri+ PCB Dredging Criteria
- 2016/2017 Geometric Mean
- 2021 Geometric Mean
- River Section Bound

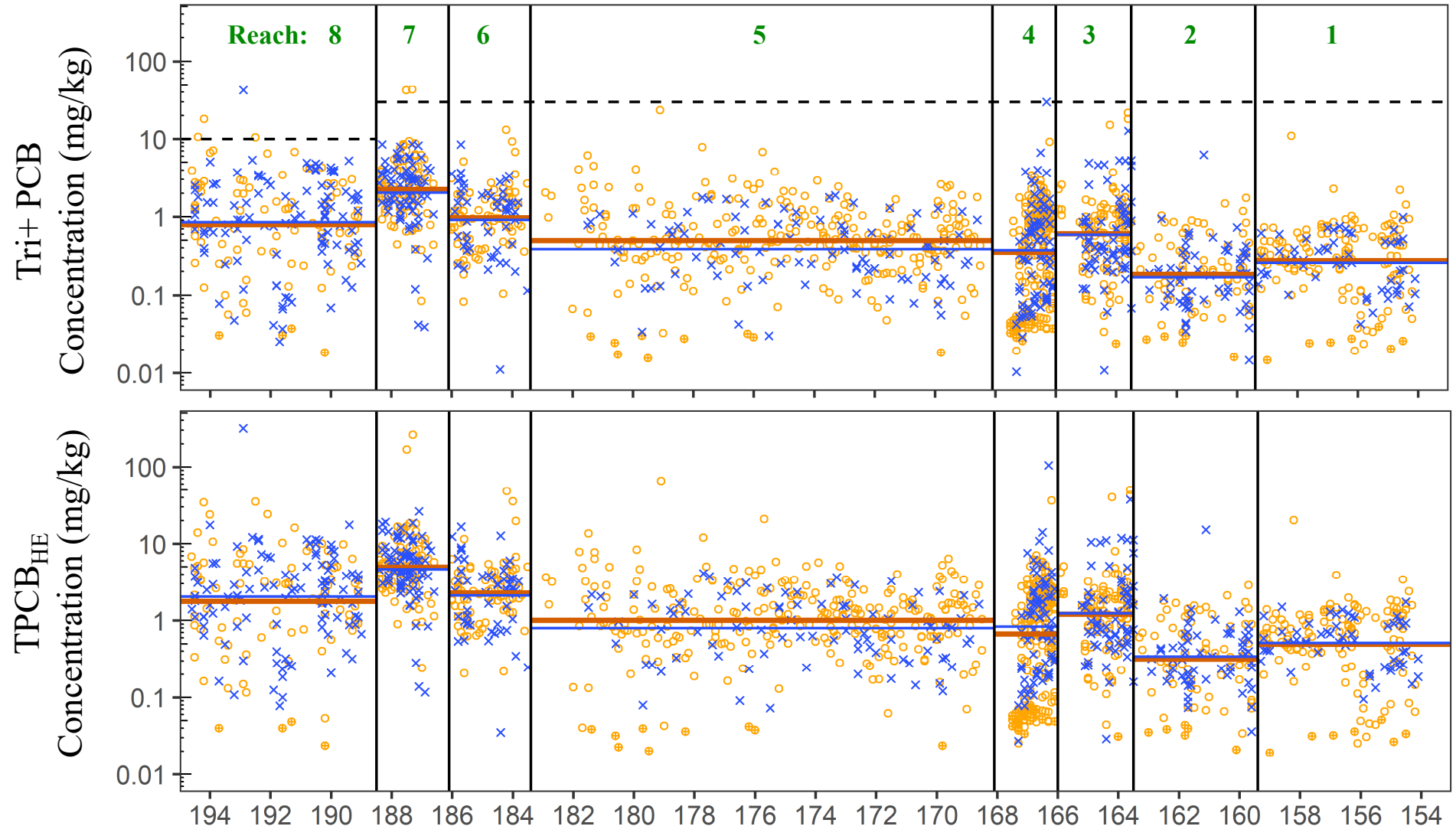
Notes:

- All 2021 results were detected.
- Samples <0.01 mg/kg are not shown.

PCB Concentrations in Recoverable Sediments *versus* River Mile: Non-Dredged Areas by River Section

Figure A2-5a

July 2024



Legend

- 2016/2017 Detect
- 2016/2017 Non-Detect
- 2021 Detect
- Tri+ PCB Dredging Criteria
- 2016/2017 Geometric Mean
- 2021 Geometric Mean
- Reach Bound

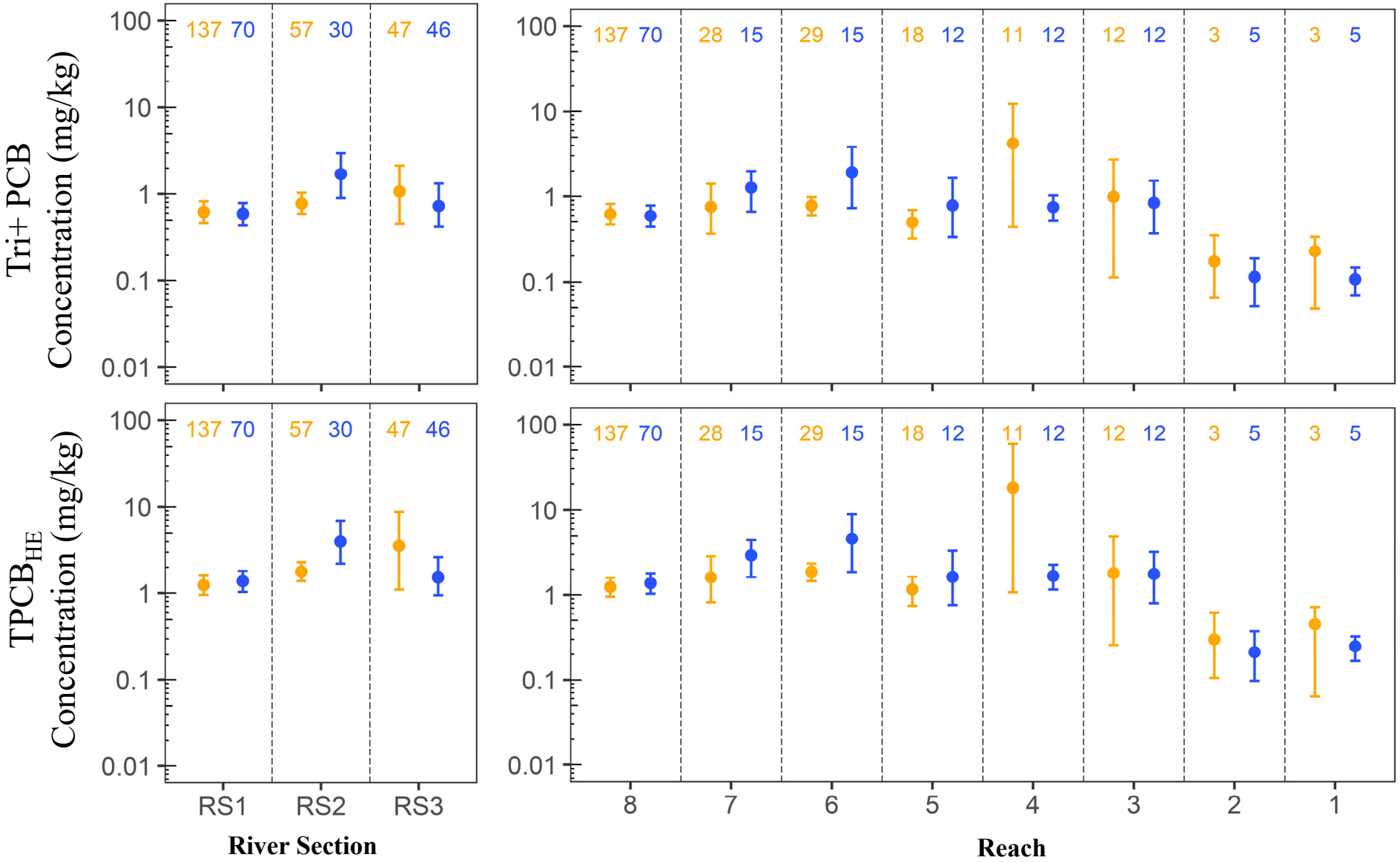
Notes:

- All 2021 results were detected.
- Samples <0.01 mg/kg are not shown.

PCB Concentrations in Recoverable Sediments *versus* River Mile: Non-Dredged Areas by Reach

Figure A2-5b

July 2024



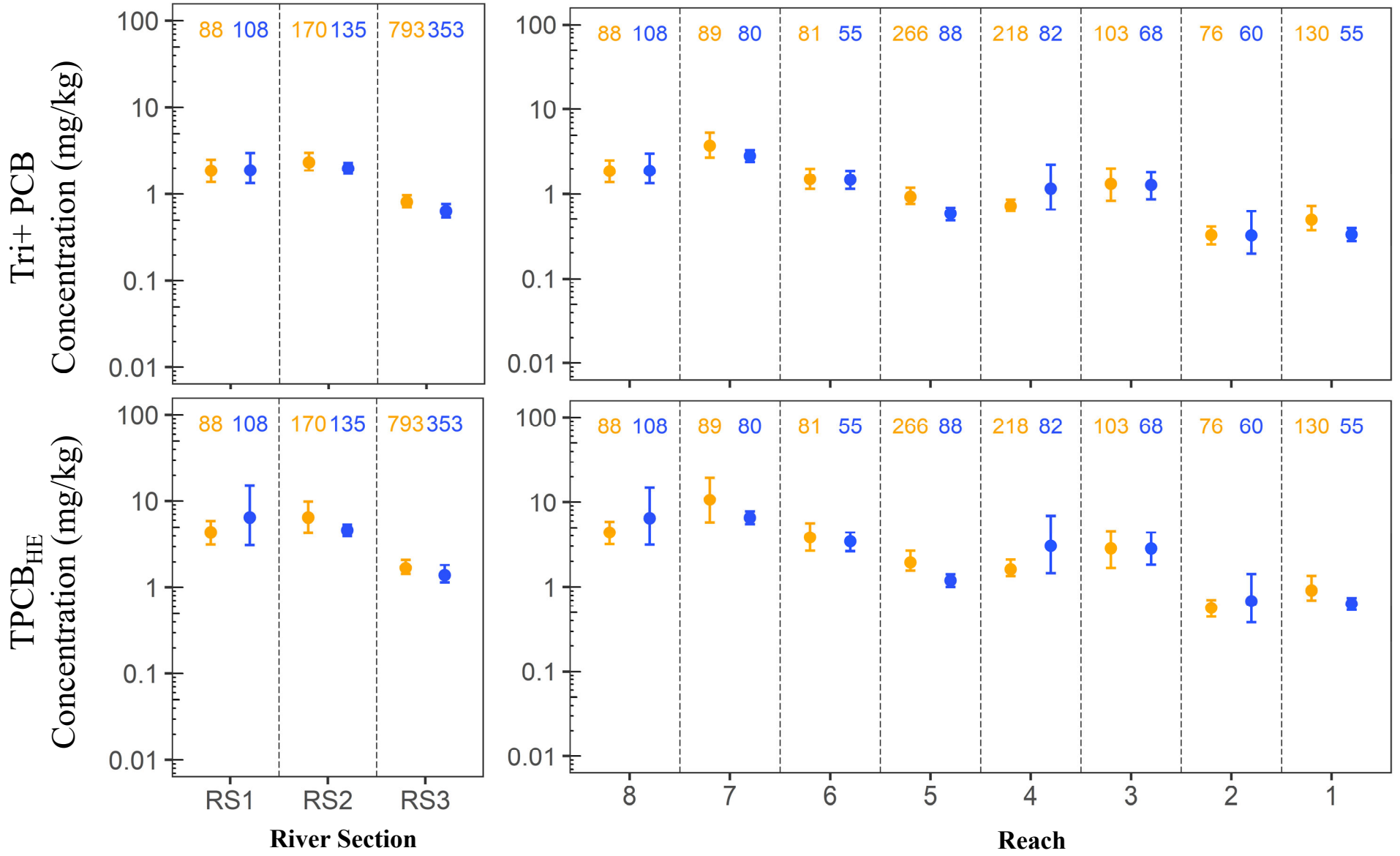
Notes:

- Numbers shown on the plot represent number of samples.
- See text in Section 3.2.1 for the calculation of RSA-weighted averages and 95% confidence limits
- UCL: Upper Confidence Limit
- LCL: Lower Confidence Limit

Recoverable-Sediment-Area (RSA)-Weighted Average PCB Concentrations by River Section and Reach: Dredged Areas

Figure A2-6a

July 2024



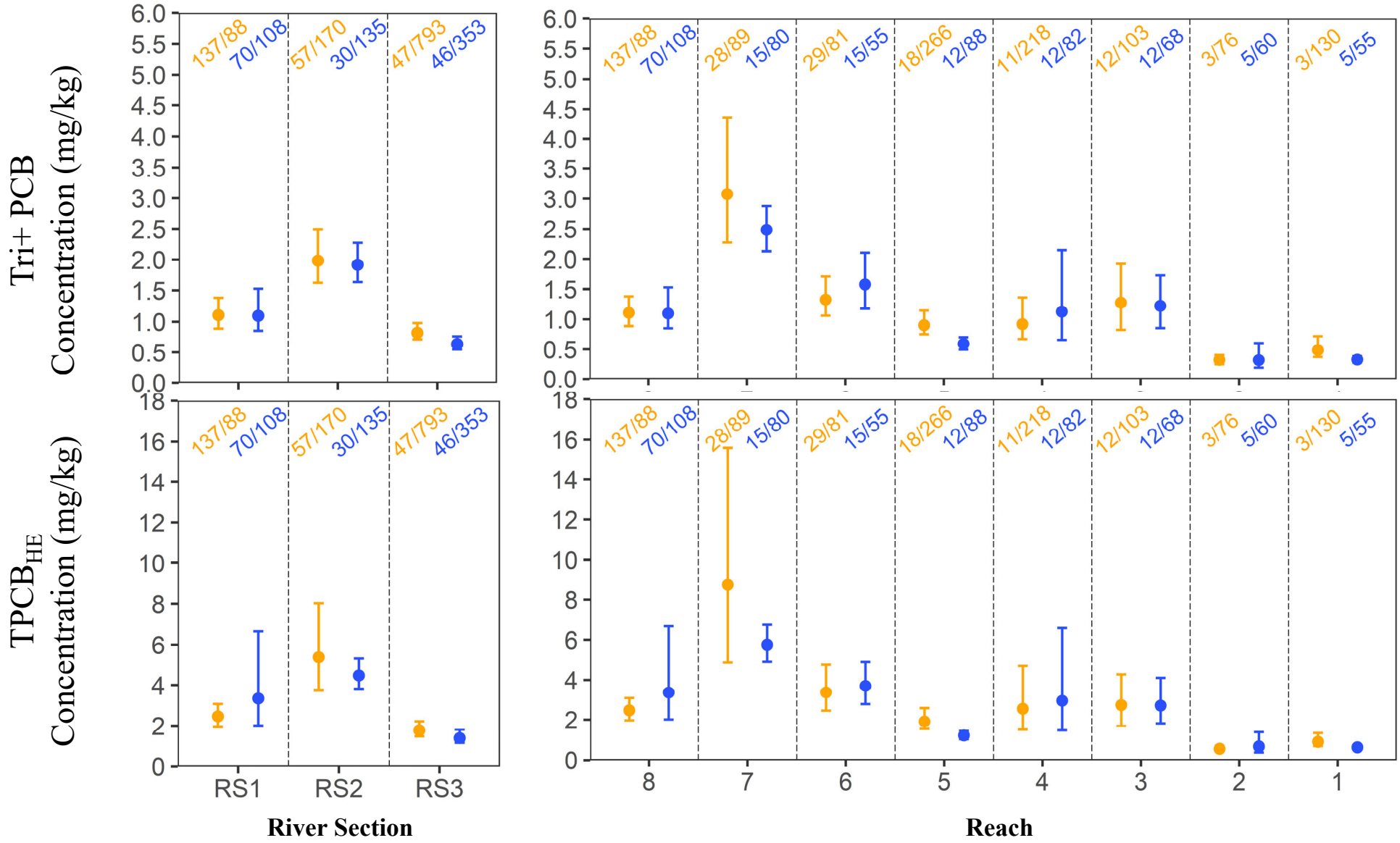
Notes:

- Numbers shown on the plot represent number of samples.
- See text in Section 3.2.1 for the calculation of RSA-weighted averages and 95% confidence limits
- UCL: Upper Confidence Limit
- LCL: Lower Confidence Limit

Recoverable-Sediment-Area (RSA)- Weighted Average PCB Concentrations by River Section and Reach: Non-Dredged Areas

Figure A2-6b

July 2024



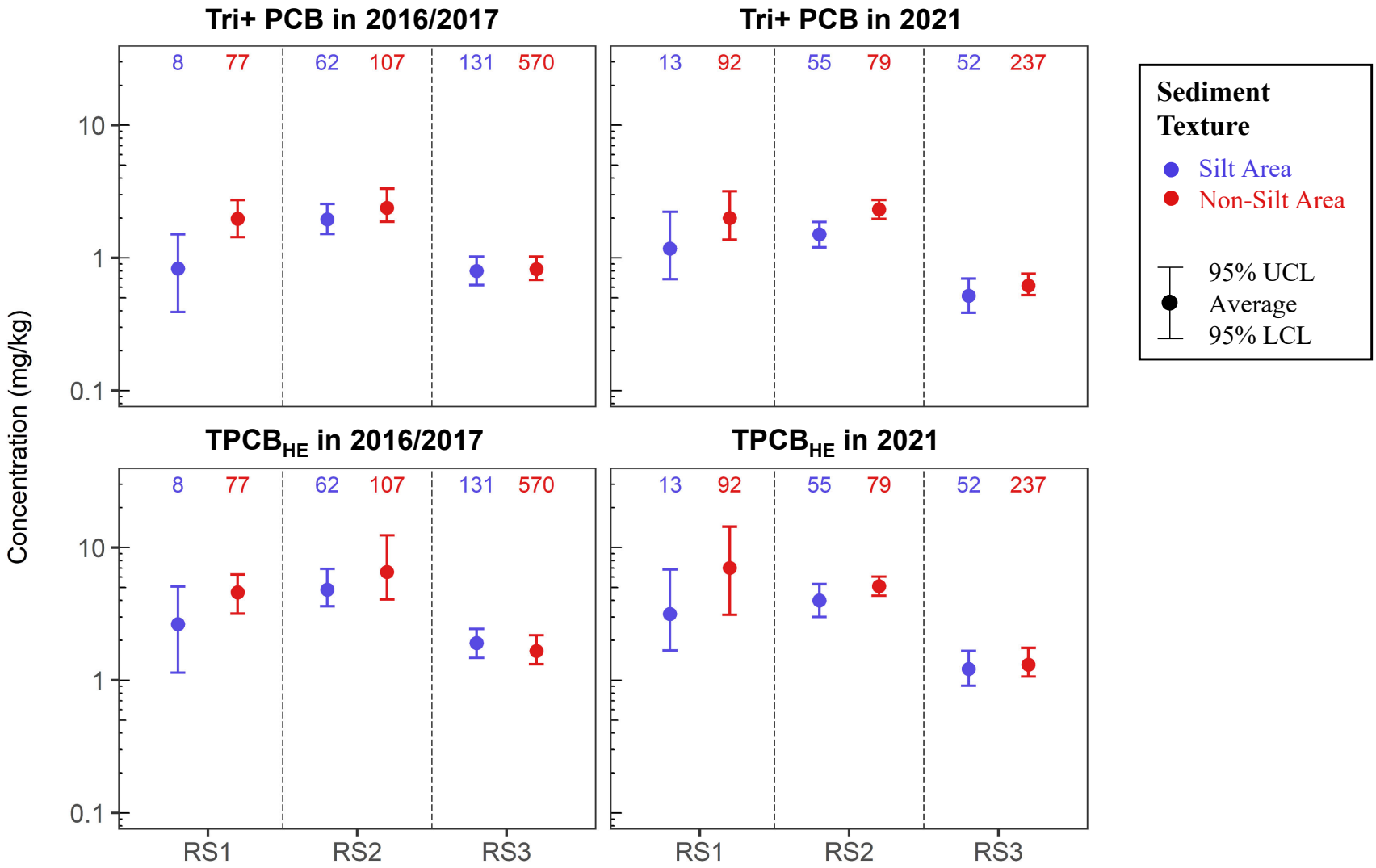
Notes:

- Numbers shown on the plot (x/x) represent number of samples in dredged and non-dredged areas, respectively.
- See text in Section 3.2.1 for the calculation of RSA-weighted averages and 95% confidence limits
- UCL: Upper Confidence Limit
- LCL: Lower Confidence Limit

Recoverable-Sediment-Area (RSA)- Weighted Average PCB Concentrations by River Section and Reach: Dredged and Non-Dredged Areas Combined

Figure A2-6c

July 2024



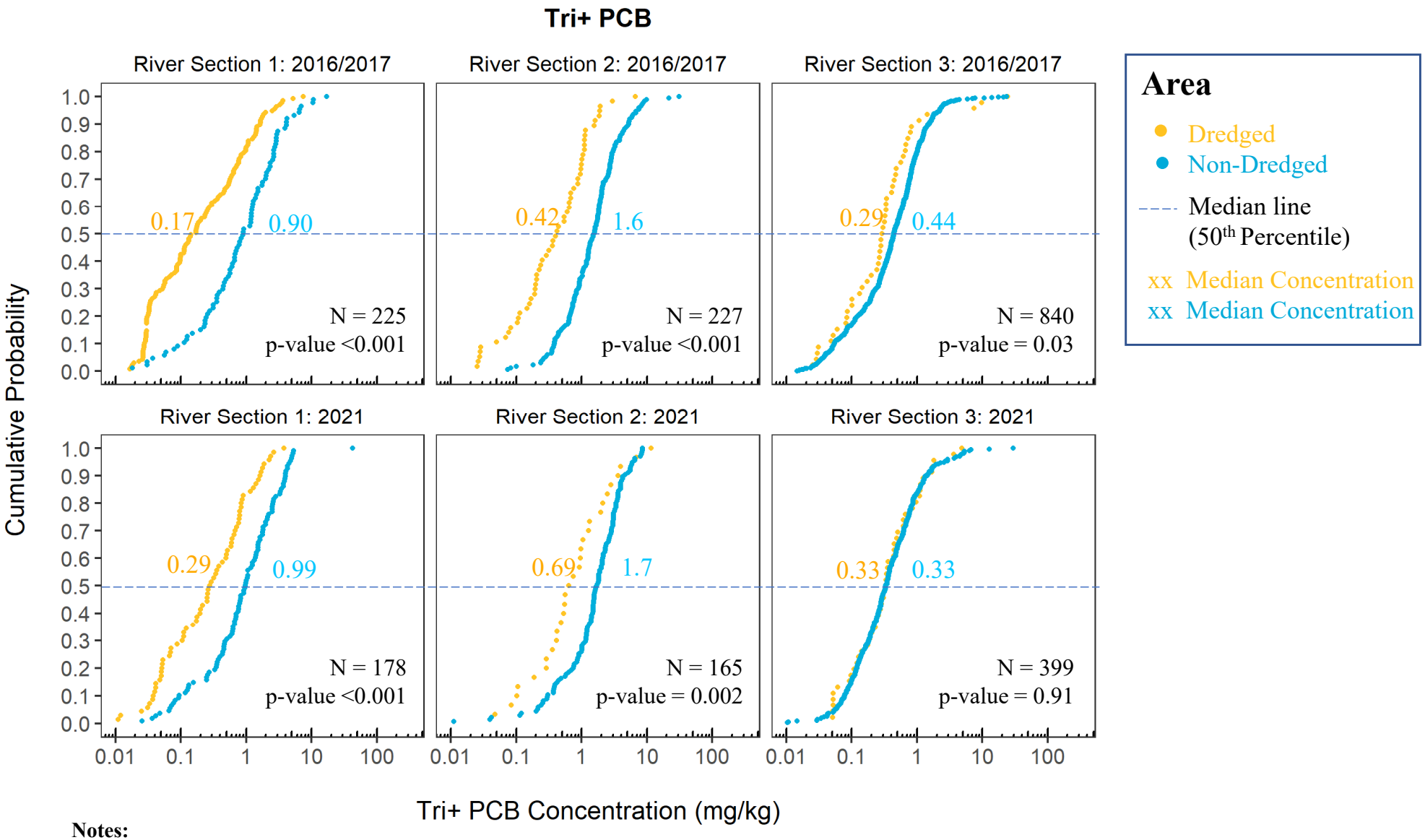
Notes:

