

## Ambient PFAS Levels in the Ohio River

6/17/22

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### **Background**

Per- and polyfluoroalkyl substances (PFAS) are man-made substances and do not exist naturally in the environment. This group of chemicals has been used in industry and consumer product manufacturing since the 1950s because of their non-stick, water resistant, low surface tension, and surface spreading properties to name a few.

Because these substances are very stable, they do not break down but rather persist in the environment. PFAS compounds can enter waterbodies through direct discharge, runoff, or air deposition. As a result, some question whether PFAS compounds are present in significant levels in natural waterbodies since this may be a route of exposure for humans.

Because these substances are very stable, they do not readily break down and their persistence in the environment is concerning. PFAS compounds can contaminate waterbodies through direct discharge, runoff or air deposition. Nationally, there is an increased awareness over whether PFAS contaminants are present in significant levels in natural waterbodies since this may be a route of exposure for humans.

This project seeks to characterize, under present water quality conditions, ambient levels of twenty-eight (28) PFAS compounds in Ohio River surface water. To accomplish the goals of this project, ORSANCO staff collected Equal Discharge Increment (EDI) and discrete grab surface water samples from the Ohio River during two seasonal sampling events. United States Environmental Protection Agency (US EPA) and their subcontractor conducted laboratory analytical testing to analyze these samples for PFAS. ORSANCO will use these data to develop a status report of findings of select PFAS levels in the Ohio River.

### **Study Objectives**

The primary objective of this effort was to characterize ambient levels of select PFAS compounds in the Ohio River at 20 sampling locations. The survey was not intended to focus on drinking water, but rather to develop an understanding of ambient baseline conditions of PFAS in Ohio River surface water. The study was not intended to identify sources or determine ecological and health risks. The results from this effort may help to inform state and federal agencies, water utilities and other interested parties on the status of PFAS in the river and provide a base understanding to evaluate the potential need for future PFAS monitoring in the Ohio River. A secondary objective of the study was to investigate the distribution of PFAS in the Ohio River water column.

Two additional sampling sites, one on the Monongahela River and one on the Allegheny River, were added to the study plan as part of a separate sampling effort in partnership with the West Virginia Water Research Institute. Sampling at these two sites was conducted by ORSANCO in coordination with the primary sampling effort for consistency in sample collection methods and laboratory analysis.

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## **Sampling Locations – Equal Discharge Increment Sampling (EDI)**

Sample site selection was based on a modified, spatially-balanced probabilistic sampling design. In this approach, the river was divided into 20 equal length segments of 49.05 miles (i.e. 981 river miles / 20 sampling sites). The initial sampling site in the most upstream segment (i.e. Ohio River mile 0.00 to mile 49.05) was randomly determined by Tony Olsen, a national expert on probabilistic study design with the US EPA NHEERL in Corvallis, OR. This first sampling point was established at Ohio River mile 11.70. Thereafter, each additional sampling point was determined by adding 49.05 miles to the previously selected site until the remaining 19 sites had been selected within subsequent river segments. This approach allowed for 20 equidistant sites spanning the full length of the Ohio River.

Following the initial site selection, each Ohio River site was evaluated individually to determine if the initial site was suitable for sampling. Adjustments to some sites were necessary to ensure Equal Discharge Increment (EDI) sampling could be done safely and without interferences that could impact representative sample collection. Adjustments were made in the event that a specific site was in a location in which the sampling could not be performed safely (e.g. within a restricted zone near a lock & dam), or if a physical structure (e.g. bridge or island) prevented proper EDI cross-sectional sampling. Sites were also to be moved if they fell within a regulatory mixing zone so as to represent ambient conditions, however, this did not occur. Sampling points that had to be adjusted for any of the above noted reasons were moved to the nearest suitable point which allowed for the EDI sampling to be completed safely and free of impediments.

Table 1. below lists each initial sampling point and the final adjusted locations by river mile and latitude/longitude coordinates. Sampling was conducted at the final adjusted locations based on latitude and longitude coordinates.

The locations of the two tributary EDI sampling sites, one on the Allegheny and one on the Monongahela River, were established by the West Virginia Water Research Institute to meet their specific and separate sampling objectives.

## **Sampling Locations – Discrete Sampling**

In addition to the PFAS sample collection by EDI, discrete water samples were collected at three of the Ohio River EDI sampling locations per round (this was increased to five sites during Round Two sampling in an effort to broaden our discrete sampling range and provide more data for sampling method comparison). The objective of the discrete sampling was to investigate how PFAS may be distributed throughout the water column at a given EDI cross-section. Selection of discrete sampling collection sites was based on guidance from the ORSANCO PFAS Working Group. The PFAS Working Group recommended the three discrete sampling sites be located at the EDI sampling locations that were either near locations with historic data which might indicate that detections would be expected, and at locations downstream of significant tributaries where incomplete mixing in the water column might be expected. Sites selected based on these criteria included ORM 256.95 (downstream of Parkersburg, WV), ORM 551.25 (downstream of Kentucky River), and ORM 600.3 (Louisville area). During Round Two, discrete sampling was performed at the above three locations, with two additional sites being added at ORM 306.00