- Silt and non-silt areas are from GE's 2002-2003 side-scan sonar survey. GE's survey did not cover the entire river bottom bank to bank.
- Non-silt area includes "Silt and Sand", "Gravel", "Transitional" and "Bedrock" areas.
- Numbers shown on the plot represent number of samples.
- See text in Section 3.2.1 for the calculation of averages and 95% confidence limits
- UCL: Upper Confidence Limit LCL: Lower Confidence Limit

Comparison of PCB Average Concentrations Between Silt and Non-Silt Areas Within the Non-Dredged Area Boundary

Figure A2-7

July 2024



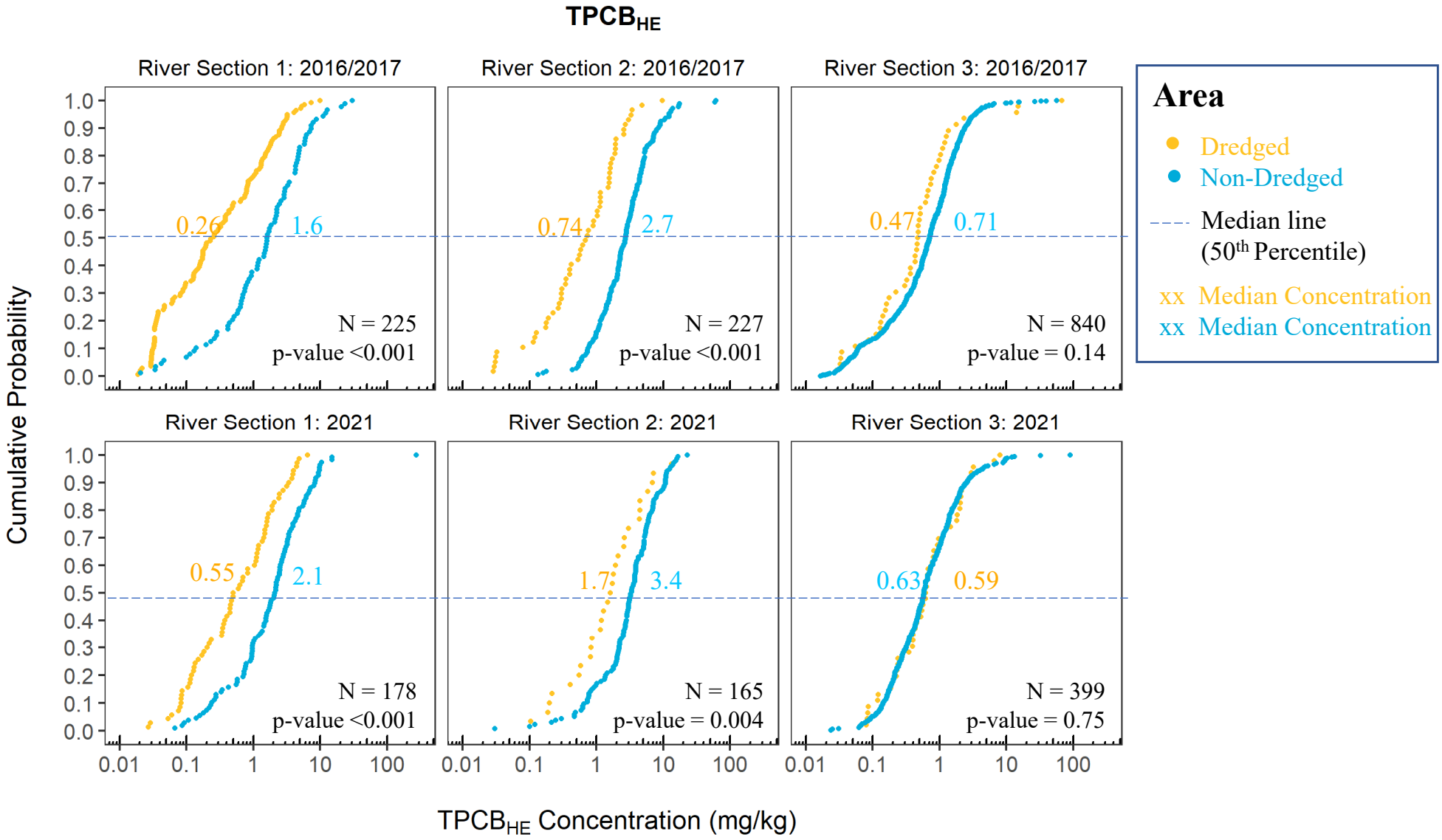
Notes:

- Non-parametric two-sample Wilcoxon rank sum test was used to test the difference in concentrations between two groups of samples.
- N: total number of samples included in the test
- p-value less than 0.05 indicates a statistically significant difference in concentrations between two groups.
- Samples < 0.01 mg/kg are not shown.

Cumulative Probability Distribution of Tri+ PCB Concentrations by Sampling Area

Figure A2-8a

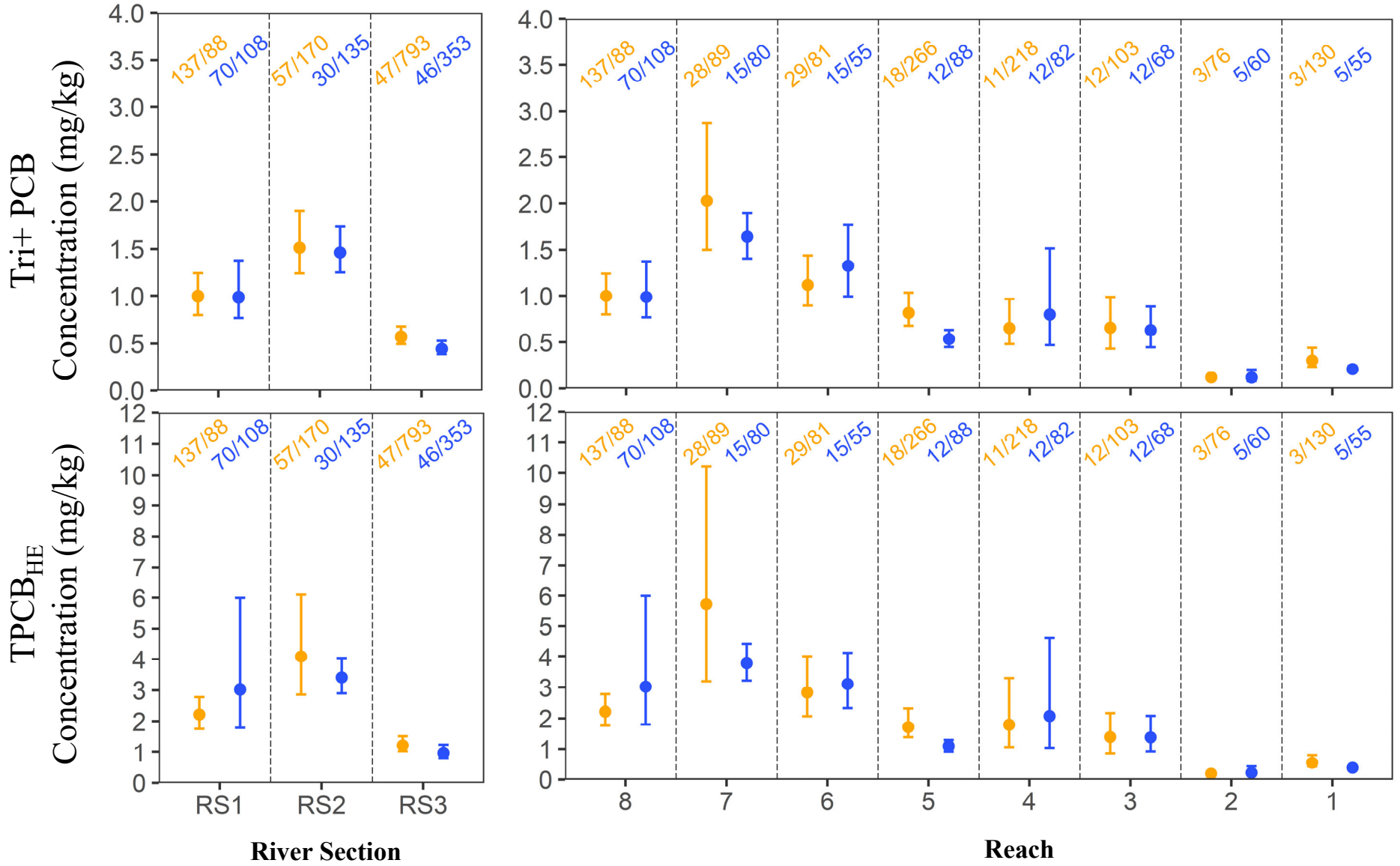
July 2024



Notes:

- Non-parametric two-sample Wilcoxon rank sum test was used to test the difference in concentrations between two groups of samples.
- N: total number of samples included in the test
- p-value less than 0.05 indicates a statistically significant difference in concentrations between two groups.
- Samples < 0.01 mg/kg are not shown.

	Cumulative Probability Distribution of TPCB$_{HE}$ Concentrations by Sampling Area	**Figure A2-8b**
		July 2024



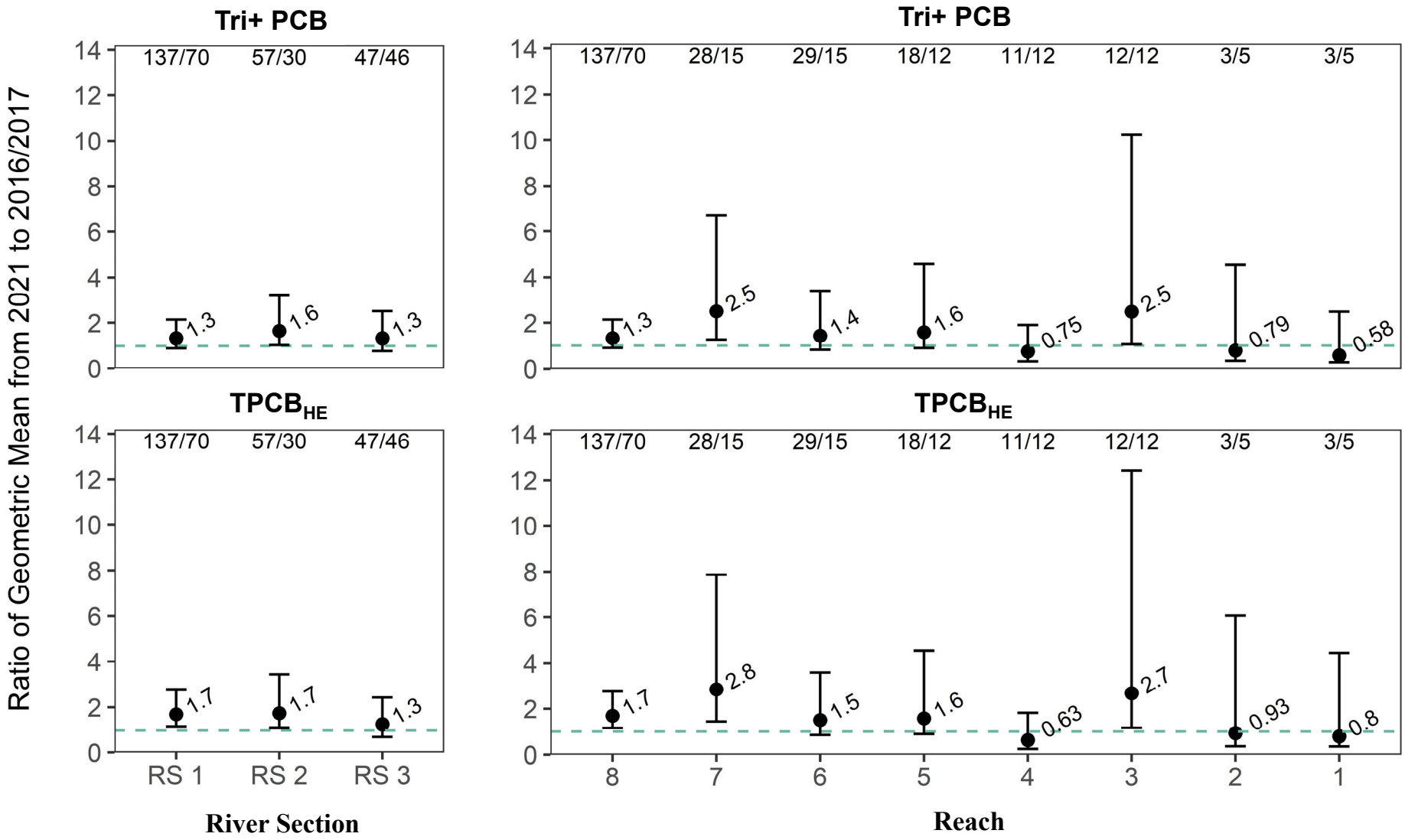
Notes:

- Numbers shown on the plot (x/x) represent number of samples in dredged and non-dredged areas, respectively.
- See text in Section 3.2.1 for the calculation of RWA-weighted averages and 95% confidence limits.
- UCL: Upper Confidence Limit
- LCL: Lower Confidence Limit

River-Wide-Area (RWA)-Weighted Average PCB Concentrations by River Section and Reach

Figure A2-9

July 2024



Legend

- 95% Upper Confidence Limit
- Ratio of Geometric Mean
- 95% Lower Confidence Limit
- Ratio of 1

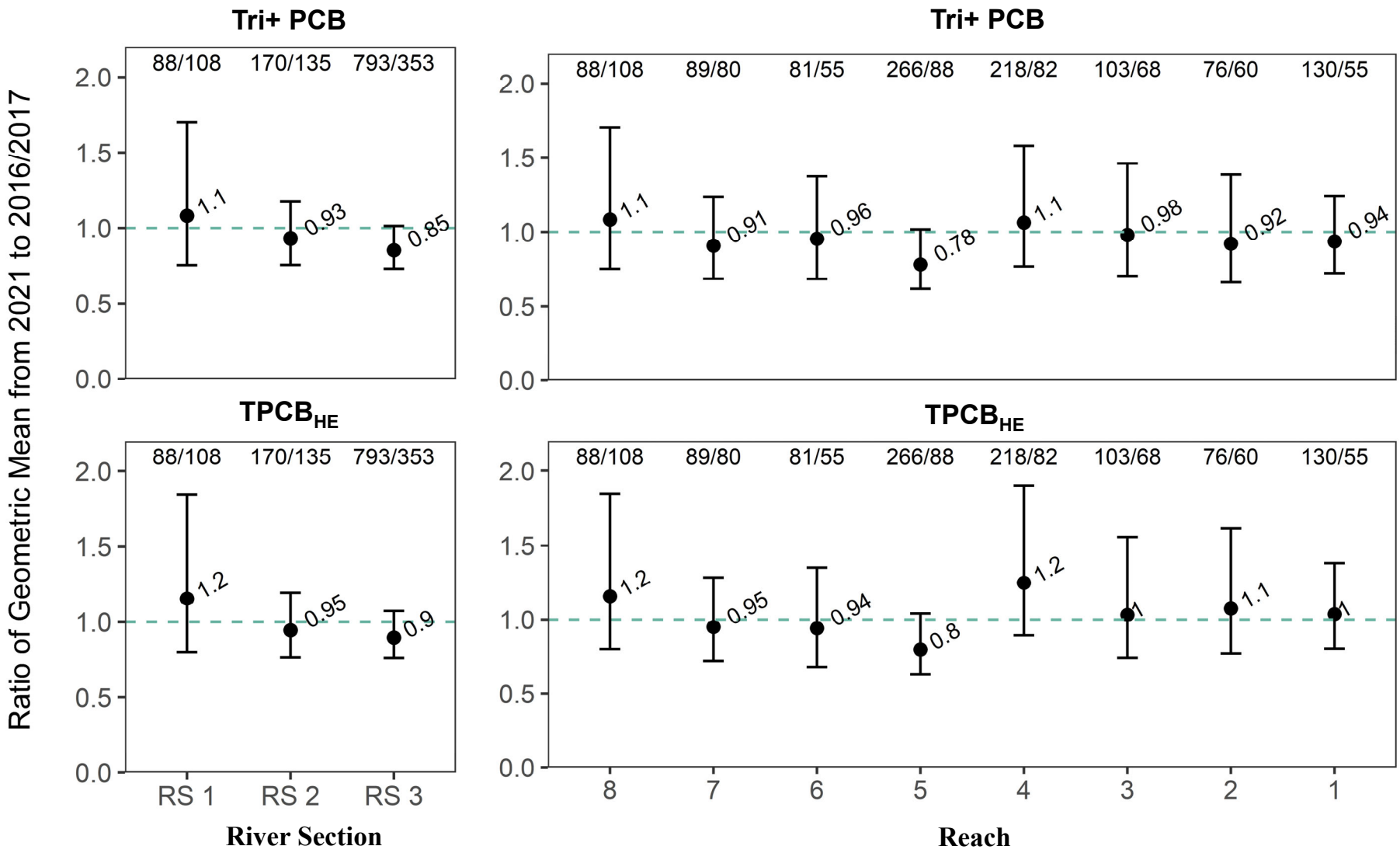
Note:

- Numbers shown on the plot (x/x) represent number of samples in 2016/2017 and 2021, respectively.

Ratio of Geometric Mean PCB Concentrations in 2021 to 2016/2017 in Dredged Areas

Figure A2-10a

July 2024



Legend

- 95% Upper Confidence Limit
- Ratio of Geometric Mean
- 95% Lower Confidence Limit
- Ratio of 1

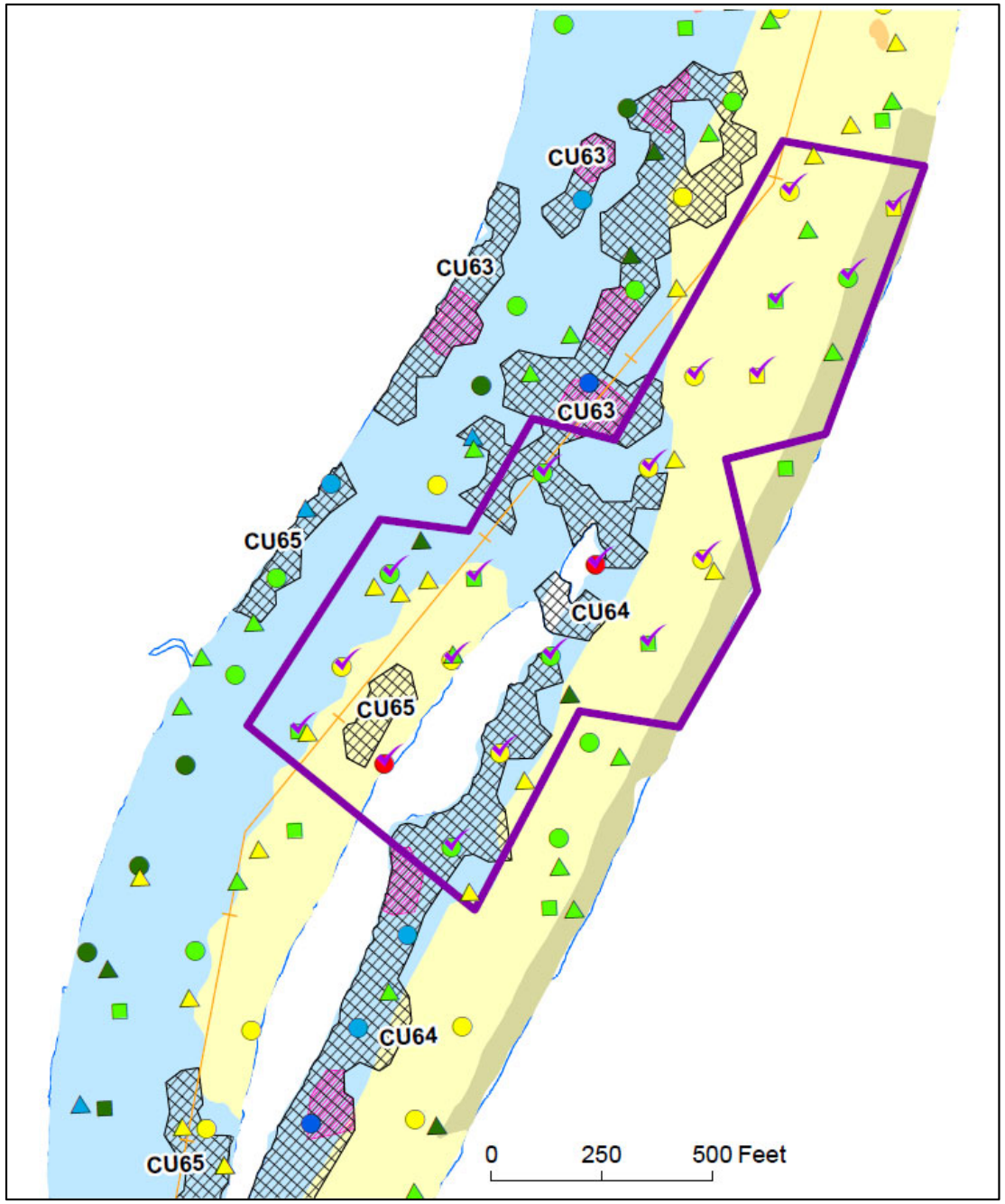
Note:

- Numbers shown on the plot (x/x) represent number of samples in 2016/2017 and 2021, respectively.

Ratio of Geometric Mean PCB Concentrations in 2021 to 2016/2017 in Non-Dredged Areas

Figure A2-10b

July 2024



Shoreline
Dredged Areas
Backfilled Areas
Capped Areas
Dams and Locks
Area of Interest
2016 Tri+ PCB Aroclors
2017 Tri+ PCB Aroclors
2021 Tri+ PCB Aroclors

Tri+ PCB (mg/kg)

- < 0.1
- 0.1-0.3
- 0.3-1.0
- 1.0-3.0
- 3.0-10.0
- 10.0-30.0
- > 30.0

Sediment Type

Silt
Silt and Sand
Gravel
Transitional
Bed Rock
River Mile

✓ Locations with comparatively higher concentrations

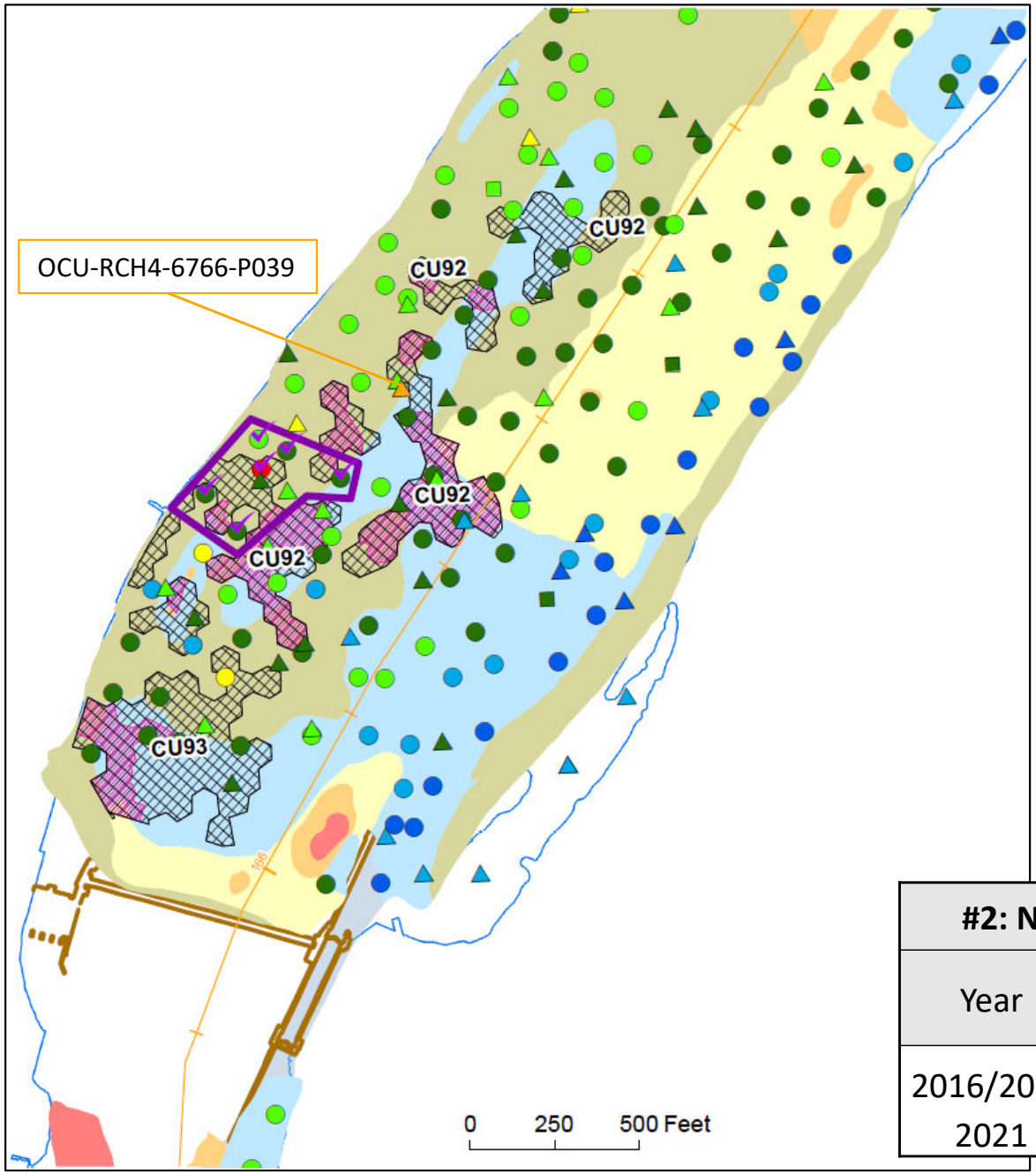
N

#1: Near Galusha Island (~21 acres)				
Year	Count	Tri+ PCB (mg/kg)		
		Max	Min	Average
2016/2017	20	43	1.0	8.1
2021	15	8.0	0.69	3.5

Area of Interest Near Galusha Island between RM 188 and 187 in RS 2/Reach 7

Figure A2-11a

July 2024



Shoreline
Dredged Areas
Backfilled Areas
Capped Areas
Dams and Locks
Area of Interest
2016 Tri+ PCB Aroclors
2017 Tri+ PCB Aroclors
2021 Tri+ PCB Aroclors

Tri+ PCB (mg/kg)

- < 0.1
- 0.1-0.3
- 0.3-1.0
- 1.0-3.0
- 3.0-10.0
- 10.0-30.0
- > 30.0

Sediment Type

- Silt
- Silt and Sand
- Gravel
- Transitional
- Bed Rock
- River Mile

✓ Locations with comparatively higher concentrations

N

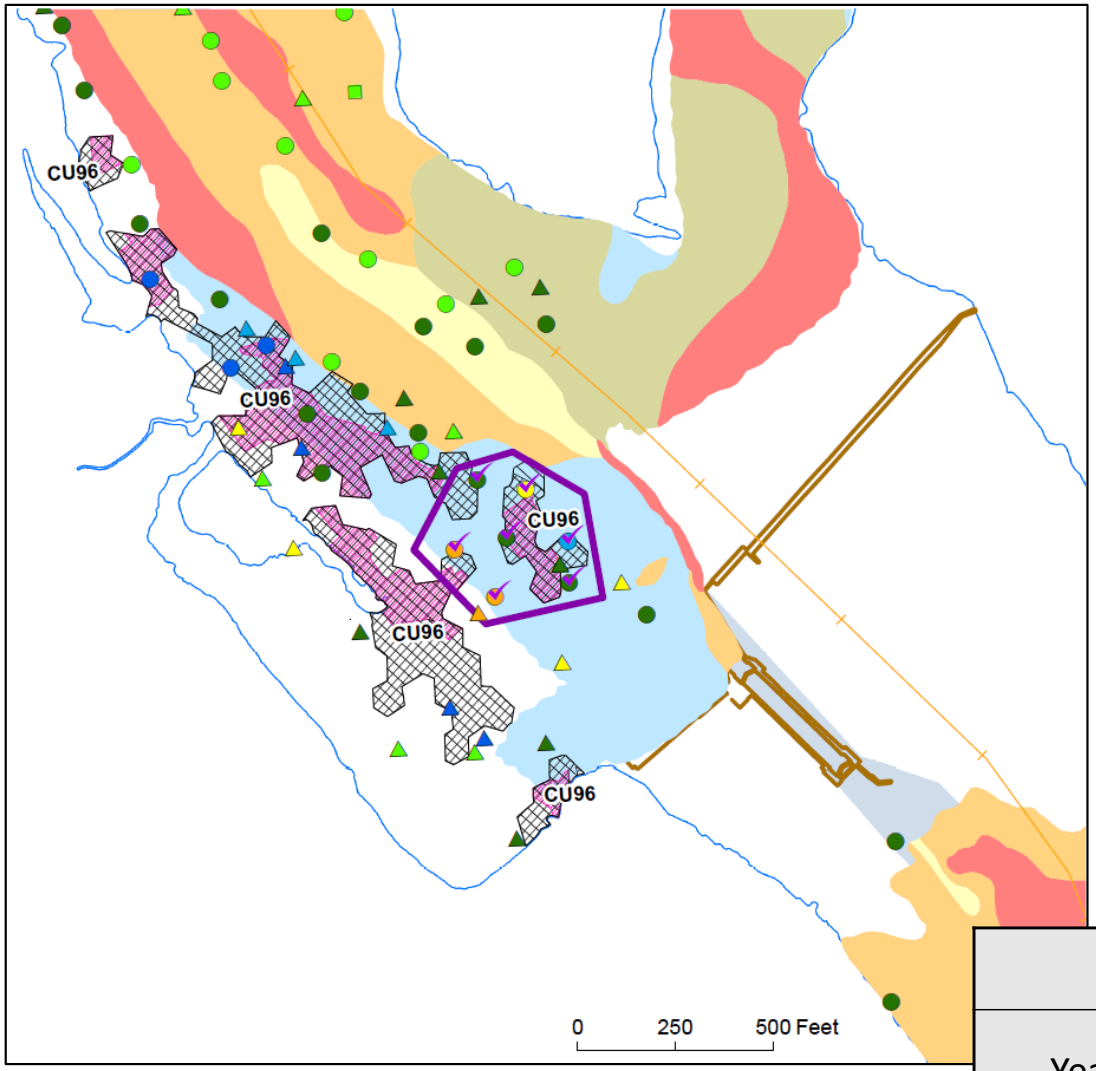
#2: Near Upper Mechanicville Dam (~2.5 acres)

Year	Count	Tri+ PCB (mg/kg)		
		Max	Min	Average
2016/2017	6	33	0.71	6.4
2021	5	3.7	0.44	1.7

Area of Interest Near the Upper Mechanicville Dam, north of RM 166 in RS 3/Reach 4

Figure A2-11b

July 2024



Shoreline
Dredged Areas
Backfilled Areas
Capped Areas
Dams and Locks
Area of Interest
2016 Tri+ PCB Aroclors
2017 Tri+ PCB Aroclors
2021 Tri+ PCB Aroclors

Tri+ PCB (mg/kg)

- < 0.1
- 0.1-0.3
- 0.3-1.0
- 1.0-3.0
- 3.0-10.0
- 10.0-30.0
- > 30.0

Sediment Type

- Silt
- Silt and Sand
- Gravel
- Transitional
- Bed Rock

River Mile

✓ Locations with comparatively higher concentrations

N

#3: near Lower Mechanicville Dam (~3 acres)				
Year	Count	Tri+ PCB (mg/kg)		
		Maximum	Minimum	Average
2016/2017	7	22	0.15	7.3
2021	4	13	0.45	4.0

Area of Interest Near the Lower Mechanicville Dam, between RM 164 and 163 in RS 3/Reach 3

Figure A2-11c

July 2024

Third Five-Year Review Report for the Hudson River PCBs Superfund Site

APPENDIX 2

ATTACHMENT A

RE-QUANTIFICATION OF AROCLOR 1221 IN 2017 SAMPLES

Prepared by:
WSP USA Solutions Inc.

July 2024

THIRD FIVE-YEAR REVIEW REPORT FOR THE HUDSON RIVER PCBs SUPERFUND SITE

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1 INTRODUCTION

During the data evaluation in 2021, the U.S. Environmental Protection Agency (EPA) revisited the high surrogate 2,4,5,6-Tetrachloro-Meta-Xylene (TCMX) recovery issue in the 2017 New York State Department of Environmental Conservation (NYSDEC) surface sediment data, which was initially identified in 2019. This new review identified that Aroclor 1221 was being under reported (overall biasing the results low) due to coelution of the chromatographic PCB Peak 2 used in quantifying Aroclor 1221 and the surrogate TCMX. Pace Analytical Services in Minneapolis analyzed these samples. The standard operating procedure (SOP) of the GE Hudson River (GEHR) Method 8082 (M8082) requires Aroclor 1221 to be quantified by five chromatographic PCB Peaks, as shown in Figure 1-1. Two surrogates, TCMX and decachlorobiphenyl (DCBP), are routinely added to each sample to monitor sample recovery. When comparing the retention times of five Peaks to that of TCMX, Peak 2, used for the Aroclor 1221 quantification, elutes immediately before the TCMX peak. The unlabeled peak that falls between Peak 1 and Peak 2 is not used in quantifying Aroclor 1221.

When comparing the EPA/GE 2021 and NYSDEC 2017 data, it was noted that the laboratory incorrectly identified the Peak 2 in quantifying Aroclor 1221 in the 2017 samples. An incorrect Peak 2 was selected because the correct Peak 2 was not adequately resolved (i.e., separated) from the TCMX peak. The coelution of the correct Peak 2 and the TCMX peak resulted in apparent high TCMX recoveries, a phenomenon which was first observed during the initial review of the NYSDEC 2017 data (EPA, 2019). At the time EPA was unaware that the steps used by General Electric Company's (GE's) laboratory (also a division of Pace Analytical), pursuant to M8082, to separate Peak 2 and TCMX were not conducted by the Pace Analytical laboratory used by NYSDEC. EPA concluded at the time that there was no data quality issue, as it appeared Peak 2 was resolved from TCMX.

To properly resolve the correct Peak 2 from the TCMX peak, the laboratory needs to use the appropriate column with correct operating parameters (e.g., hydrogen gas flow and temperature program) as documented in the M8082 SOP. This SOP requires the use of column ZB-1MS (diameter 0.18 mm), while Pace Analytical working for NYSDEC used column ZB-1-579513 (diameter 0.32 mm). To illustrate the issue, the chromatograms of Aroclor 1221 calibration standards from both datasets are presented in Figure 1-2. The chromatograms show that the correct Peak 2 was distinctly resolved from the TCMX peak in the 2021 Aroclor 1221 standard run for GE, but not in the 2017 Aroclor 1221 standard run for NYSDEC. Consequently, in the 2017 Aroclor 1221 quantification, the unknown peak located between Peak 1 and the coeluting Peak 2/TCMX peak was erroneously identified as Peak 2 and used in the quantification.

This misidentification of Peak 2 is not expected to affect the calibration results, because both peaks exhibit similar responses (i.e., peak area) in the calibration standards (top panel of Figure 1-1 and left panel of Figure 1-2). That is, the peak areas determined for the correct Peak 2 and the unknown

peak (misidentified Peak 2) are similar enough in the Aroclor 1221 standard that the ratio of the calibration standard mass to instrument response (i.e., the Aroclor 1221 response factor) is expected to be the same regardless of which peak is used.

However, this is not the case for actual Upper Hudson River (UHR) samples. As a result of PCB dechlorination in field samples, which increases the proportion of lower-chlorinated congeners, the correct Peak 2 generally has a higher peak area than the misidentified Peak 2. This can be seen in the example chromatogram from a GE 2021 sample shown in Figure 1-3 (left panel), and a more thorough comparison using a subset of GE 2021 samples presented in Figure 1-4. The 2021 sample data used the correct Peak 2 but also reported the peak area for the incorrect peak misidentified and used in the NYSDEC 2017 data. In Figure 1-4, the ratios of areas from the correct Peak 2 to the misidentified Peak 2 were plotted against Aroclor 1221 concentrations. The plot illustrates that for nearly all of the samples, the correct Peak 2 area is larger than the misidentified peak area (i.e., ratios greater than 1), and in most instances the correct Peak 2 area is more than 10 times greater than the misidentified peak.[1] Moreover, the ratio of the two areas increases as the Aroclor 1221 concentration increases. This observation indicates that the misidentification of Peak 2 generally leads to biased-low results for Aroclor 1221 in the NYSDEC 2017 field samples.

It should be noted that this quantification issue is specific to Aroclor 1221. All other Aroclors were quantified using the correct peaks following M8082 for the NYSDEC 2017 samples. This attachment describes the procedures EPA has taken to correct the reported Aroclor 1221 results for the NYSDEC 2017 samples. It also discusses the impact of this correction on the concentrations of Aroclor 1221, Tri+ PCB, and TPCB.

2 METHODS USED FOR RE-QUANTIFYING AROCLOR 1221

Estimation of the Correct Peak 2 Area

To correct the Aroclor 1221 data, the first step is to correctly identify Peak 2 and determine its area. The method for estimating the correct Peak 2 area varies depending on the chromatographic resolution of the correct Peak 2 observed in the sample. The resolution of Peak 2 is essentially defined by three conditions, resulting in three separate correction processes. The 2017 NYSDEC samples were grouped according to these conditions. Figure 2-1 shows an example sample chromatogram from each of these three groups.

For the first group of samples, defined as Group 1, Aroclor 1221 is not detected, and the correct Peak 2 is absent. Therefore, there is no need for re-quantification. The reporting limit does not

[1] While this plot indicates a substantial underestimation of the Peak 2 area, it does not translate directly to a proportional increase in the Aroclor 1221 concentration. This is because Peak 2 is one of five peaks used to quantitate Aroclor 1221. As a result, while it is clear that incorrectly identifying Peak 2 leads to underestimation of Aroclor 1221, it is not possible to directly infer the exact degree of underestimation of Aroclor 1221 from the change in Peak 2 area alone.

need adjustment either, because the reporting limit is based on the lowest calibration standard and the misidentification of Peak 2 does not affect the calibration data, as noted above. There are a total of 182[2] NYSDEC samples under this category. These samples are considered accurately quantitated, and no additional uncertainty is associated with the reported reporting limit.

For the second group of samples, defined as Group 2, Aroclor 1221 is detected, and the correct Peak 2 can be identified as either partially or fully resolved from the TCMX peak.[3] There are two samples with fully resolved Peak 2 and 68 samples with partially resolved Peak 2. For these samples, the correct Peak 2 was identified as the front split of the TCMX peak (in the case of partially resolved samples) or as a peak that eluted immediately before the TCMX peak (in the case of fully resolved samples). In such cases, the area of the correct Peak 2 (although misidentified) was reported in the laboratory package and does not require any estimation. This correct Peak 2 area was then used along with other peak areas to re-calculate the Aroclor 1221 concentrations per Equation 3 discussed in the next subsection. There is no additional uncertainty associated with such a calculation.

For the third group of samples, defined as Group 3, Aroclor 1221 is detected but the correct Peak 2 is not resolved from TCMX. A total of 1,026 samples fall into this group. For these samples, the correct Peak 2 area had to be estimated using Equation 1, based on the surrogate recoveries ($\%R_{TCMX}$ *and* $\%R_{DCBP}$) in the batch-specific method blank and in the field sample, as well as the peak area of TCMX in the sample.

The explanation and derivation for the basis of this equation is as follows:

$$A_{Peak2,sample} = \frac{\%R_{Peak2+TCMX,sample} - \left(\frac{\%R_{TCMX}}{\%R_{DCBP}}\right)_{blank} \times \%R_{DCBP,sample}}{\%R_{Peak2+TCMX,sample}} \times A_{Peak2+TCMX,sample} \qquad \text{(Eq. 1)}$$

Where,

$A_{Peak2,sample}$ is the estimated correct Peak 2 area in the sample.

$\%R_{Peak2+TCMX,sample}$ is the reported TCMX recovery in the sample, which represents the recovery from the coeluting TCMX peak and correct Peak 2.

$\%R_{DCBP,sample}$ is the reported DCBP recovery in the sample.

$A_{Peak2+TCMX,sample}$ is the reported TCMX peak area in the sample, which represents the area from the coeluting TCMX peak and correct Peak 2.

$\left(\frac{\%R_{TCMX}}{\%R_{DCBP}}\right)_{blank}$ is the ratio of TCMX recovery to DCBP recovery in the batch-specific method blank

[2] Sample counts discussed in this section include all NYSDEC samples collected in 2017, although only samples from main stem are used in the FYR evaluation.
[3] As discussed above, the original quantification of these samples did not correctly identify this peak as Peak 2.

This estimation method is based on several underlying premises:

- The recovery rates of TCMX and DCBP are closely correlated with each other. They do not need to be the same, but the recovery of DCBP needs to be a good predictor of the recovery of TCMX. This is expected because most factors impacting surrogate recovery will tend to impact both of these surrogates in a similar manner.
- The ratio of the recovery rates for a sample group can be best approximated by the associated method blank. That is, variations relative to the mean recovery ratio are largely specific to a sample delivery group (including the associated method blank). A sample delivery group generally reflects a specific set of laboratory operating conditions (i.e., extraction equipment, operating procedures, instrument parameters and laboratory staff) that influence the overall rates of surrogate and PCB recoveries.
- The recovery rate of a surrogate compound is proportional to its peak area under the same analytical run. This is true per the calculation presented in Equation 2.

Given the above three premises, Figure 2-2 illustrates the steps by which Equation 1 was derived.

The terms used in Equation 1 were available in the laboratory deliverables provided by NYSDEC. The surrogate recoveries in the method blank $\left(\frac{\%R_{TCMX}}{\%R_{DCBP}}\right)_{blank}$ and the peak area of the coeluting Peak 2/TCMX in the sample ($A_{TCMX+Peak2,sample}$) were obtained from laboratory packages. The surrogate recoveries in the samples were found in the laboratory electronic database (EDD).

However, for a subset of 16 samples, the surrogate recoveries reported in the EDD were not those associated with the Aroclor 1221 analysis but rather were derived from a different analysis run using a different dilution factor from those used in Aroclor 1221 reporting. For these samples, the surrogate recoveries were re-calculated using the information associated with the Aroclor 1221 run, per Equations 2a and 2b below.

$$Measured\ Surrogate\ Concentration = \frac{Area}{RF} \times DF_{A1221} \times \frac{5{,}000}{1 \times W} \quad \text{(Eq. 2a)}$$

$$\%\ R_{i,sample} = \frac{Measured\ Surrogate\ Concentration}{Spiked\ Surrogate\ Concentration} \quad \text{(Eq. 2b)}$$

Where,

$\%R_{i,sample}$ is the surrogate recovery in the sample as defined in Equation 1.

i is either Peak2+TCMX or DCBP

Area is the peak area of the surrogate (Peak2+TCMX or DCBP) from the sample chromatogram that was used to quantify Aroclor 1221.

RF is the average response factor of the surrogate (Peak2+TCMX or DCBP) for the calibration standards. Response factor was calculated as the ratio of peak area to concentration (in µg/mL) in the calibration standard.

DF_{A1221} is the dilution factor associated with the Aroclor 1221 analysis.

5,000 is volume of final extract in microliter (µL).

1 is volume injected for analysis in µL.

W is the weight of sample extracted in grams.

Spiked Surrogate Concentration is the actual lab-spiked concentrations in the sample.

Area and RF were obtained from the laboratory packages, and other input parameters were from the EDD.

After determining all the input values for these 16 samples per Equations 2a and 2b, Equation 1 was used to calculate the area of the correct Peak 2.

In general, the estimated area of the correct Peak 2 from Equation 1 is expected to be equal to or greater than the area of the misidentified Peak 2 due to the increased presence of lower molecular weight PCB congeners in the sample as a result of dechlorination in the environment (as illustrated in Figure 1-4). This was the case for 856 of the 1,026 (83 percent) NYSDEC samples in this category (i.e., Group 3). However, the recalculation resulted in zero or negative estimated Peak 2 area values for 162 samples, as well as smaller positive estimated Peak 2 area than the misidentified Peak 2 area for eight samples. The negative values are primarily due to uncertainty in the surrogate recoveries in the sample and method blank when the Peak 2 contribution to the coeluting Peak 2/TCMX was small. Uncertainty in the Peak 2 value increases when the areas of the estimated TCMX peak and the coeluting Peak 2/TCMX approach each other, sometimes resulting in negative values for Peak 2. A value of zero was assigned for samples where a negative Peak 2 area was obtained.

In the instances where the estimated Peak 2 area was positive but less than the misidentified Peak 2 area, the calculated Peak 2 area was used. This is based on the fact that the lighter congeners present in UHR sediment samples are largely the result of dechlorination and not the release of Aroclor 1221. Thus, no strict relationship should be expected between Peak 2 and other peaks in the Aroclor 1221 spectrum. The misidentified Peak 2 has not been established as a basis for quantitation of Aroclor 1221 or Aroclor-1221-like PCBs and thus should not be used.

Application of the Corrected Peak 2 Areas

After obtaining the correct Peak 2 areas for Group 2 (fully/partially resolved Peak 2) and Group 3 (unresolved Peak 2) samples, the values were used along with the areas of the other four Peaks to recalculate the Aroclor 1221 concentration for each sample per Equation 3 below.

$$C_{.A1221} = \frac{\frac{(A_{Total} - A_{p2,wrong} + A_{p2,\,correct}) - b}{a} \times DF \times V_t}{V_i \times W_S \times (\frac{100 - M}{100})} \qquad \text{(Eq. 3)}$$

Where,

A_{Total} : sum of areas of misidentified Peak 2 and the other four Peaks, obtained from the laboratory package

$A_{p2,wrong}$: area of the misidentified Peak 2, obtained from the laboratory package

$A_{p2,correct}$: area of the correct Peak 2, obtained from the laboratory package for Group 2 and Equation 1 for Group 3

a : slope of calibration curve, obtained from the laboratory package

b : intercept of calibration curve, obtained from the laboratory package

DF : dilution factor, unitless, obtained from the EDD

V_t : volume of final extract in µL, obtained from the EDD

V_i : volume injected in µL, obtained from the EDD

W_s : weight of sample extracted in grams, obtained from the EDD

M : % moisture, obtained from the EDD

Out of the 1,097 samples collected by NYSDEC in 2017 that showed detectable Aroclor 1221 results, one sample, HR17-OU2-R5-083_20170720, was missing its raw chromatogram data. As a result, this particular sample was not included in either Group 2 or Group 3. The reported Aroclor 1221 concentration for this sample was 55.9 micrograms per kilogram (µg/kg), which is an estimated "J" value below the quantitation limit of 57.8 µg/kg. Additionally, the TCMX surrogate recovery in this sample was low, at 64 percent. The low Aroclor 1221 concentration and the low TCMX surrogate recovery suggest that Peak 2 component in the coeluting Peak 2/TCMX is small. Therefore, even though Peak 2 was misidentified, it is unlikely to have a significant impact on the Aroclor 1221 concentration in this sample. As a result, the original reported Aroclor 1221 value was used for this sample due to the lack of raw data.

3 RESULTS FOR AROCLOR 1221 RE-QUANTIFICATION

Figure 3-1 compares the original and recalculated Aroclor 1221 concentrations in the samples where Aroclor 1221 was detected (i.e., Groups 2 and 3 combined). The results show that the vast majority of the recalculated Aroclor 1221 concentrations are higher than the original concentrations. For a subset of the samples (225 samples, 20 percent of Groups 2 and 3 combined), the corrected Aroclor 1221 value was more than twice the original value.

Table 3-1 presents the effects of this adjustment on the geometric means of Aroclor 1221, total PCB (TPCB), and Tri+ PCB concentrations in dredged and non-dredged areas at the river section scale as well as the entire UHR, using samples from the main stem of the UHR. TPCB was calculated as the sum of all Aroclors reported by M8082. Tri+ PCB was estimated from GE's equation below (GE, 2011):

$$\text{Tri+ PCB} = 0.13 \times \text{Aroclor 1221} + 0.89 \times (\text{Aroclor 1242} + \text{Aroclor 1254}) \qquad \text{(Eq. 4)}$$

The results shown in Table 3-1 indicate that the geometric mean concentration of Aroclor 1221 increased by 35 to 90 percent across the six strata evaluated: three river sections and two areas (dredged and non-dredged). The level of adjustment is greater in the dredged areas than in the non-dredged areas. Among the six strata, the largest increase was observed in RS 3 dredged area, while the smallest increase was observed in RS 1 non-dredged area. TPCB concentrations increased by 15 to 36 percent, while Tri+ PCB concentrations increased by 3 to 9 percent.

The data suggest that Aroclor 1221 showed the most significant increase, followed by TPCB, with Tri+ PCB exhibiting the smallest increase. This is because Aroclor 1221 constituted about 40 percent of TPCB on average (as shown in the Aroclor composition chart discussed in Section 4 below), while only 13 percent of Aroclor 1221 concentration is factored into the Tri+ PCB calculation (as per Equation 4).

4 VALIDATION OF RECALCULATED AROCLOR 1221

Comparison to congener-based measurements

One approach to assess the validity of the recalculated Aroclor 1221 results in 2017 samples is to compare them with the congener-based measurements. A subset of samples from 2017 and 2021 (i.e., matched pairs) were analyzed for PCBs using both M8082 and a congener-based method (M1668). It is expected that the difference between the Aroclor-based and congener-based measurements should be consistent in the post-dredging samples collected in 2017 and 2021, because the general PCB pattern is not expected to change rapidly during this relatively short interval.

To compare the Aroclor-based and congener-based measurements between programs, the ratios of the congener-based to Aroclor-based results were calculated for TPCB and Tri+ PCB using the matched pair samples in 2017 and 2021. The congener to Aroclor ratio in 2017 samples was calculated using both the original and the recalculated Aroclor 1221 concentrations. The results in Figure 4-1 show that the geometric mean of the TPCB ratios derived from the original 2017 Aroclor 1221 is about 17 percent higher than the ratios from the recalculated 2017 Aroclor 1221 concentrations and the 2021 data, and the ratios from the recalculated 2017 concentrations are more consistent with those from the 2021 samples. Unlike the TPCB ratio, the changes in the Tri+ PCB ratio in the 2017 samples using the recalculated Aroclor 1221 concentrations were

insignificant. This reflects the small contribution of Aroclor 1221 to the Tri+ PCB calculation (13 percent).

It is also expected that the adjustment of Aroclor 1221 in the 2017 samples should not weaken the correlation between Aroclor-based and congener-based concentrations. To evaluate such correlation, Aroclor-based results (using both original and recalculated Aroclor 1221) were plotted against congener-based results for TPCB in Figure 4-2a and for Tri+ PCB in Figure 4-2b. The Pearson correlation coefficient was calculated based on the log-transformed concentrations. The results in Figure 4-2a indicate that the correlation between the Aroclor-based and congener-based TPCB results remains similar regardless of whether the original Aroclor 1221 concentrations or the recalculated Aroclor 1221 concentrations were used. This suggests that the re-quantification of Aroclor 1221 and the introduction of the uncertainties associated with the re-quantification process did not weaken the correlation of Aroclor-based results with congener-based results. The Tri+ PCB results were presented in Figure 4-2b for completeness, but given the small contribution of Aroclor 1221 to the Tri+ PCB concentrations, no change in the Pearson correlation coefficient was expected.

Comparison of Aroclor composition

Another approach to evaluate the recalculated Aroclor 1221 concentrations in the 2017 samples is to examine the Aroclor composition. It is anticipated that the Aroclor composition should remain similar among samples collected during the post-dredging period in 2016, 2017, and 2021, because (as noted above) the general pattern of PCB congeners is not expected to change rapidly during this relatively short interval. In this analysis, the Aroclor composition reported in the 2017 samples were compared to those reported in the 2016 and 2021 samples, where there was no error in the quantification of Aroclor 1221.

The Aroclor composition was expressed as the mass fraction of Aroclors, which was derived by normalizing the concentration of individual Aroclors to TPCB. To simplify the comparison, the average Aroclor mass fraction was computed for a specific group of samples. For this evaluation, the average mass fraction of Aroclors was calculated for the 2017 samples using both the original and recalculated Aroclor 1221 concentrations and compared to the average mass fraction derived for 2016 and 2021 samples. The results of these calculations are summarized in Figure 4-3. The 2016 and 2021 samples showed that Aroclor 1221 should account for approximately 45 to 50 percent of the TPCB. However, when using the original Aroclor 1221 concentrations in the 2017 samples, Aroclor 1221 only accounted for about 30 percent of TPCB. After adjusting the Aroclor 1221 concentrations in the 2017 samples, its contribution increased to 40 percent of TPCB, which was substantially closer to percentages observed in the 2016 and 2021 samples. The comparison suggests that the original Aroclor 1221 concentrations in the 2017 samples are biased low, and the correction has made the results more consistent with those observed in 2016 and 2021.

5 CONCLUSION

In the analysis of the NYSDEC 2017 sediment samples, the laboratory incorrectly quantified Aroclor 1221 due to the use of a misidentified Peak 2, which was incorrectly used as a basis to quantify this Aroclor. In general, this misidentified peak was less intense than the correct Peak 2 that coeluted with the TCMX surrogate. This resulted in a low bias in the Aroclor 1221 results. Regardless of its relationship to the correct Peak 2, however, the use of the misidentified peak in the analysis was incorrect. To address this error, EPA as agreed upon with NYSDEC, evaluated the entire set of Aroclor 1221 results for the NYSDEC 2017 samples. Where Aroclor 1221 was reported as detected, EPA re-quantified the Aroclor 1221 result for all sediment samples.[4] EPA's review of the non-detect results for Aroclor 1221 indicated that no adjustment was required for these samples and their associated reporting limits.

With the incorporation of the revised results, mean PCB concentrations increased throughout the UHR. On a geometric mean basis, TPCB increased by 15 to 36 percent on a river section basis whereas Tri+ PCB concentrations increased by 3 to 9 percent. The smaller change in Tri+ PCB concentrations reflects the smaller contribution of Aroclor 1221 to this PCB parameter.

The re-quantification of Aroclor 1221 in 2017 samples has made the 2017 results more consistent with the results in 2016 and 2021. Specifically, the ratios of the congener-based to Aroclor-based results, and the composition of Aroclors have become more similar across these different datasets.

The recalculated Aroclor 1221 concentrations in the 2017 samples are provided in the Excel file attached to this document.

6 REFERENCES

EPA (United States Environmental Protection Agency). 2019. Technical Memorandum Evaluation of 2016 EPA/GE and 2017 NYSDEC Surface Sediment Data, Hudson River PCBs Superfund Site. Prepared by: Louis Berger and Kern Statistical Services. April.

General Electric (GE). 2011. Corrective Action Memorandum (CAM) No. 3 – Modification of Sediment Residual Monitoring Program – Discontinuing mGBM Analysis of Sediment Samples and Updates of the Regression Coefficients. Memorandum from Emily Chen, Anchor QEA to Bob Gibson, General Electric. August 15, 2011.

_____. 2021. Addendum to Surface Sediment Sampling Work Plan. Hudson River PCBs Superfund Site. Prepared for General Electric by Anchor QEA. October.

[4] A single sample, HR17-OU2-R5-083_20170720, with a "J" flagged concentration of Aroclor 1221 could not be corrected due sample information that was not included in the NYSDEC materials. The remaining 1,096 samples with detectable concentration of Aroclor 1221 were corrected.

APPENDIX 2
ATTACHMENT A
Tables and Figures

Tables

Table 3-1
Comparison of Geometric Mean Concentrations for Aroclor 1221, Tri+ PCB and TPCB using Original and Re-Calculated Aroclor 1221 in NYSDEC 2017 Surface Sediment Samples

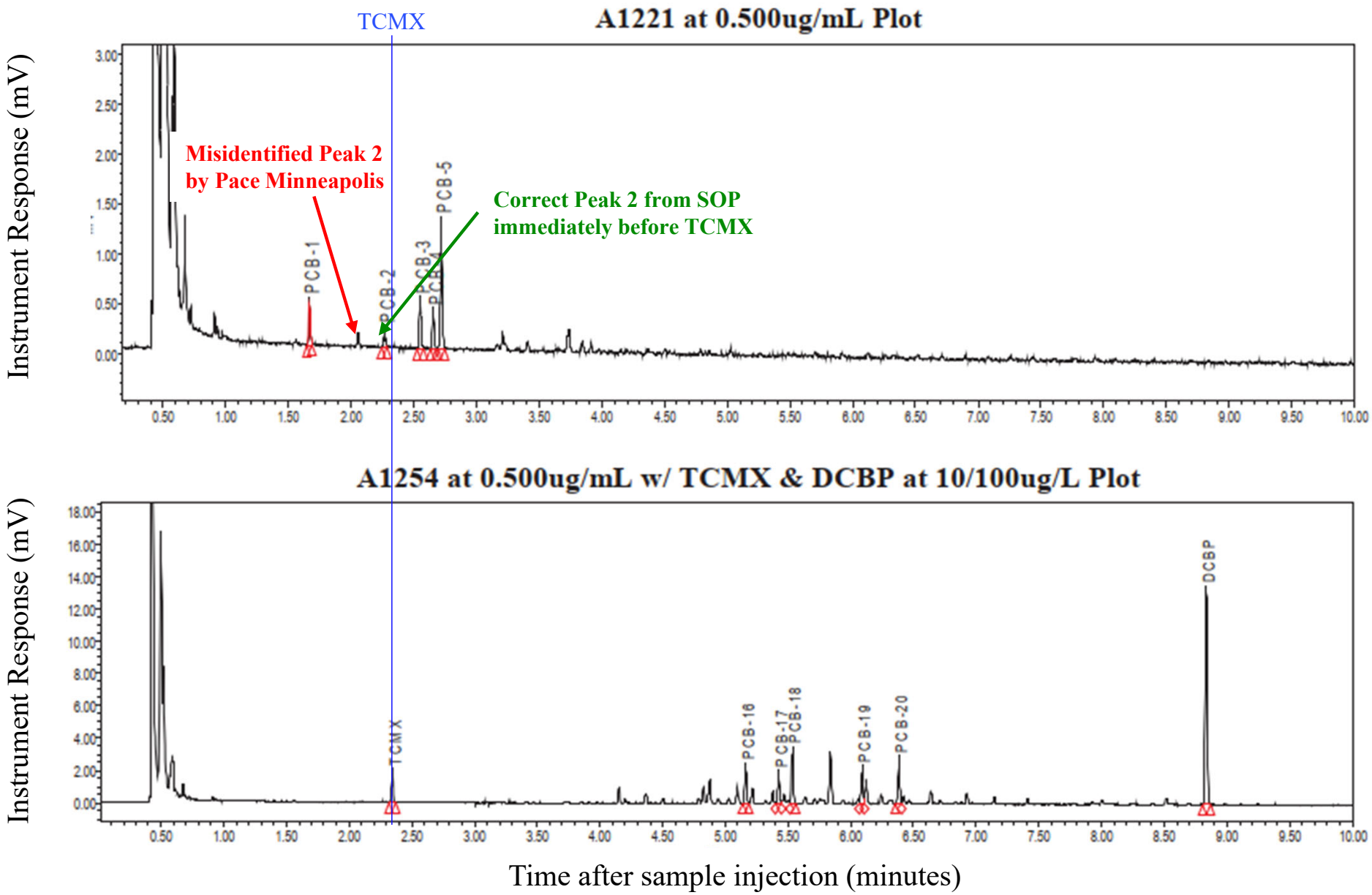
Dredged Areas										
River Section	N	Aroclor 1221			TPCB			Tri+ PCB		
		Original Conc (mg/kg)	Re-Calculated Conc (mg/kg)	Increase (%)	Original Conc (mg/kg)	Re-Calculated Conc (mg/kg)	Increase (%)	Original Conc (mg/kg)	Re-Calculated Conc (mg/kg)	Increase (%)
RS 1	137	0.12	0.17	42%	0.27	0.32	16%	0.19	0.19	4%
RS 2	57	0.30	0.51	70%	0.73	0.94	30%	0.44	0.47	7%
RS 3	47	0.18	0.34	90%	0.48	0.66	36%	0.30	0.32	9%
UHR	**241**	0.16	0.26	62%	0.39	0.49	25%	0.25	0.27	6%

Non-Dredged Areas										
River Section	N	Aroclor 1221			TPCB			Tri+ PCB		
		Original Conc (mg/kg)	Re-Calculated Conc (mg/kg)	Increase (%)	Original Conc (mg/kg)	Re-Calculated Conc (mg/kg)	Increase (%)	Original Conc (mg/kg)	Re-Calculated Conc (mg/kg)	Increase (%)
RS 1	55	0.41	0.55	35%	1.3	1.4	16%	0.77	0.81	4%
RS 2	100	0.98	1.5	51%	2.7	3.2	22%	1.6	1.7	6%
RS 3	682	0.22	0.30	38%	0.66	0.76	15%	0.44	0.45	3%
UHR	**837**	0.33	0.47	43%	0.95	1.1	17%	0.60	0.63	4%

Notes:

1. Samples collected from the main stem were included in the calculation. Samples from landcuts and tributaries were excluded.
2. Parent and field duplicate samples results were averaged before calculating the statistics.
3. Half reporting limits (RL) were assigned to samples with non-detected concentrations.
4. River Section data represents the reach geometric means weighted by reach areas across reaches in a specific river section.
5. Upper Hudson River (UHR) data represents the reach geometric means weighted by reach areas across eight reaches.

Figures



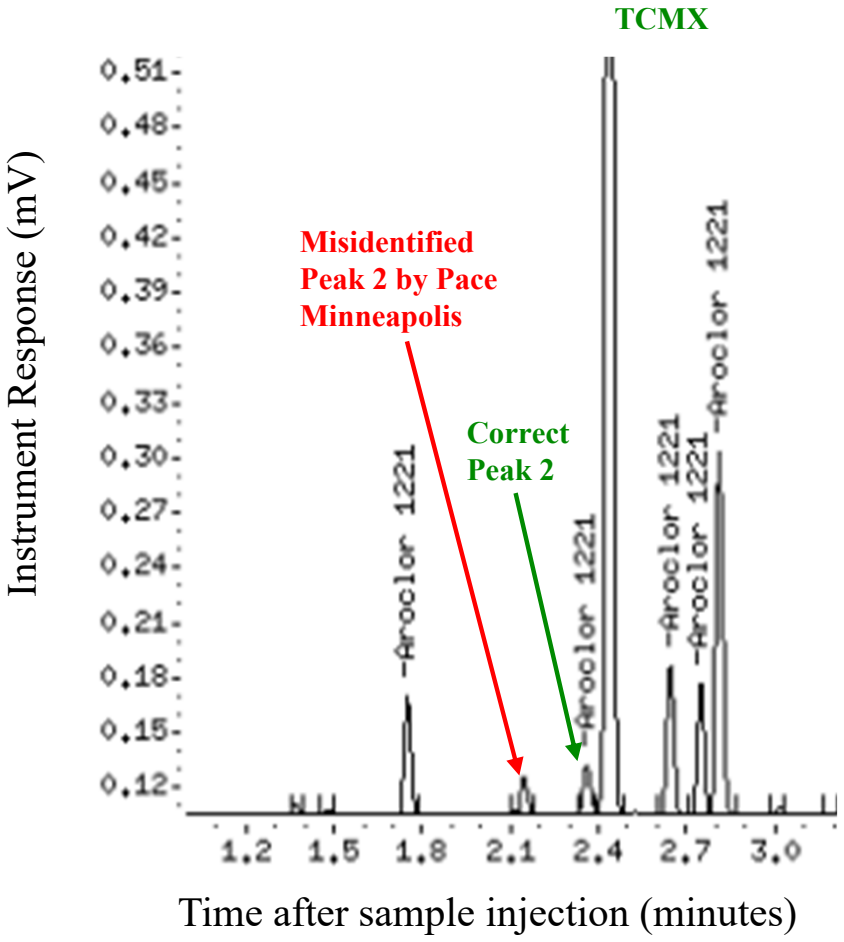
Source: Attachment 4 to GE (2021)

Chromatograms for Aroclor 1221 and Aroclor 1254 Calibration Standards from M8082 SOP

Figure 1-1

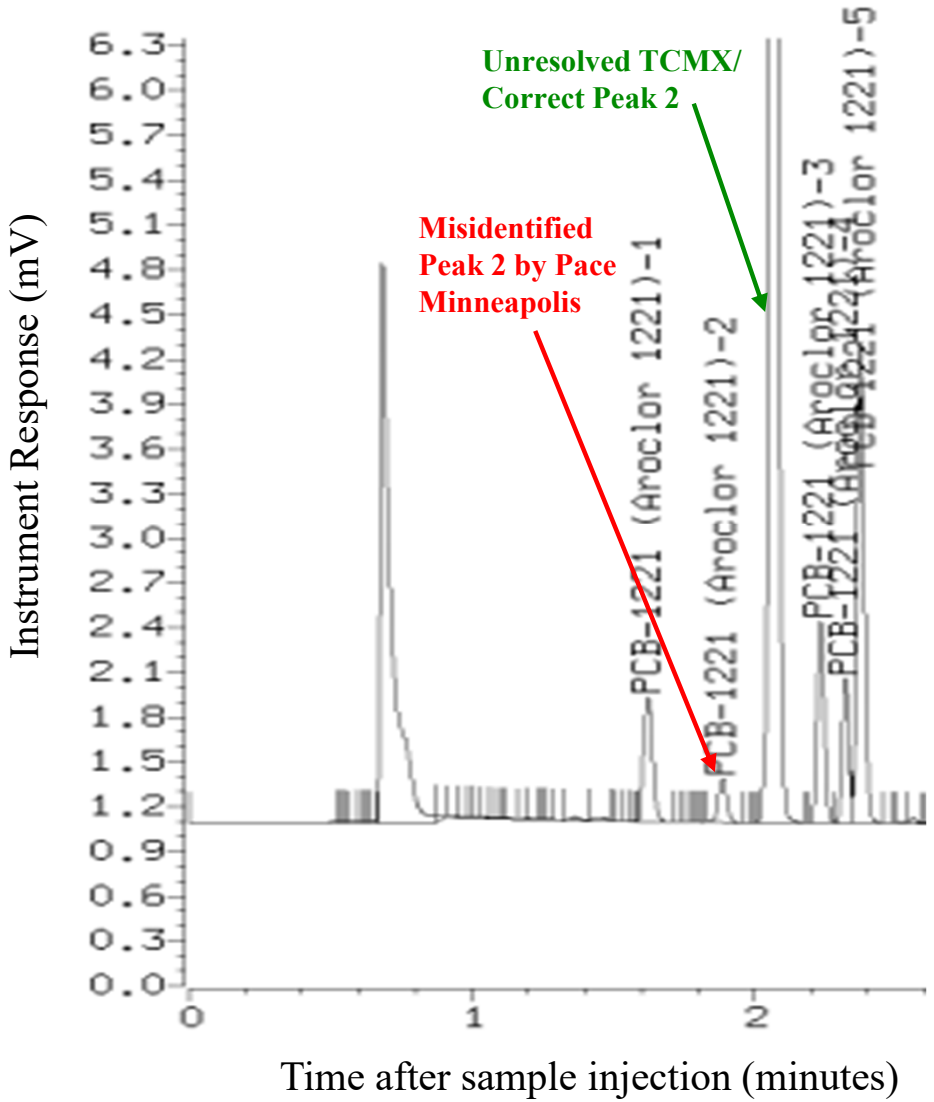
July 2024

Aroclor 1221 Calibration Standard GE 2021



The correct Peak 2 has similar response to the misidentified Peak 2 in the calibration standard

Aroclor 1221 Calibration Standard NYSDEC 2017



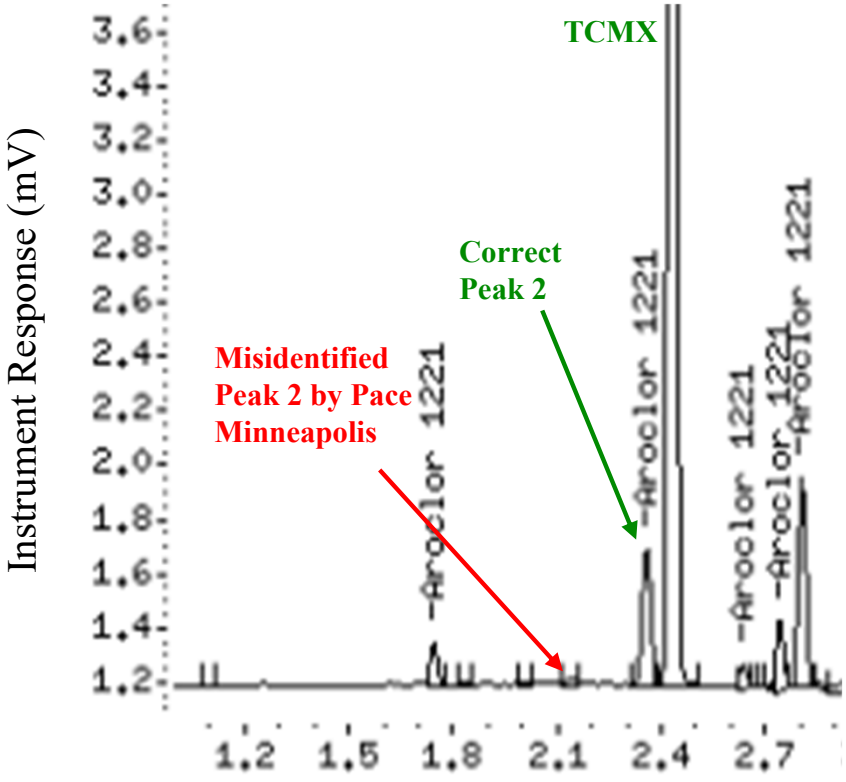
Example Chromatograms for Aroclor 1221 Calibration Standard in 2021 and 2017

Figure 1-2

July 2024

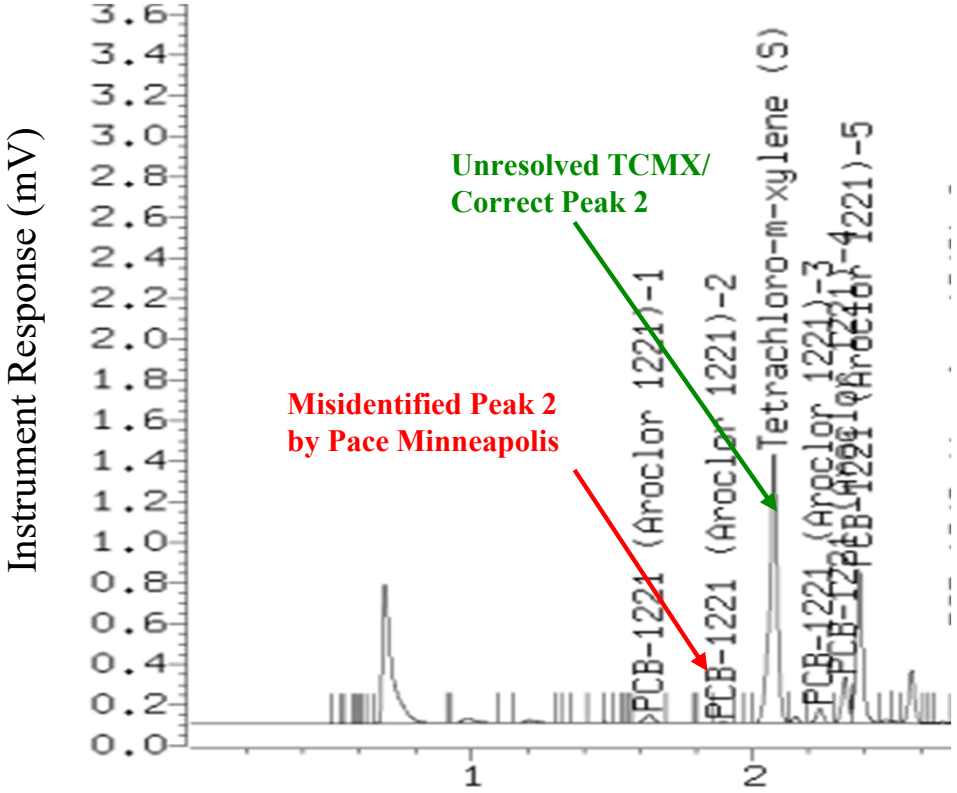
GE 2021 Sample

Sample: ICU-RCH6-8685-P007



NYSDEC 2017 Sample

Sample: HR17-OU2-R7-034

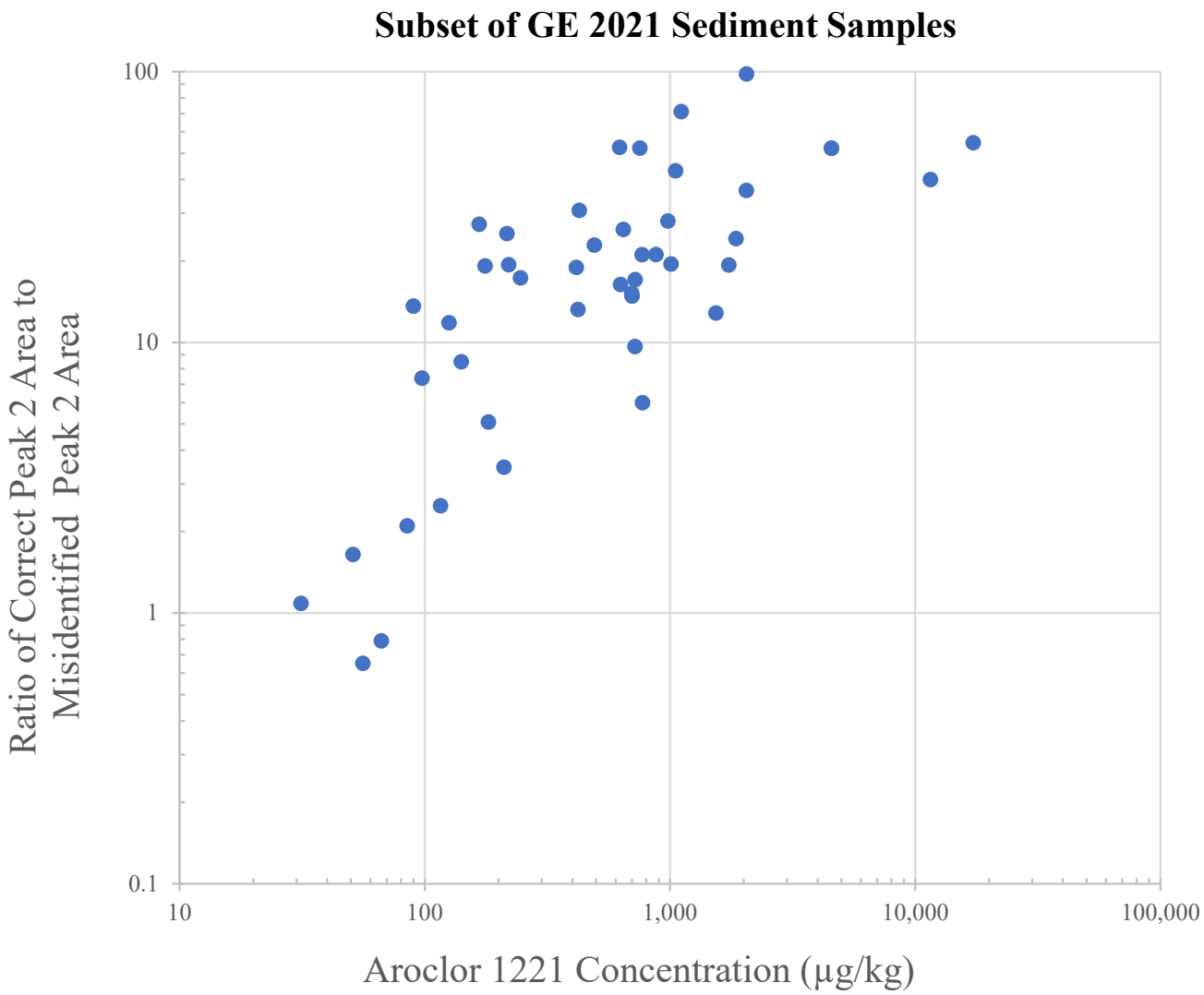


The correct Peak 2 has a higher response than the misidentified Peak 2 in the field sample

Example Chromatograms for GE 2021 and NYSDEC 2017 Field Samples

Figure 1-3

July 2024



Note:
This plot only includes 2021 0-2 inch sediment samples that were selected for the analysis of PCB congeners. This subset of samples covers a wide range of PCB concentrations and is also spatially representative.

Areas of Correct Peak 2 vs. the Misidentified Peak 2 in Surface Sediment Samples Collected by GE in 2021

Figure 1-4

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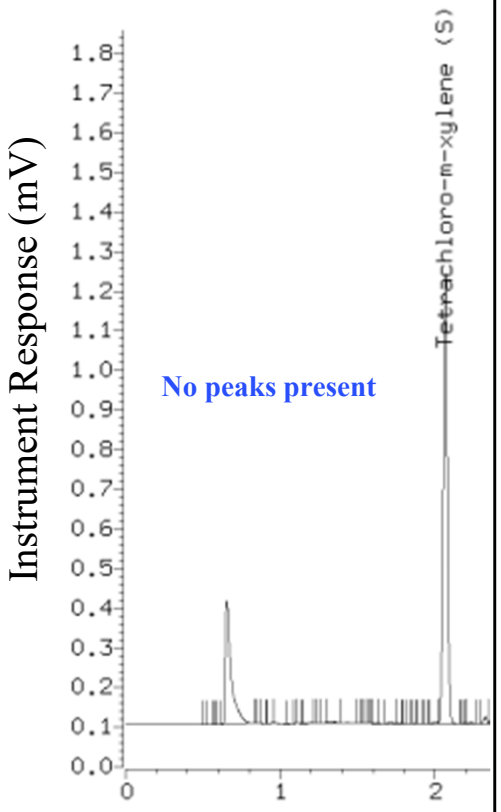
Group 1
Non-Detect Aroclor 1221
(Total: 182 Samples)

Sample: HR17-OU2-R1-083

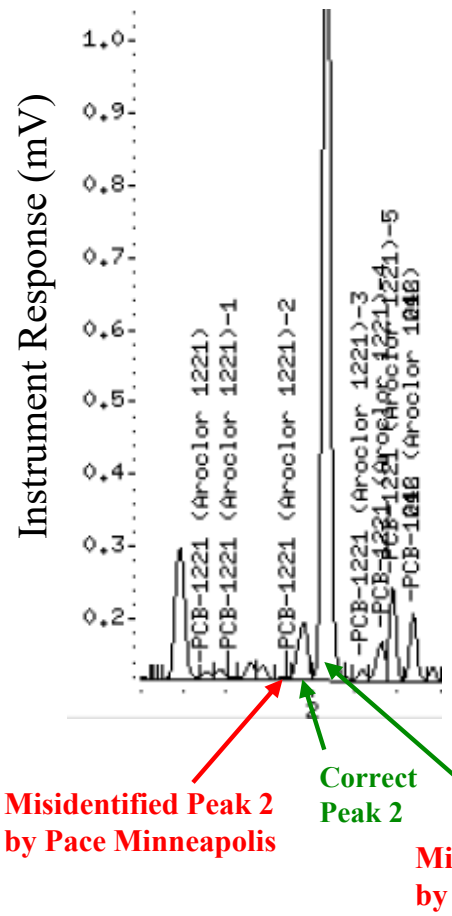


X-axis label for all plots:
Time after sample injection (minutes)

Group 2

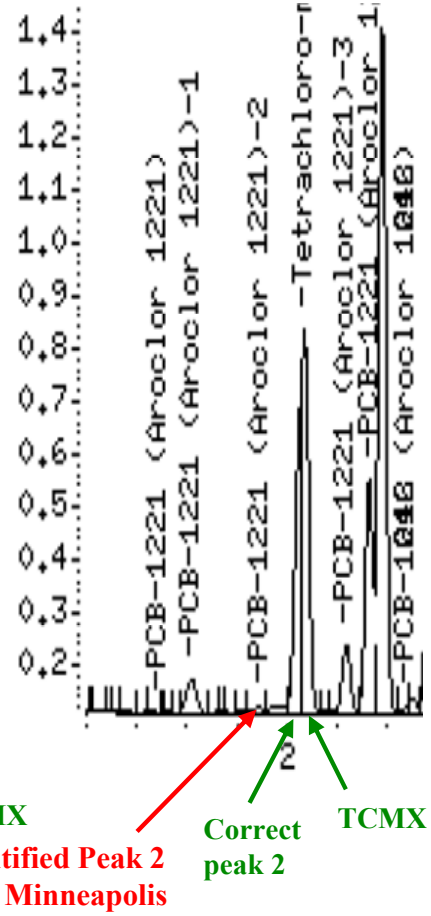
Detected Aroclor 1221 with
Fully Resolved Peak 2
(Total: 2 Samples)

Sample: HR17-OU2-R1-089



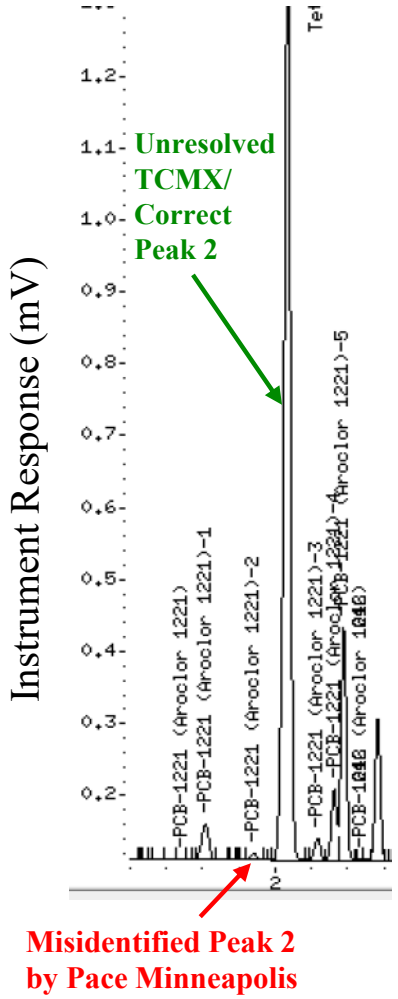
Detected Aroclor 1221 with
Partially Resolved Peak 2
(Total: 68 Samples)

Sample: HR17-OU2-R5-168



Group 3
Detected Aroclor 1221 with
Unresolved Peak 2
(Total: 1,026 Samples)

Sample: HR17-OU2-R5-229



Example Chromatogram from Each of the Three Sample Groups in NYSDEC 2017

Figure 2-1

July 2024

Step 1. Peak 2 area is calculated by subtracting the actual TCMX area from the measured area of co-eluting Peak 2 and TCMX (noted as Peak2+TCMX):

$$A_{Peak2,sample} = A_{Peak2+TCMX,sample} - A_{TCMX,sample} \quad \text{(Eq. 1)}$$

Re-arrange Eq. 1:

$$A_{Peak2,sample} = A_{Peak2+TCMX,sample} \times \left(1 - \frac{A_{TCMX,sample}}{A_{Peak2+TCMX,sample}}\right) \text{(Eq. 2)}$$

Step 2. Because concentration (C) is determined by peak area (A) and response factor (RF) as $C=A/RF$, and the RF is the same for TCMX and Peak2+TCMX, the ratio of peak areas from the TCMX to Peak 2+TCMX is equal to the ratio of their concentrations:

$$\frac{A_{TCMX,sample}}{A_{Peak2+TCMX,sample}} = \frac{C_{TCMX,sample}}{C_{Peak2+TCMX,sample}} \quad \text{(Eq. 3)}$$

Step 3. Because the surrogate recovery is calculated as the ratio of measured concentration to the spiked true concentration, and the spiked concentration is the same for TCMX and Peak 2+TCMXrat, the ratio of the TCMX concentration to Peak 2+TCMX concentration is equal to the ratio of their recoveries:

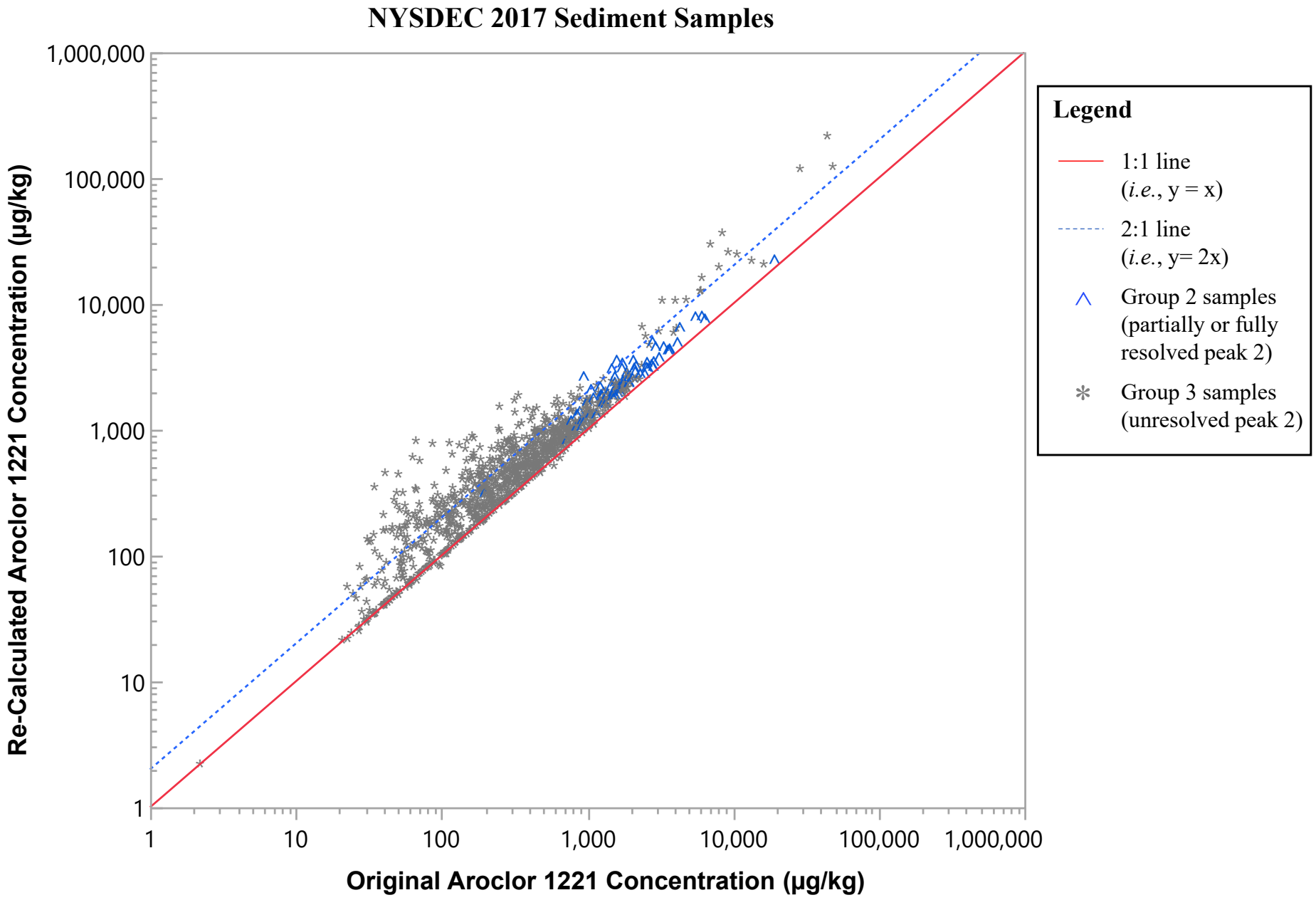
$$\frac{C_{TCMX,sample}}{C_{Peak2+TCMX,sample}} = \frac{\%R_{TCMX,sample}}{\%R_{Peak2+TCMX,sample}} \quad \text{(Eq. 4)}$$

Step 4. Because the ratio of the recovery of TCMX ($\%R_{TCMX,sample}$) to the recovery of DCBP ($\%R_{DCBP,sample}$) in the sample assumes to be the same as their ratio in the method blank, TCMX recovery in the sample can be calculated by multiplying the ratio of surrogate recoveries in the method blank with the DCBP recovery in the sample:

$$\%R_{TCMX,sample} = \left(\frac{\%R_{TCMX}}{\%R_{DCBP}}\right)_{blank} \times \%R_{DCBP,sample} \text{ (Eq. 5)}$$

Step 5: Combining Equations 2 through 5 to derive the final equation (i.e., Equation 1 in the text):

$$A_{Peak2,sample} = \frac{\%R_{Peak2+TCMX,sample} - \left(\frac{\%R_{TCMX}}{\%R_{DCBP}}\right)_{blank} \times \%R_{DCBP,sample}}{\%R_{Peak2+TCMX,sample}} \times A_{Peak2+TCMX,sample}$$



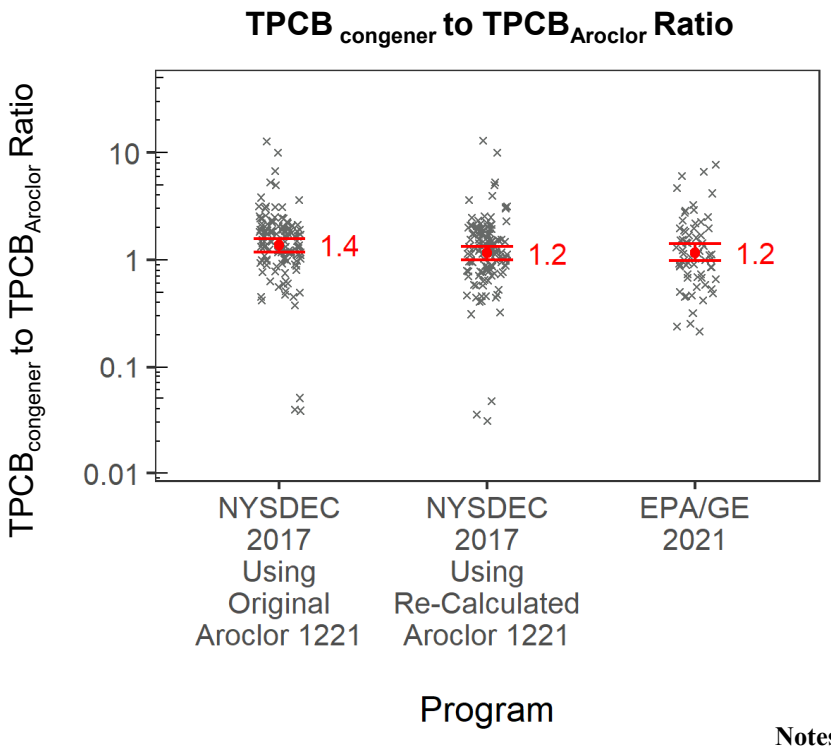
Note:
This figure includes all Group 2 and Group 3 samples, comprised of samples taken from the main stem, tributaries, and landcuts.

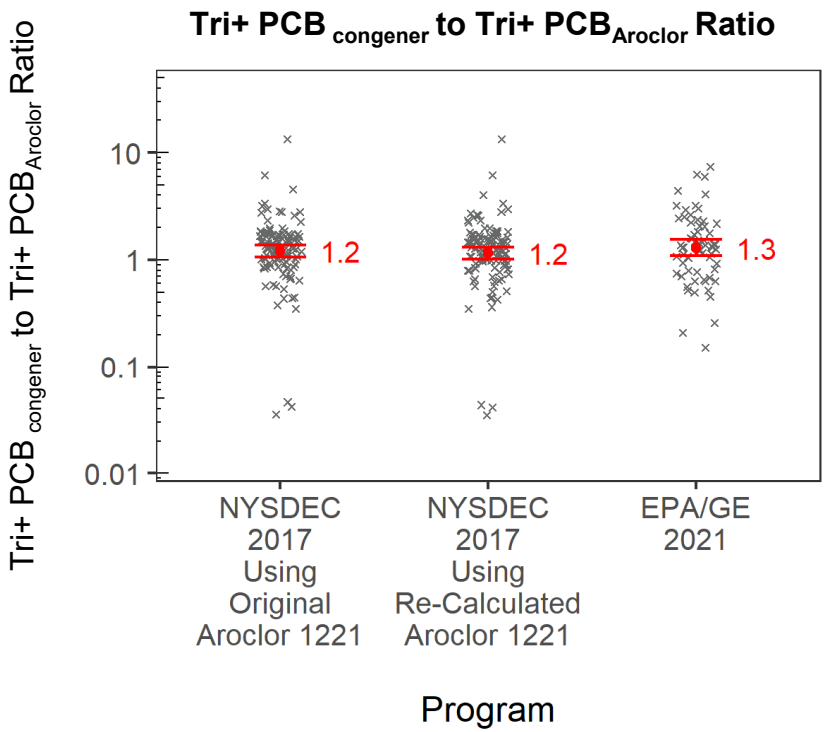
Comparison of the Original and the Re-Calculated Aroclor 1221 Concentrations in NYSDEC 2017 Sediment Samples

Figure 3-1

July 2024

Matched Pair Samples by Program





Legend

- 95% Upper Confidence Limit
- Geometric mean of the ratio
- 95% Lower Confidence Limit
- Individual value

Notes:

- For Aroclor-based results:
  - TPCB is the sum of all Aroclors reported by M8082. Non-detect results were set to zero in the summation.
  - Tri+ PCB concentration is estimated using GE's 2011 equation as: Tri+ PCB = 0.13 × A1221 + 0.89 × (A1242+A1254).
- For congener-based results:
  - TPCB concentration is the sum of 209 congeners reported by M1668. Non-detect results were set to zero in the summation.
  - Tri+ PCB concentration is the sum of congeners with 3 or more chlorine atoms. Non-detect results were set to zero in the summation.
- Figure only includes matched pair samples where both Aroclor-based and congener-based results are detected.
- 95% confidence limits on the geometric mean of the ratio are the bias-corrected and accelerated (BCa) bootstrap 2.5th to 97.5th percentile values.

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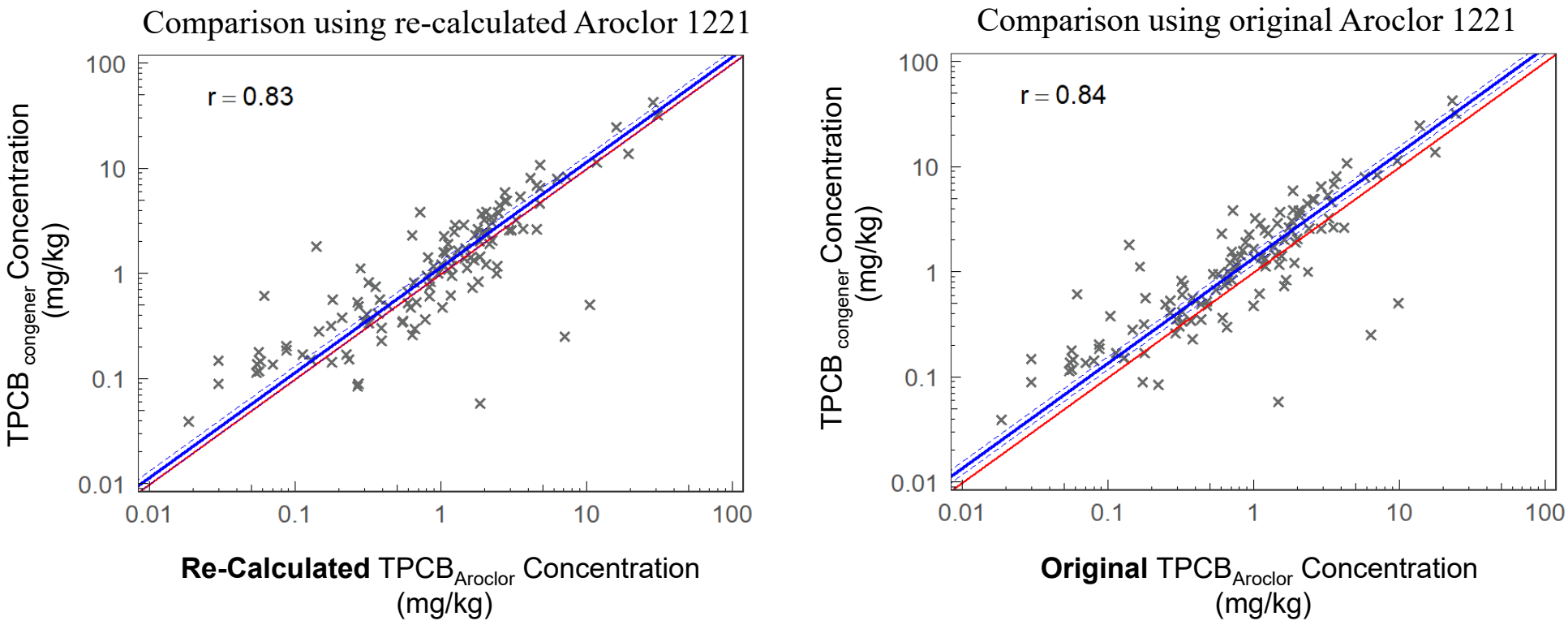
WSP

Ratio of Congener-Based to Aroclor-Based Measurements Using Original and Re-Calculated Aroclor 1221

Figure 4-1

July 2024

NYSDEC 2017 Matched Pair Samples



Legend

- 1: 1 line
- Geometric mean of the ratio
- 95% confidence limits on the geometric mean ratio
- Individual value

Notes:

- This figure only includes samples where both Aroclor-based and congener-based (matched pair) results are detected.
- $TPCB_{congener}$ is the sum of 209 congeners reported by M1668. Non-detect congener result was set to zero in the summation.
- $TPCB_{Aroclor}$ is the sum of all Aroclors reported by M8082. Non-detect Aroclor result was set to zero in the summation.
- *r*: Pearson correlation coefficient based on log-transformed concentration data
- 95% confidence limits on the geometric mean of the ratio are the bias-corrected and accelerated (BCa) bootstrap 2.5th to 97.5th percentile values.

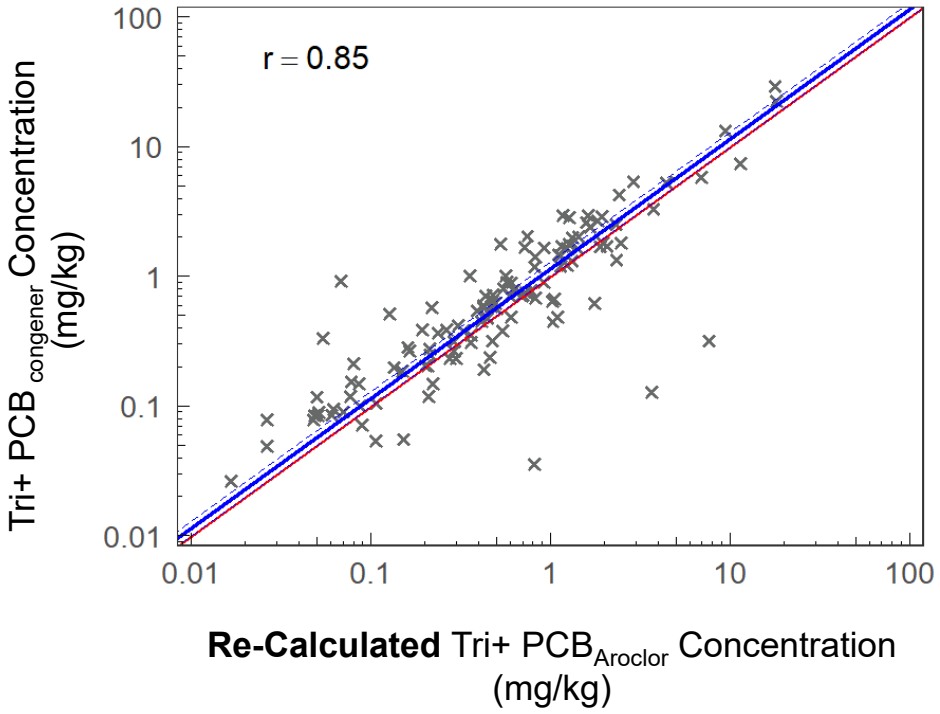
Correlation Between Arolcor-Based and Congener-Based TPCB Concentrations Using Original and Re-Calculated Aroclor 1221

Figure 4-2a

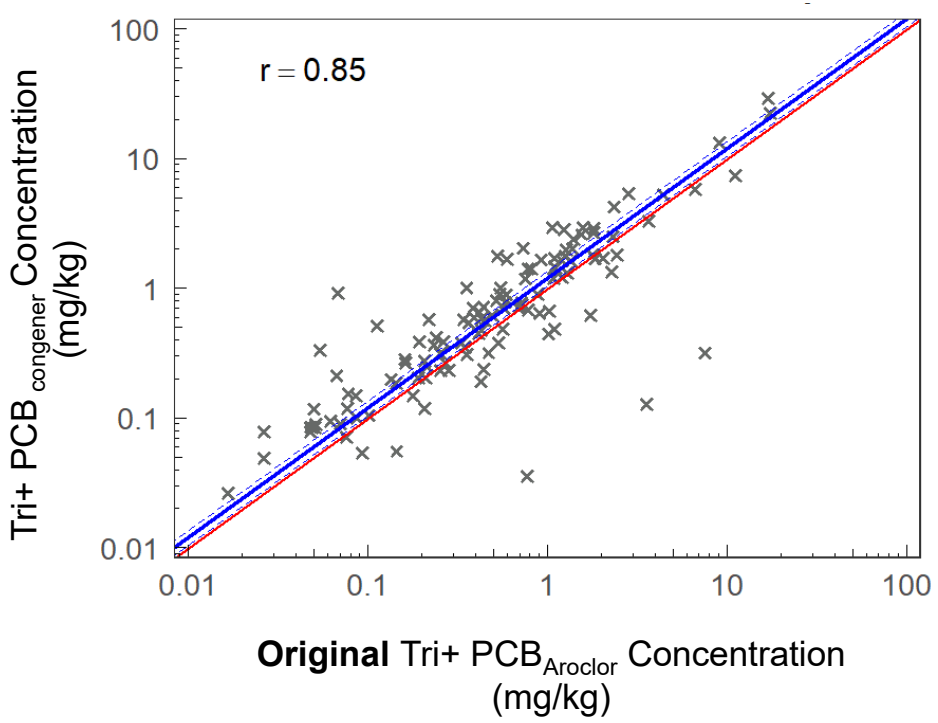
July 2024

NYSDEC 2017 Matched Pair Samples

Comparison using re-calculated Aroclor 1221



Comparison using original Aroclor 1221



Legend

- 1: 1 line
- Geometric mean of the ratio
- 95% confidence limits on the geometric mean ratio
- Individual value

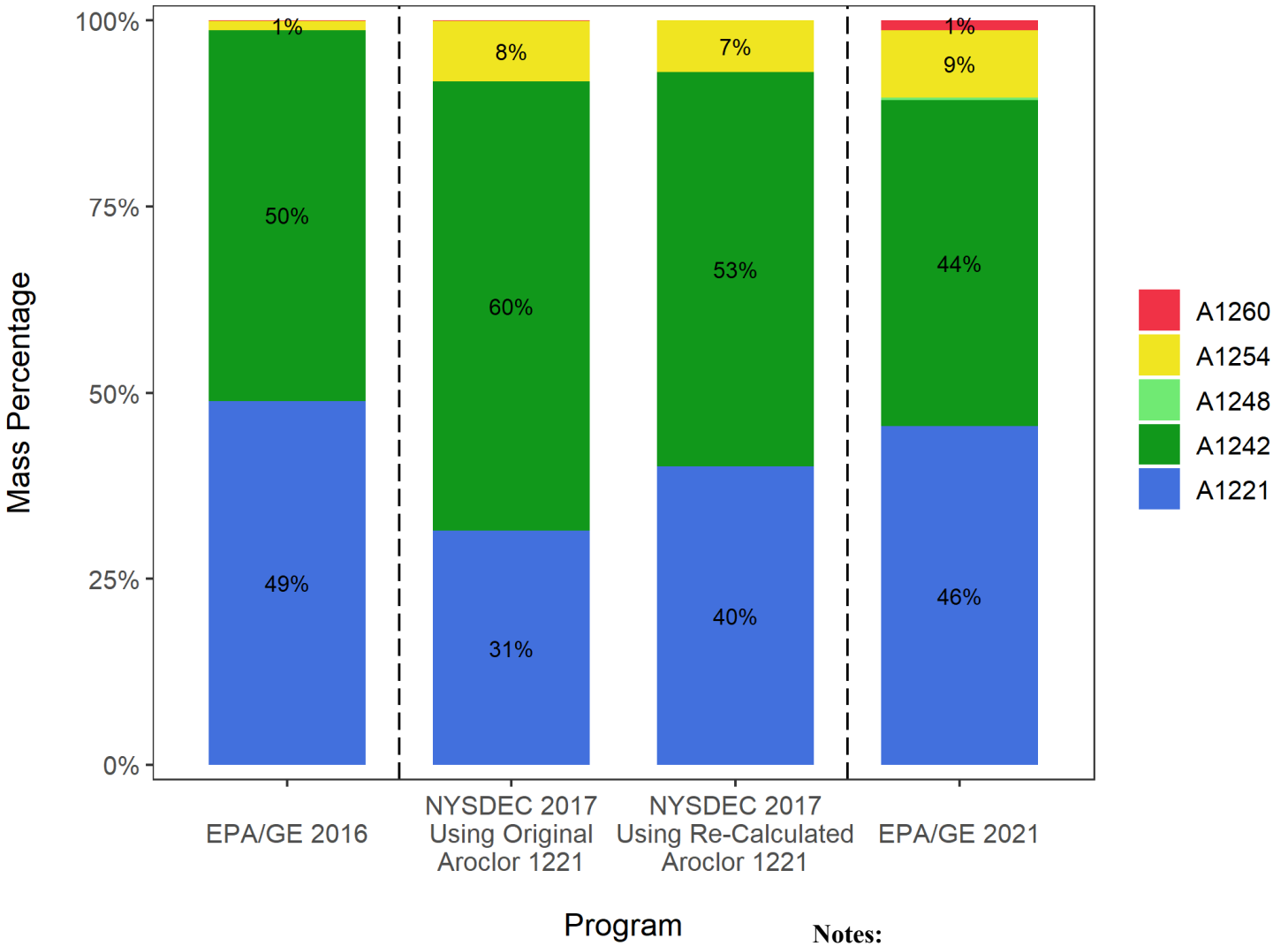
Notes:

- This figure includes matched pair samples where both Aroclor-based and congener-based results are detected.
- Tri+ $PCB_{congener}$ is the sum of congeners with three or more chlorine atoms reported by M1668. Non-detect congener result was set to zero in the summation.
- Tri+ $PCB_{Aroclor}$ is calculated from GE's equation: Tri+ PCB = 0.13 × A1221 + 0.89 × (A1242+A1254). Non-detect Aroclor result was set to zero in the summation.
- *r*: Pearson correlation coefficient based on log-transformed concentration data
- 95% confidence limits on the geometric mean of the ratio are the bias-corrected and accelerated (BCa) bootstrap 2.5th to 97.5th percentile values.

Correlation between Aroclor-Based and Congener-Based Tri+ PCB Concentrations Using Original and Re-Calculated Aroclor 1221

Figure 4-2b

July 2024



Notes:

- Label not shown when percentage is less 1 percent.
- Figure only includes samples collected from the main stem.
- Field duplicates averaged.
- Non-detect at half of reporting limits.

Comparison of Average Aroclor Mass Percentage Using Original and Re-Calculated Aroclor 1221

Figure 4-3

July 2024

Third Five-Year Review Report for the Hudson River PCBs Superfund Site

APPENDIX 2

ATTACHMENT B

SEDIMENT

PCB DATA TREATMENT

Prepared by:
WSP USA Solutions Inc.

July 2024

THIRD FIVE-YEAR REVIEW REPORT FOR THE HUDSON RIVER PCBs SUPERFUND SITE

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THIRD FIVE-YEAR REVIEW REPORT FOR THE HUDSON RIVER PCBs SUPERFUND SITE

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1 NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY (NIST) STANDARD REFERENCE MATERIAL (SRM) RESULTS

1.1 Introduction

In 2021, NIST SRM 1944 samples were included for the analysis of both congeners and Aroclors to monitor and evaluate long-term trends and data comparability of sediment polychlorinated biphenyl (PCB) data. NIST SRM 1944 consists of a mixture of New York and New Jersey waterway sediments collected in October 1994 and has been analyzed by multiple laboratories to yield a suite of 29 certified and four reference congener values.

1.2 Assessment of Aroclor Results

NIST SRM 1944 samples were analyzed for Aroclors by GE Hudson River (GEHR) Method 8082 (M8082) at a rate of one per 40 sediment samples collected in 2021, resulting in a total of 21 NIST SRM Aroclor analyses conducted in February and March 2022. Because NIST does not certify the total PCBs as sum of Aroclors ($TPCB_{Aroclor}$) or individual Aroclor concentrations, seven NIST SRM 1944 samples were analyzed prior to the analysis of 2021 sediment samples. These seven samples were extracted and analyzed on three different days (January 12, 13, and 14, 2022), and served as a baseline dataset against which subsequent sample groups were compared. Out of the seven Aroclors reported by M8082, only Aroclor 1248, Aroclor 1254, and Aroclor 1260 were detected. Therefore, this section addresses these three Aroclors and $TPCB_{Aroclor}$.

In the following discussion, the 21 NIST SRM samples analyzed along with the 2021 sediment samples will be referred to as "2021 NIST SRM samples," despite being analyzed in 2022. The seven NIST SRM samples will be referred to as "baseline samples."

To assess the consistency of the Aroclor measurements over time, the arithmetic mean concentration from the 2021 NIST SRM samples was compared to the 95-percent confidence limits of the arithmetic mean from the baseline samples. The baseline mean was calculated by averaging the Aroclor concentrations from the seven NIST SRM 1944 samples, and the 95-percent confidence limits were calculated as the baseline mean ± 2 times the standard error. Per the 2021 Sediment Work Plan, the arithmetic mean concentration for the 2021 NIST SRM samples should be within the 95-percent confidence limits of the baseline mean (GE, 2021). As shown in Figure 1-1, the 2021 mean was found to be lower than the 95-percent lower confidence limit of the baseline mean for $TPCB_{Aroclor}$ and individual Aroclors, indicating low bias in the 2021 NIST SRM samples. The percent deviation from the baseline mean is -12 percent, -10 percent, -9 percent, and -11 percent for Aroclor 1248, Aroclor 1254, Aroclor 1260, and $TPCB_{Aroclor}$, respectively (Table 1-1).

To evaluate the precision of the 2021 NIST SRM Aroclor results, each individual result was compared to the ± 20 percent of the baseline mean. The acceptance criterion of ± 20 percent was

set based on the calibration acceptance criteria for M8082 (EPA, 2007). Figure 1-1 shows that five results (approximately 25 percent of the data) were outside the ± 20 percent range of the baseline mean, indicating a higher variability.

In summary, analysis of NIST SRM samples associated with the 2021 samples showed that the arithmetic means for individual Aroclors and $TPCB_{Aroclor}$ were outside the 95-percent confidence limits of their respective baseline means, biased low. About 25 percent of individual results fall outside of the ± 20 percent baseline mean. The variability of the NIST SRM sample results associated with the 2021 sediment samples are larger compared to the baseline NIST SRM samples. The laboratory procedure needs to be refined to ensure that individual results are within ± 20 percent of the baseline mean.

1.3 Assessment of Congener Results

NIST SRM 1944 samples were analyzed for PCB congeners by Method 1668 (M1668) at a rate of one per 20 sediment samples collected in 2021, resulting in a total of five NIST SRM congener analyses. Table 1-2 provides certified values for 29 PCB congeners and reference values for 4 PCB congeners, as specified in the NIST SRM 1944 standard. Measured PCB congener results were compared to their certified or reference values using percent deviation (%D) to assess the accuracy of congener results. An acceptance criterion of ±25 percent for %D was used, which was based on the quality control acceptance criterion for calibration verification required by M1668 (EPA, 2010). The percent deviation (%D) was calculated according to Equation 1:

$$\%D = \frac{C_{Measured} - C_{Certified\ or\ reference}}{C_{Certified\ or\ reference}} \times 100\% \qquad \text{(Eq. 1)}$$

Where:

- $C_{Measured}$ is the measured concentration for a specific congener; and
- $C_{Certified\ or\ reference}$ is the certified or reference concentration for a specific congener.

Because some of the 33 congeners that have certified or references values are co-eluted with other congeners from data reported by Vista Analytical Laboratory, the accuracy assessment focused only on 19 single-elute[1] congeners. Figure 1-2a shows the plot of the %D for the 19 single-elute congeners, arranged by PCB congener number. In Figure 1-2b, these %D values were plotted against the certified or reference concentrations. The results indicated that about 98 percent of individual congener measurements (93 out of 95 measurements) had %D within the acceptance criterion of ±25 percent. The two measurements that were outside the acceptance criterion belonged to the same congener, PCB 174. Figure 1-2b shows that there was no correlation between %D and certified or reference concentrations.

[1]A single-elute congener is a congener that is quantified by Method 1668 based on a single chromatographic peak.

To evaluate the accuracy of congener results in terms of totals, the concentrations of 19 single-elute congeners were summed for the five NIST SRM 1944 samples analyzed by the Vista laboratory and compared to the sum of NIST certified or reference concentrations. The data revealed that the total concentration of 19 single-elute congeners ranged from 0.60 to 0.68 mg/kg in the five NIST SRM 1944 samples analyzed by the Vista laboratory. This resulted in a %D ranging from -4 percent to 7 percent when compared to the sum of NIST certified/reference concentration of 0.63 mg/kg. The low %D values observed for both individual congeners and the sum of congeners demonstrates that the PCB congener measurements performed at Vista laboratory were sufficiently accurate.

To assess the precision of the congener results, the concentration range of the sum of 209 congeners, known as total PCBs congeners ($TPCB_{congener}$), was used. The results indicate that the $TPCB_{congener}$ concentrations ranged from 1.9 to 2.2 mg/kg, with an average of 2.1 mg/kg (Table 1-3). Compared to the range reported for $TPCB_{Aroclor}$ (from 1.5 to 2.7 mg/kg), the congener-based measurements demonstrated a higher precision than the Aroclor-based measurements for the NIST SRM 1944 samples.

1.4 Conclusion

This section examined the accuracy and precision of the results of NIST SRM 1944 samples, which were analyzed along with the 0 to 2-inch surface sediment samples collected in 2021.

The accuracy for PCB congener measurements was assessed by comparing the results to certified or reference values. The results showed that PCB congener concentrations reported by Vista laboratory were within ±25 percent of their certified or reference values, indicating high accuracy. The precision for PCB congener measurements was also evaluated, and the results showed that they were very precise, with $TPCB_{congener}$ ranging from 1.9 to 2.2 mg/kg.

The accuracy of PCB Aroclor measurements was not assessed, as NIST does not certify Aroclor concentrations. Instead, the consistency of Aroclor-based measurements was evaluated by comparing the arithmetic mean concentrations in the 2021 NIST SRM samples to the baseline means. The comparison showed that the Aroclor measurements in the 2021 NIST SRM samples had biased low means compared to the baseline values. The precision of PCB Aroclor measurements was assessed by comparing individual Aroclor concentrations in the 2021 NIST SRM samples to the baseline means. Approximately 25 percent of the data was outside the ± 20 percent of the baseline mean, indicating a higher variability.

Overall, the congener-based measurements in 2021 NIST SRM 1944 samples met the project accuracy and precision criteria, while Aroclor-based measurements were biased low compared to the baseline values and showed a higher variability. The laboratory procedure needs to be refined to improve the consistency of Aroclor measurements.

2 EXAMINATION OF AROCLOR-CONGENER MATCHED PAIR DATA

2.1 Introduction

The majority of the Upper Hudson River (UHR) sediment samples were analyzed for PCBs as Aroclors using M8082. Historically, GE used the modified Green Bay Method (mGBM), a congener-based method, to directly measure Tri+ PCB and establish a conversion basis for the M8082 results. However, the mGBM method was discontinued at the end of 2016, and it is no longer available to the Hudson River project. In 2021, GE implemented a more accurate and rigorous congener-based method (i.e., M1668) for the determination of Tri+ PCB and TPCB. Besides the change in the congener analytical method from mGBM to M1668, the approach to quantify Aroclor concentrations by M8082 was also changed. For samples collected in 2017 or earlier, the concentration of Aroclor was determined by the sum of five peak areas, while for samples collected in 2021 and beyond, the quantitation of Aroclor uses the average of concentrations obtained from each of the five peaks. Due to these changes, this attachment evaluates the consistency of Aroclor-based concentrations with congener-based concentrations for both Tri+ PCB and TPCB.

The formula to convert the Aroclor data to a Tri+ PCB estimate in UHR sediments is as follows:

$$\text{Tri+ PCB}_{\text{Aroclor}} = 0.13 \times \text{Aroclor 1221} + 0.89 \times (\text{Aroclor 1242+ Aroclor 1254}) \qquad \text{(Eq. 2)}$$

This equation, also known as GE's equation, was developed by regressing Tri+ PCB concentrations derived from congener data (reported via mGBM) against Aroclor concentrations (reported via M8082) using 445 sediment samples collected between 2004 and 2011 under the Sediment Sampling and Analysis Program [SSAP] and Remedial Action Monitoring Program [RAMP] (GE, 2011).

To compare the Tri+ PCB and TPCB results obtained through two different methods, a subset of samples collected in 2017 and 2021 was analyzed using both M8082 and M1668 (i.e., matched pairs). These matched pair samples were used to compare the Aroclor-based Tri+ PCB concentrations derived from GE's equation ($\text{Tri+ PCB}_{\text{Aroclor}}$) to congener-based measurements ($\text{Tri+ PCB}_{\text{congener}}$), as well as Aroclor-based TPCB concentrations ($\text{TPCB}_{\text{Aroclor}}$) to congener-based measurements ($\text{TPCB}_{\text{congener}}$).

2.2 Comparison of Aroclor- and Congener-based Tri+ PCB and TPCB Results from 2017 and 2021 Programs

Table 2-1 summarizes the analytical methods and laboratories used to analyze the matched pair samples. The selected samples for congener analysis covered a range of TPCB concentrations (Figure 2-1). Under the 2017 sampling program, a total of 131 samples and field duplicates were analyzed for PCB congeners using M1668, resulting in 122 quantitated pairs (i.e., detectable

results by both methods). Under the 2021 program, a total of 66 samples and field duplicates were analyzed for PCB congeners using M1668, resulting in 66 quantitated pairs.

Note that the results of the 2017 matched pair samples were discussed in EPA's *Technical Memorandum* (EPA, 2019). However, EPA/GE recently identified a quantitation error for Aroclor 1221 data in 2017 samples and subsequently re-quantified all the Aroclor 1221 results for that year (Attachment A). As a result, the previously reported results were no longer accurate. The analyses presented in this attachment are based on the adjusted 2017 Aroclor 1221 results.

The estimated Tri+ PCB (Tri+ $PCB_{Aroclor}$) using Equation 2 above, were compared to the measured congener-based Tri+ PCB (Tri+ $PCB_{congener}$) to assess whether GE's equation is still applicable to the post-dredging data. This was done by evaluating the correlation between the two measurements (Tri+ $PCB_{congener}$ and Tri+ $PCB_{Aroclor}$) and calculating the geometric mean of the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratio along with its 95-percent confidence limits. The 95-percent confidence limits on the geometric mean of the ratio are the bias-corrected and accelerated (BCa) bootstrap 2.5th to 97.5th percentile values. Figure 2-2a shows a scatter plot comparing the two measurements (Tri+ $PCB_{congener}$ and Tri+ $PCB_{Aroclor}$) with lines representing the geometric mean of the ratio and its 95-percent confidence limits. The results showed that the estimated Tri+ $PCB_{Aroclor}$ were strongly correlated with measured Tri+ $PCB_{congener}$ concentrations. Pearson correlation coefficients based on log-transformed concentration data were 0.85 and 0.91 for 2017 and 2021 matched pair samples, respectively. The geometric mean of the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratio was 1.16 in 2017 and 1.29 in 2021, indicating that estimates for Tri+ PCB concentrations using GE's equation are slightly biased low. However, the similar geometric mean ratios with overlapping 95-percent confidence limits from the two datasets (2017 and 2021) suggest that this bias is consistent over time and will not likely impact the detection of trends.

In addition to comparing Tri+ PCB, TPCB concentrations obtained from the two different analytical methods were also compared by evaluating the correlation and geometric mean of the ratio. The results showed that $TPCB_{Aroclor}$ and $TPCB_{congener}$ concentrations were well correlated in both 2017 and 2021, and the geometric mean of the $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratio was consistent between the two years, at a value of 1.16 (Figure 2-2b). This suggests that $TPCB_{Aroclor}$ concentrations were consistent over time, although they were 16 percent lower than $TPCB_{congener}$ concentrations.

It is worth noting that the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratio and $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratio showed significant variability in individual samples (Figure 2-3). For instance, the 2021 results indicate that the estimated Tri+ PCB concentrations from GE's equation can either be overestimated or underestimated by a factor of 7 when compared to their measured concentration from M1668. This large sample-to-sample variability observed in the matched pair data is partly due to the laboratory sample extraction and analysis procedures. It is important to note that the matched pair data used for developing GE's equations (i.e., SSAP and RAMP data) were obtained

from the same extract, while the samples collected in 2017 and 2021 were extracted separately for the analysis of Aroclors and congeners. Therefore, it is expected that recent matched pair data in 2017 and 2021 showed higher variability than the earlier SSAP/RAMP data.

2.3 Factors that May Influence the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ and $TPCB_{congener}$ to $TPCB_{Aroclor}$ Ratio

The geometric mean of the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratio and $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratio suggests that on average, ratios from the post-dredging period (2017 and 2021) were greater than those from the SSAP/RAMP period (Figure 2-3). To better understand the temporal change in ratios, several factors were evaluated, including (1) $TPCB_{Aroclor}$ concentration, (2) composition of PCB as indicated by the mass fraction of Aroclor 1221 in $TPCB_{Aroclor}$, and (3) composition of PCB as indicated by the number of chlorine atoms per biphenyl molecule (CPB) for a given sample (CPB_{sample}). Here, CPB_{sample} represents a weighted-average CPB across the 10 homologues for that sample. Homologue-specific CPB (ranging from 1 to 10) was weighted by its respective molar fraction in the sample to derive the CPB_{sample} using Equation 3:

$$CPB_{sample} = \frac{\sum_{i=1}^{10} M_i \, CPB_i}{\sum_{i=1}^{10} M_i} \qquad \text{(Eq. 3)}$$

Where:

- i is an index of PCB homologues (1 to 10);
- CPB_i is the CPB for homologue i; CPB varies from 1 for monochlorobiphenyl to 10 for decachlorobiphenyls; and
- M_i is the molar concentration for homologue i, which is calculated by dividing its concentration (in mg/kg) by its molecular weight.

Figure 2-4a illustrates the relationship between the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratio (on the vertical axis) and the three factors mentioned above (Tri+ $PCB_{Aroclor}$ concentrations, Aroclor 1221 mass fraction, and CPB on the horizontal axis). Figure 2-4b shows similar plots for $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratio. Each plot includes a 95-percent confidence ellipse based on multivariate t-distribution for each dataset. The ellipse defines the region that contains 95 percent of the samples and was plotted to assist in visualizing the relationship. The plots reveal that the 95 percent confidence ellipses were overlapping in the horizontal axis direction, suggesting that both the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratio and $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratio did not vary with any of the three factors mentioned above. This finding demonstrates that the slightly higher geometric mean ratios observed during the 2017 and 2021 post-dredging samples were not due to changes in PCB composition or concentration from the earlier SSAP/RAMP samples. These plots further reveal that the 95-percent confidence ellipses for the two post-dredging datasets completely encompassed the ellipse for the SSAP/RAMP dataset in the vertical axis direction. This indicates

that, on an individual sample basis, the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratios or $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratio reported in post-dredging samples were consistent with those reported for SSAP/RAMP samples.

2.4 Conclusion

Because the majority of post-Record of Decision data has been generated using Aroclor-based method M8082, it is recommended to continue using GE's equation to estimate Tri+ PCB concentrations. There are several reasons why this approach is preferred. First, GE's equation was developed using a large dataset of 445 matched pair samples, providing a robust basis for estimating Tri+ PCB concentrations. This is an established, well-known equation that has been used extensively in the past. In contrast, the recent matched pair data in 2017 and 2021 showed a greater variability than those from earlier samples. Second, the Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ ratio in 2017 and 2021 had similar geometric means with overlapping 95-percent confidence intervals, suggesting that the ratio has not changed over time. Finally, the ratio did not vary with either concentration or composition of PCBs.

Different from Tri+ PCB, Aroclor-based TPCB results were adjusted by a factor of 1.16, which is the geometric mean of the $TPCB_{congener}$ to $TPCB_{Aroclor}$ ratios, to standardize these results to a homologue equivalent value ($TPCB_{HE}$) for post-dredging sediment samples collected in 2016, 2017 and 2021.

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APPENDIX 2
ATTACHMENT B
Tables and Figures

Tables

Table 1-1
NIST SRM 1944 Performance Evaluation Sample Results:
Aroclors by GEHR Method 8082

Program	Number of SRM Samples	Aroclor 1248		Aroclor 1254		Aroclor 1260		$TPCB_{Aroclor}$	
		Arithmetic Mean (mg/kg)	%D from Baseline Mean	Arithmetic Mean (mg/kg)	%D from Baseline Mean	Arithmetic Mean (mg/kg)	%D from Baseline Mean	Arithmetic Mean (mg/kg)	%D from Baseline Mean
Baseline (Jan 12 to 14, 2022)	7	1.1	NA	0.77	NA	0.39	NA	2.3	NA
Associated with 2021 Samples (Feb-Mar 2022)	21	1.0	-12%	0.69	-10%	0.36	-9%	2.1	-11%

Notes:

1. $TPCB_{Aroclor}$ is the sum of all Aroclors reported by M8082. Non-detect results were set to zero in the summation.
2. %D from Baseline Mean is calculated as (2021 Mean - Baseline Mean) ÷ Baseline Mean x 100%.

Table 1-2

List of Congeners with Certified and Reference Values for NIST SRM 1944

Congener number	Concentration value specified in NIST SRM 1944 (mg/kg)	Type of value (certified or reference)	Co-elute congeners reported by Vista Analytical Laboratory	Single co-elute congeners
8	0.0223	Certified	5+8	No
18	0.051	Certified	18	Yes
28	0.0808	Certified	28	Yes
31	0.0787	Certified	31	Yes
44	0.0602	Certified	44	Yes
45	0.0108	Reference	45	Yes
49	0.053	Certified	43+49	No
52	0.0794	Certified	52+69	No
66	0.0719	Certified	66+76	No
87	0.0299	Certified	87+117+125	No
95	0.065	Certified	95+98+102	No
99	0.0375	Certified	99	Yes
101	0.0734	Certified	90+101	No
105	0.0245	Certified	105	Yes
110	0.0635	Certified	110	Yes
118	0.058	Certified	106+118	No
128	0.00847	Certified	128+162	No
138	0.0621	Certified	138+163+164	No
163	0.0144	Reference		No
146	0.0101	Reference	146+165	No
149	0.0497	Certified	139+149	No
151	0.01693	Certified	151	Yes
153	0.074	Certified	153	Yes
156	0.00652	Certified	156	Yes
170	0.0226	Certified	170	Yes
174	0.016	Reference	174	Yes
180	0.0443	Certified	180	Yes
183	0.01219	Certified	183	Yes
187	0.0251	Certified	182+187	No
194	0.0112	Certified	194	Yes
195	0.00375	Certified	195	Yes
206	0.00921	Certified	206	Yes
209	0.00681	Certified	209	Yes

Table 1-3
NIST SRM 1944 Performance Evaluation Sample Results:
$TPCB_{congener}$ *vs.* $TPCB_{Aroclor}$

Program	$TPCB_{congener}$ from Method 1668C				$TPCB_{Aroclor}$ from GEHR Method 8082			
	Analysis Date	Number of SRM Samples	TPCB Average (mg/kg)	TPCB Range (mg/kg)	Analysis Date	Number of SRM Samples	TPCB Average (mg/kg)	TPCB Range (mg/kg)
Baseline	Not Required				Jan 2022	7	2.3	2.0 - 2.4
Associated with 2021 Samples	May 2022	5	2.1	1.9 - 2.2	Feb-Mar 2022	21	2.1	1.5 - 2.7

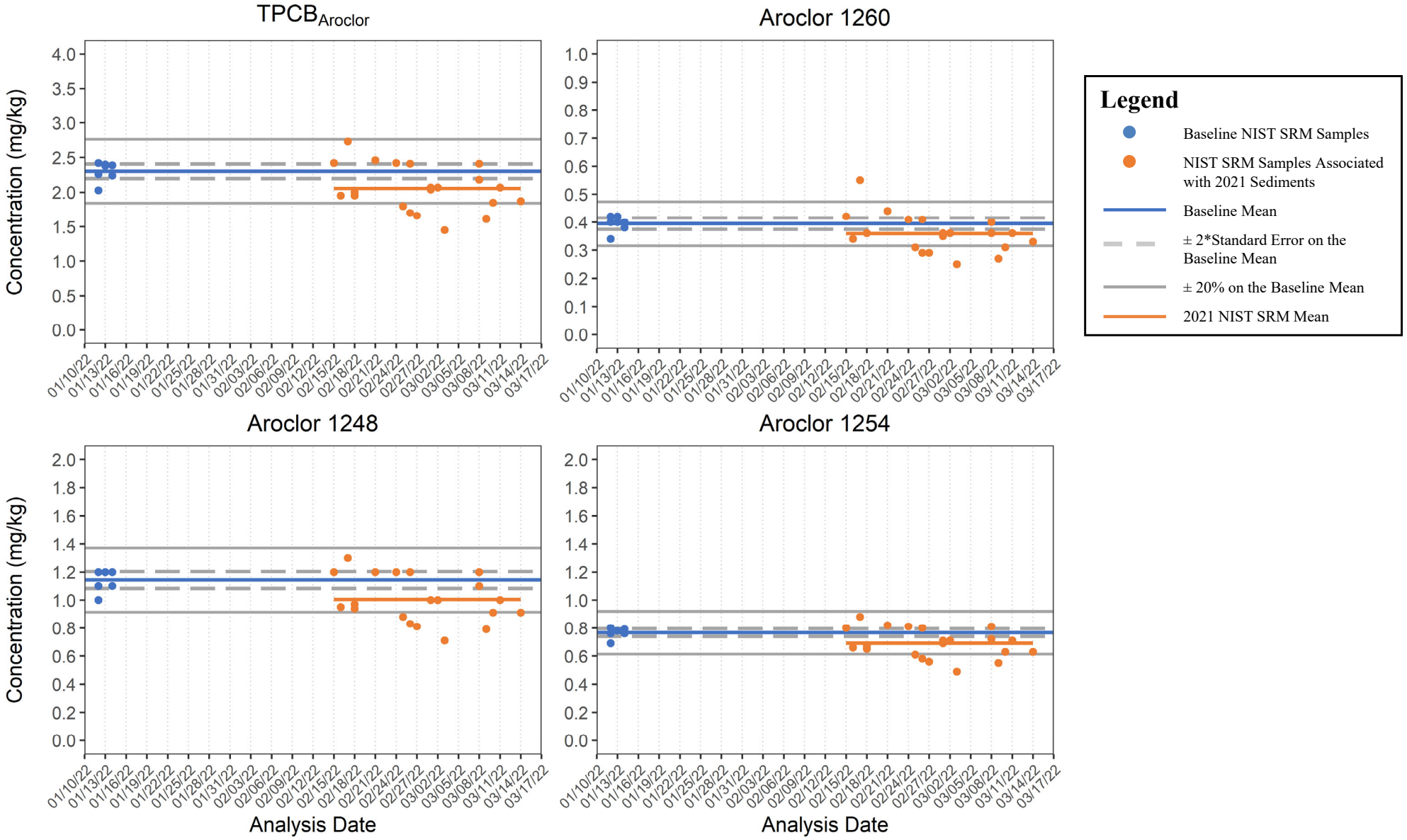
Notes:
1. $TPCB_{Aroclor}$ is the sum of all Aroclors reported by M8082. Non-detect results were set to zero in the summation.
2. $TPCB_{congener}$ is the sum of 209 congeners. Non-detect results were set to zero in the summation.

Table 2-1
Summary of Matched Pair Analyses

Program	Year	Number of Pairs	Aroclor Method	Aroclor Lab	Congener Method	Congener Lab
SSAP/RAMP	2004, 2005, 2009, 2011	445	GEHR Method 8082	Accutest Laboratories, Inc. (Dayton, NJ) Lancaster Laboratories, Inc. (Lancaster, PA) Severn Trent Laboratories, Inc. (Pittsburgh, PA) Northeast Analytical, Inc. (Schenectady, NY) Pace Analytical Services (Schenectady, NY)	modified Green Bay Method (mGBM)	Northeast Analytical, Inc. (Schenectady, NY)
NYSDEC 2017	2017	131[(1)]		Pace Analytical Services (Minneapolis, MN)	M1668A	Pace Analytical Services (Minneapolis, MN)
EPA/GE 2021	2021	66		Pace Analytical Services (Green Bay, WI)	M1668C	Vista Analytical Laboratory (El Dorado Hills, CA)

Notes:
(1) 122 pairs where both methods yield detectable results are used in the matched pair evaluation.
GEHR: GE Hudson River

Figures



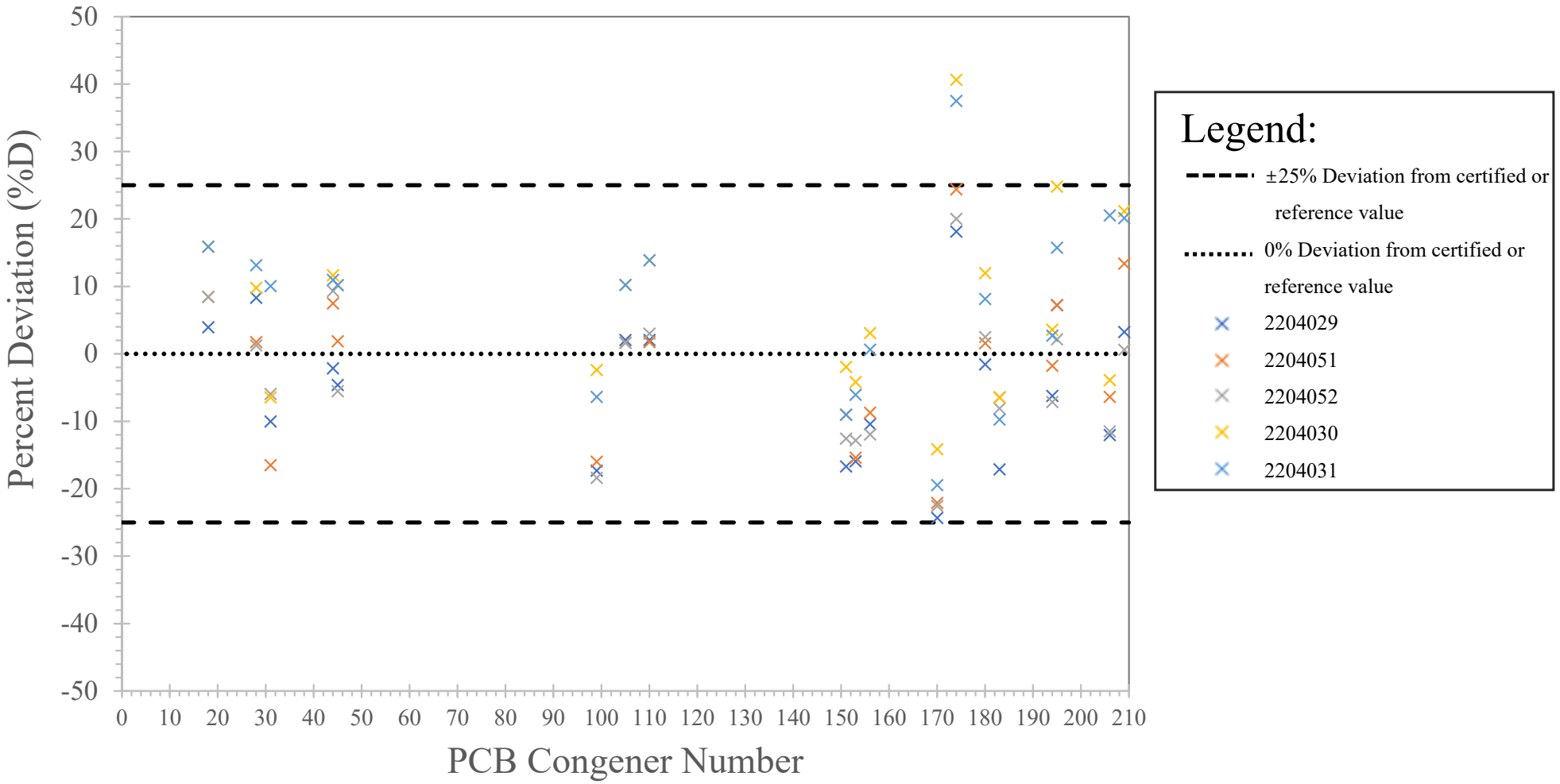
Notes:

- All results are detected.
- Note the varying y-axis scales in these plots.

NIST SRM 1944 Performance Evaluation Sample Results for PCB Aroclors

Figure 1-1

July 2024



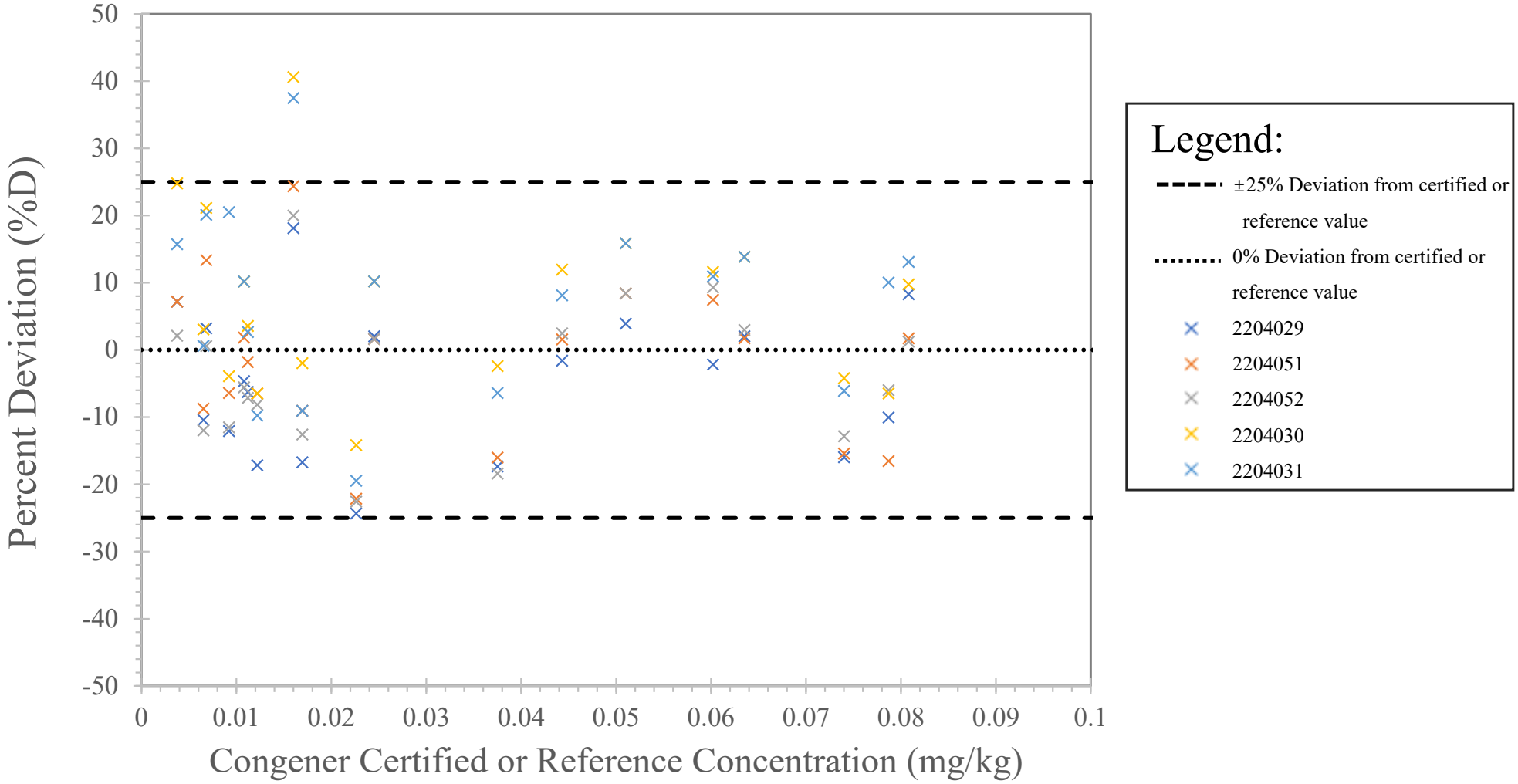
Notes:

- NIST SRM 1944 standard provides certified values for 29 PCB congeners and reference values for 4 PCB congeners (see Table 3-2). This evaluation focuses only on 19 single-elute congeners.
- The percent deviation (%D) for individual congener is calculated as (Measured concentration- Certified or reference concentration) ÷ Certified or reference concentration ×100%.
- All measured concentrations for single-elute congeners are detected.
- Percent deviations for 18 of 19 single-elute congeners are within ± 25% acceptance criterion.

NIST SRM 1944 Performance Evaluation Sample Results: Single-Elute PCB Congeners Percent Deviation *vs.* Congener Number

Figure 1-2a

July 2024



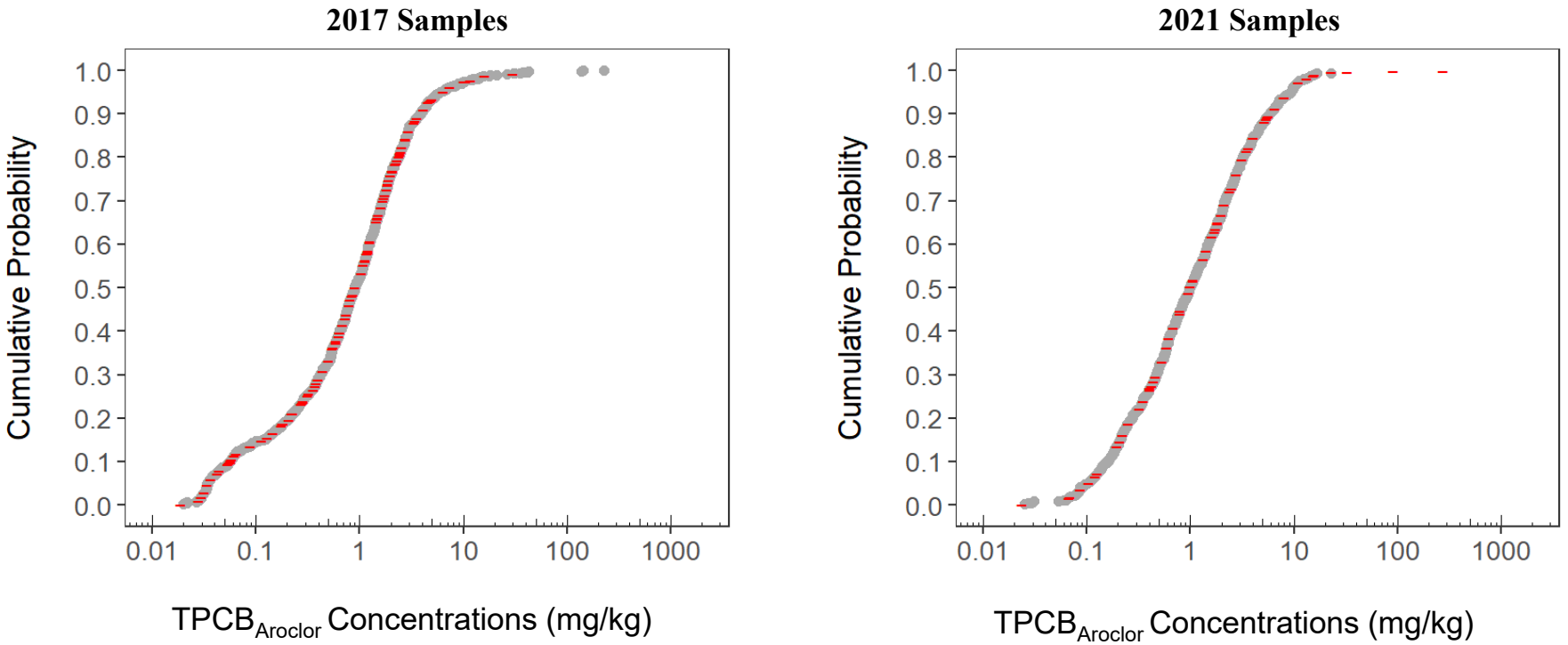
Notes:

- NIST SRM 1944 standard provides certified values for 29 PCB congeners and reference values for 4 PCB congeners (see Table 3-2). This evaluation focuses only on 19 single-elute congeners.
- The percent deviation (%D) for individual congener is calculated as (Measured concentration- Certified or reference concentration) ÷ Certified or reference concentration ×100%.
- All measured concentrations for single-elute congeners are detected.
- Percent deviations for 18 of 19 single-elute congeners are within ± 25% acceptance criterion .

NIST SRM 1944 Performance Evaluation Sample Results:
Single-Elute PCB Congeners Percent Deviation *vs.* Certified or Reference Concentration

Figure 1-2b

July 2024



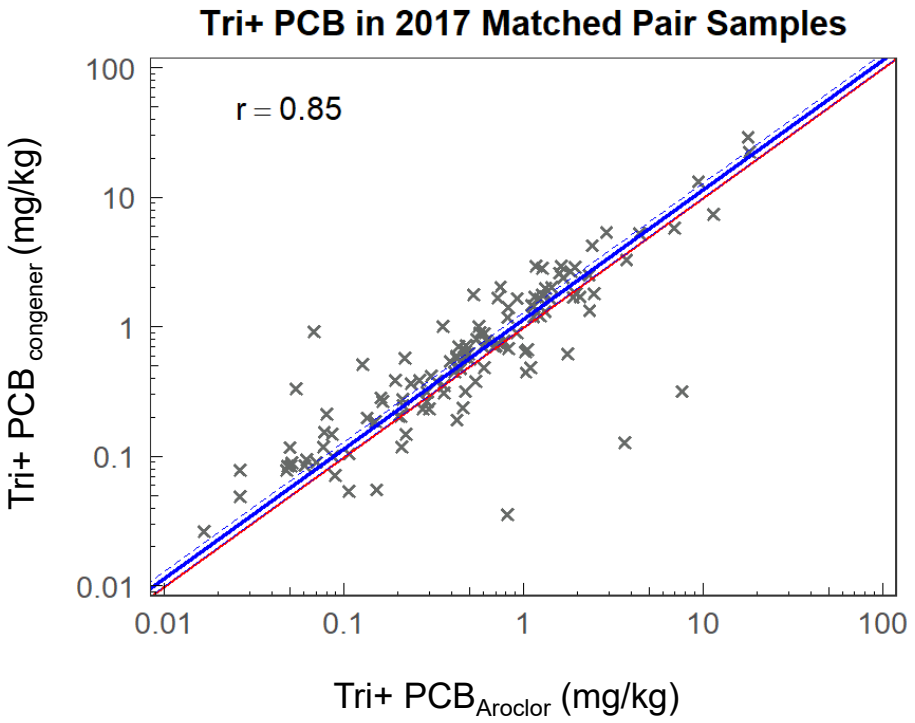
Notes:

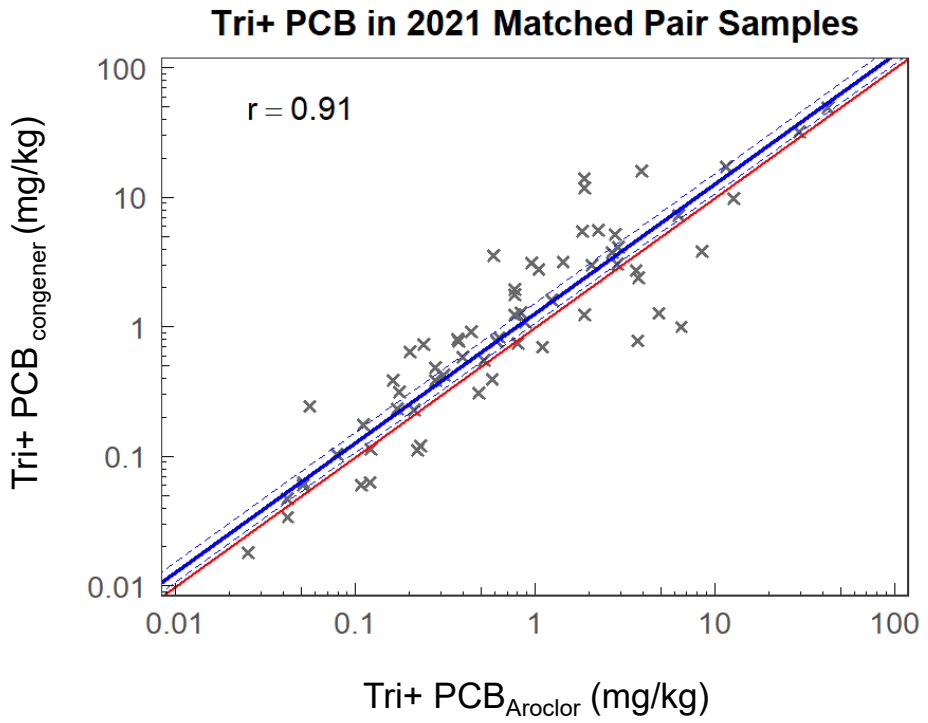
- $TPCB_{Aroclor}$ concentration is the sum of all Aroclors measured by GEHR Method 8082 (M8082). Non-detect results were set at zero in the summation.
- One 2017 sample with $TPCB_{Aroclor}$ <0.01 mg/kg was not shown.

Representativeness of Samples Selected for Congener Analysis

Figure 2-1

July 2024





Legend

- 1: 1 line
- Geometric mean of the ratio
- 95% confidence limits on the geometric mean ratio
- Individual value

Tri+ PCB ratio	NYSDEC 2017	EPA/GE 2021
Geometric Mean	1.16	1.29
(95% confidence limits)	(1.01 to 1.32)	(1.08 to 1.55)

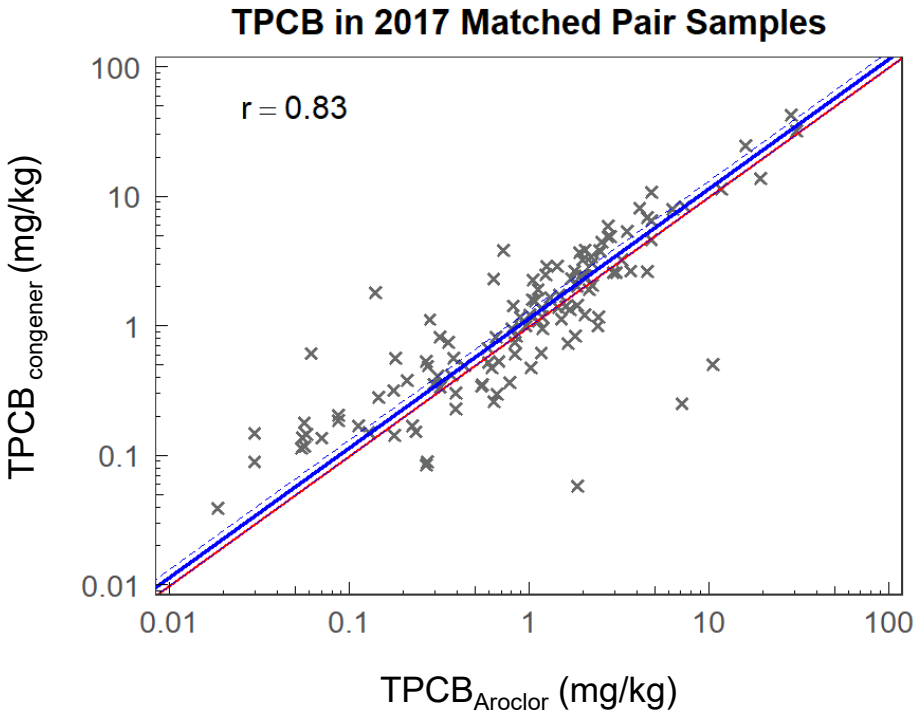
Notes:

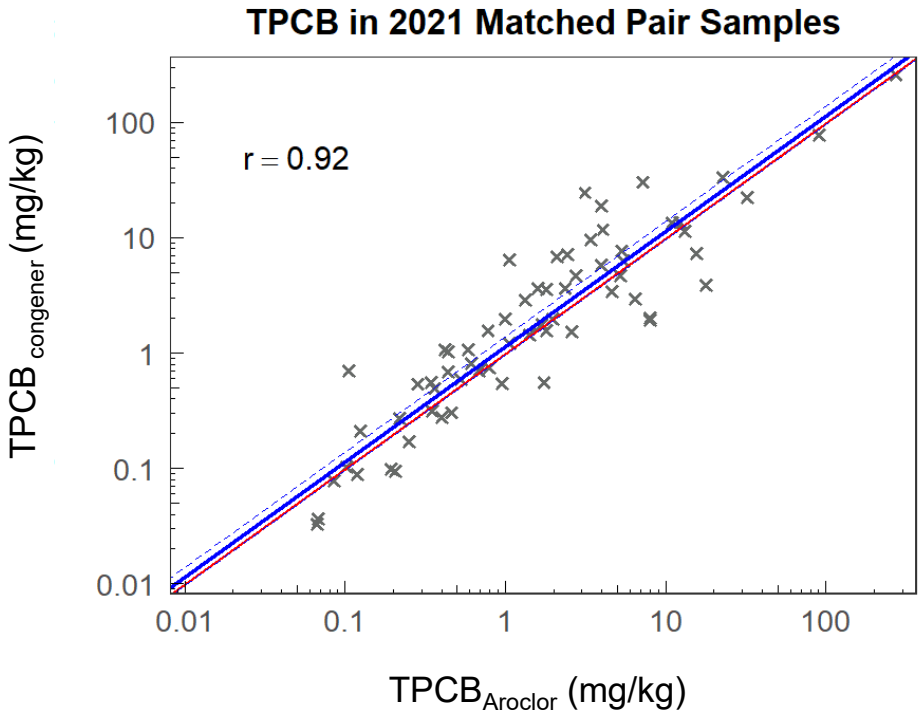
- Tri+ $PCB_{congener}$ is the sum of congeners with three or more chlorine atoms reported by EPA Method 1668 (M1668). Non-detect results were set at zero in the summation.
- Tri+ $PCB_{Aroclor}$ is calculated from GE's equation: Tri+ PCB = 0.13 × A1221 + 0.89 × (A1242+A1254).
- *r*: Pearson correlation coefficient based on log-transformed concentration data
- 95% confidence limits on the geometric mean of the ratio are the bias-corrected and accelerated (BCa) bootstrap 2.5^{th} to 97.5^{th} percentile values.
- One 2021 sample with Tri+ $PCB_{congener}$ <0.01 mg/kg was not shown.

Comparison of Aroclor-based Tri+ PCB (Tri+ $PCB_{Aroclor}$) Concentrations Derived from GE's Equation and Congener-based Tri+ PCB (Tri+ $PCB_{congener}$) Concentrations

Figure 2-2a

July 2024





Legend

- 1: 1 line
- Geometric mean of the ratio
- 95% confidence limits on the geometric mean ratio
- Individual value

TPCB ratio	NYSDEC 2017	EPA/GE 2021
Geometric Mean	1.16	1.16
(95% confidence limits)	(1.00 to 1.34)	(0.97 to 1.41)

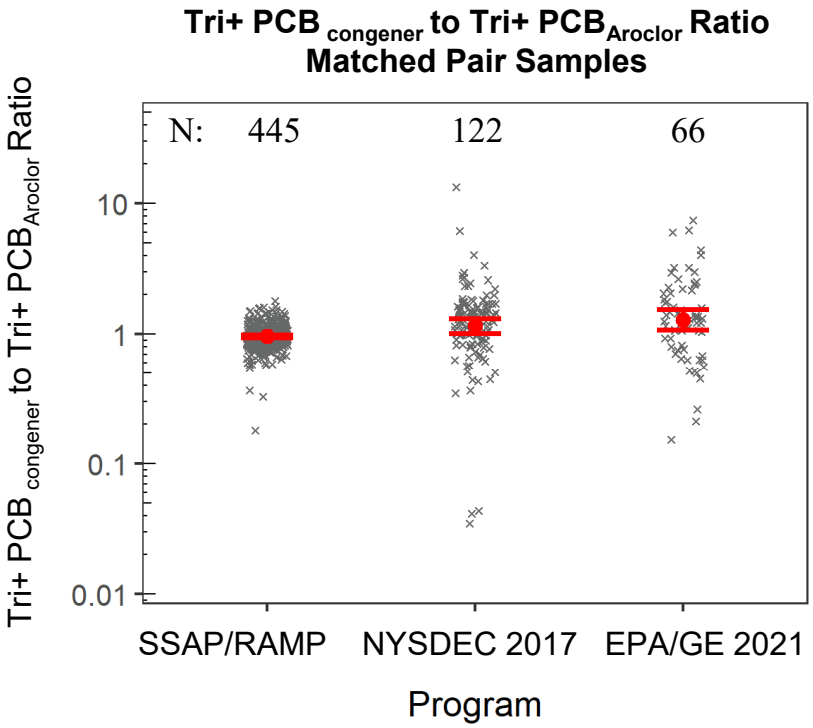
Notes:

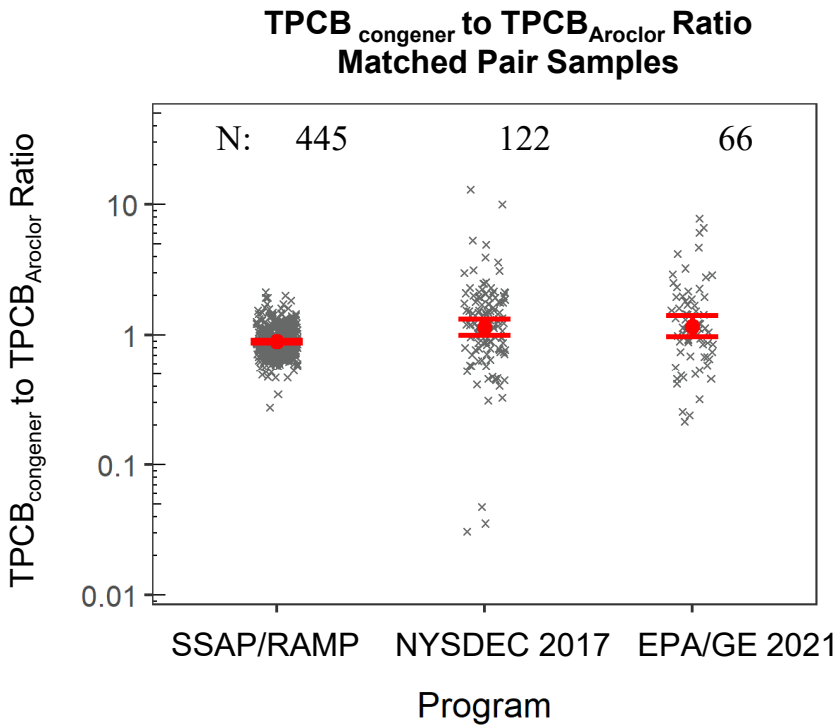
- $TPCB_{congener}$ is the sum of all congeners measured by M1668. Non-detect results were set at zero in the summation.
- $TPCB_{Aroclor}$ is the sum of all Aroclors measured by M8082. Non-detect results were set at zero in the summation.
- *r*: Pearson correlation coefficient based on log-transformed concentration data
- 95% confidence limits on the geometric mean of the ratio are the bias-corrected and accelerated (BCa) bootstrap 2.5^{th} to 97.5^{th} percentile values.
- One 2021 sample with $TPCB_{congener}$ <0.01 mg/kg was not shown.

Comparison of Aroclor-based TPCB ($TPCB_{Aroclor}$) and Congener-based TPCB ($TPCB_{congener}$) Concentrations

Figure 2-2b

July 2024





Tri+ PCB ratio	SSAP/RAMP	NYSDEC 2017	EPA/GE 2021
Geometric Mean	0.97	1.16	1.29
(95% confidence limits)	(0.95 to 0.99)	(1.01 to 1.32)	(1.08 to 1.55)

TPCB ratio	SSAP/RAMP	NYSDEC 2017	EPA/GE 2021
Geometric Mean	0.89	1.16	1.16
(95% confidence limits)	(0.87 to 0.91)	(1.00 to 1.34)	(0.97 to 1.41)

Legend

- 95% Upper Confidence Limit
- Geometric mean of the ratio
- 95% Lower Confidence Limit
- Individual value

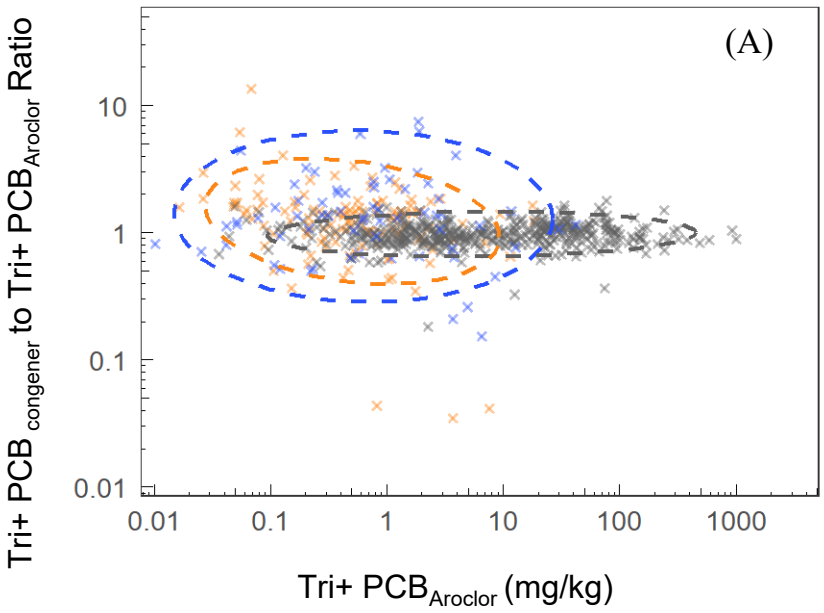
Notes:

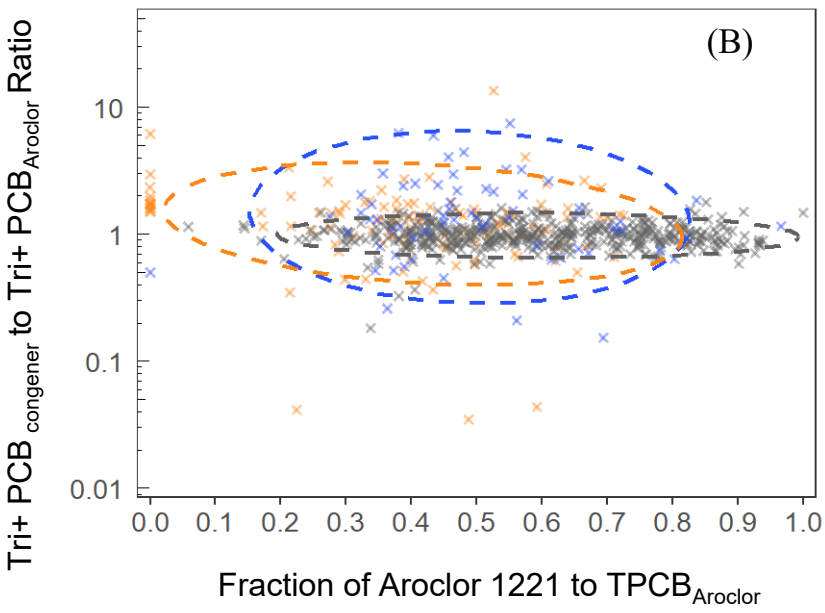
- Results from SSAP/RAMP samples are derived from same extract, therefore, exhibit less variability than those reported recently where results were derived from separate extractions.
- N: number of pairs

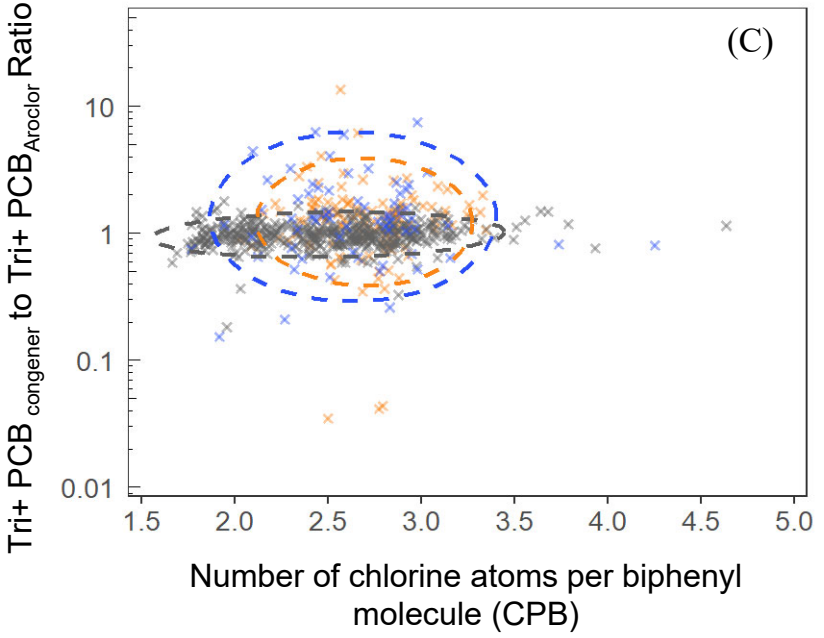
Temporal Changes in Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ Ratios and $TPCB_{congener}$ to $TPCB_{Aroclor}$ Ratios

Figure 2-3

July 2024







Legend

- SSAP/RAMP
- NYSDEC 2017
- EPA/GE 2021
- 95% confidence ellipse

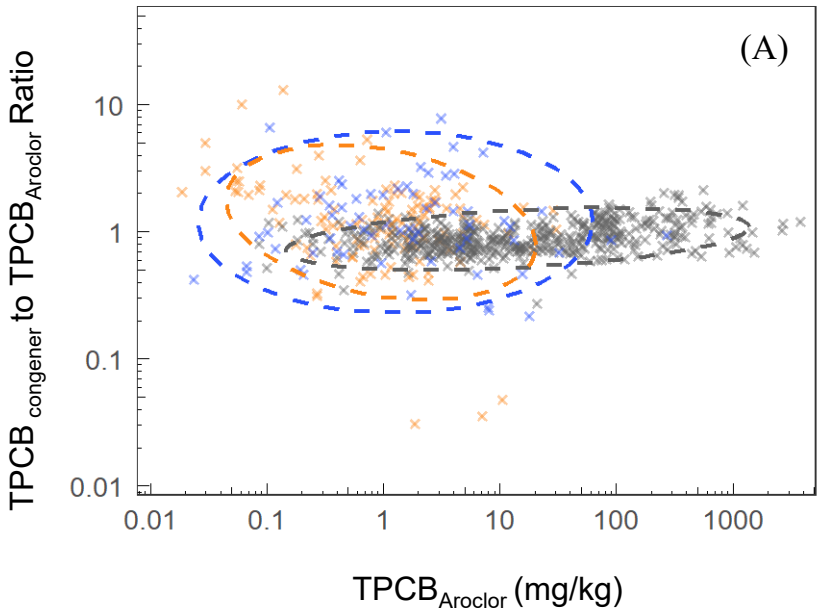
Notes:

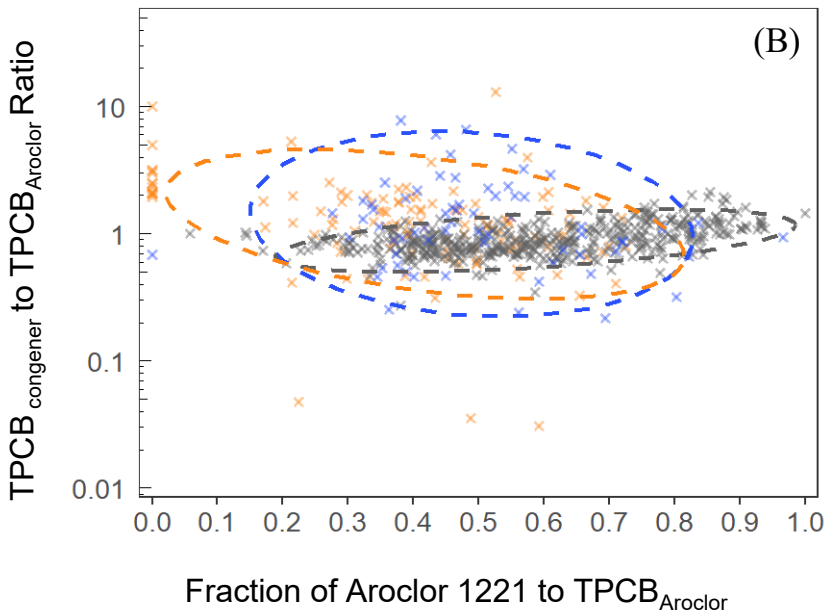
- Dashed boundary line is 95% confidence ellipse based on multivariate t-distribution. This confidence ellipse defines the region that contains 95% of all samples that can be drawn from the underlying t-distribution.
- Number of chlorine atoms per biphenyl molecule (CPB) represents a simple index to characterize the PCB composition.

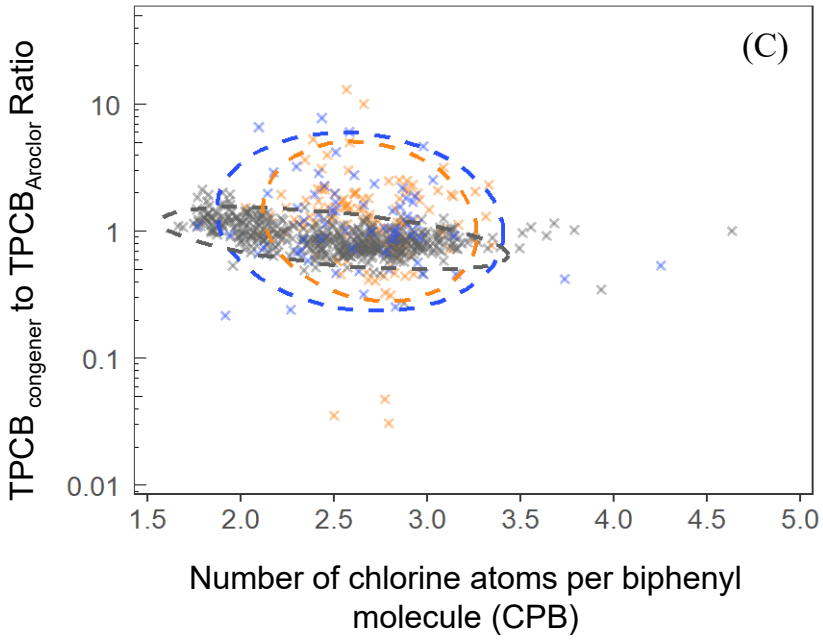
Relationship between Tri+ $PCB_{congener}$ to Tri+ $PCB_{Aroclor}$ Ratio and Potential Influential Factors

Figure 2-4a

July 2024







Legend

- SSAP/RAMP
- NYSDEC 2017
- EPA/GE 2021
- 95% confidence ellipse

Notes:

- Dashed boundary line is 95% confidence ellipse based on multivariate t-distribution. This confidence ellipse defines the region that contains 95% of all samples that can be drawn from the underlying t-distribution.
- Number of chlorine atoms per biphenyl molecule (CPB) represents a simple index to characterize the PCB composition.

Relationship between $TPCB_{congener}$ to $TPCB_{Aroclor}$ Ratio and Potential Influential Factors

Figure 2-4b

July 2024