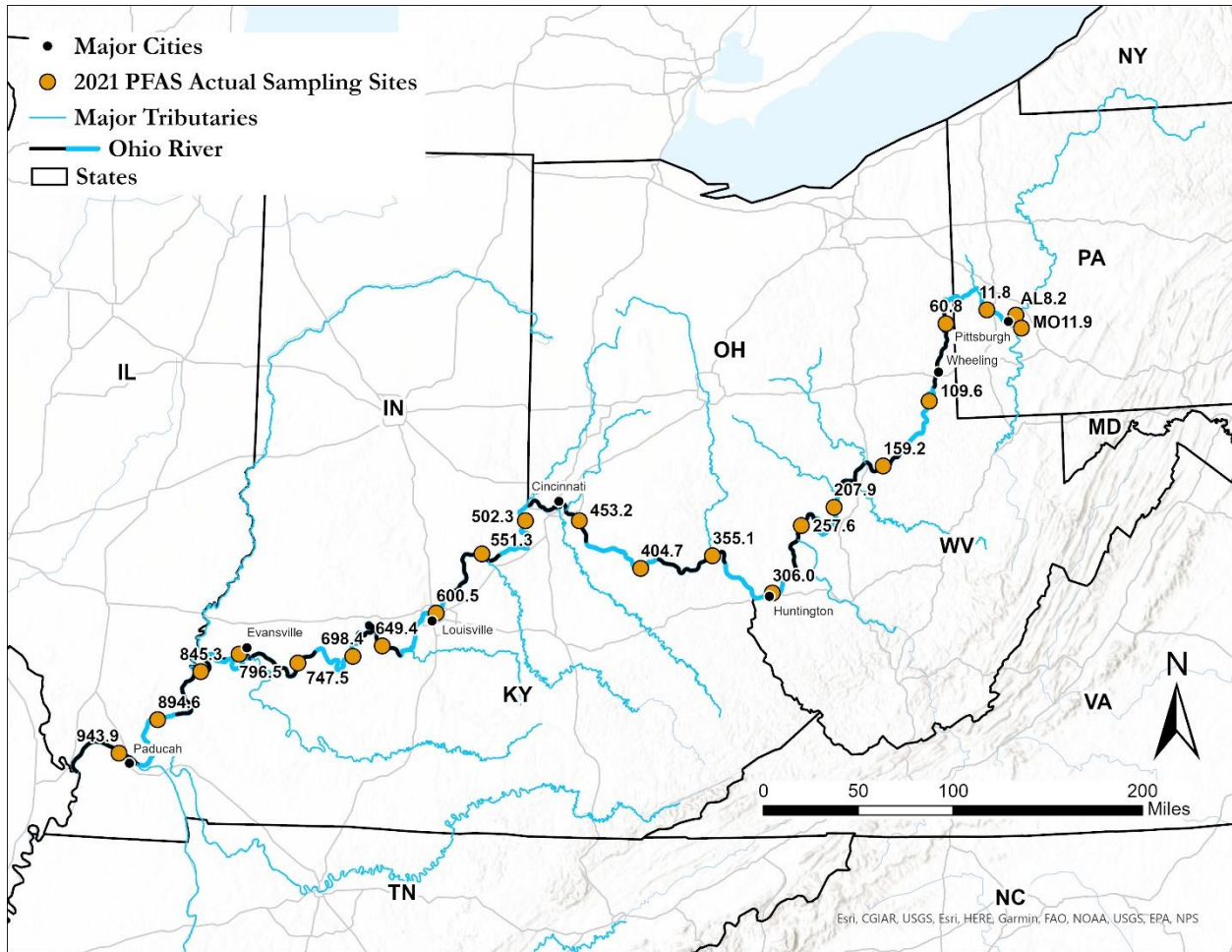
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(Huntington, WV) and ORM 355.1 (Portsmouth, OH). Sampling locations are described in Table 1. and Figure 1.

**Table 1. Ohio River PFAS Sampling Locations**

| Site I.D. | Nearest City and State | Initial Site Mile Point | Reason for Selecting Alternate Site                            | Final Adjusted Site Mile Point | Final Latitude | Final Longitude |
|-----------|------------------------|-------------------------|--|--------------------------------|----------------|-----------------|
| 1         | Sewickly, PA           | 11.70                   | Initial site close to bridge; may cause interference with ADCP | 11.76                          | 40.532275      | -80.186281      |
| 2         | Toronto, OH            | 60.75                   | No change  | 60.75                          | 40.442611      | -80.607167      |
| 3         | Powhatan Point, OH     | 109.80                  | Initial site in barge fleeting area                            | 109.60                         | 39.858006      | -80.800511      |
| 4         | Eureka, WV             | 158.85                  | Cross-section obstructed by island                             | 159.22                         | 39.377575      | -81.280039      |
| 5         | Long Bottom, OH        | 207.90                  | No change  | 207.90                         | 39.077333      | -81.780783      |
| 6         | Cheshire, OH           | 256.95                  | Initial site in barge fleeting area                            | 257.60                         | 38.944531      | -82.106594      |
| 7         | Huntington, WV         | 306.00                  | No change  | 306.00                         | 38.438200      | -82.404522      |
| 8         | Portsmouth, OH         | 355.05                  | No change  | 355.05                         | 38.725794      | -82.987878      |
| 9         | Maysville, KY          | 404.10                  | Initial site in barge fleeting area                            | 404.71                         | 38.633753      | -83.695864      |
| 10        | Blairsville, OH        | 453.15                  | No change  | 453.15                         | 38.994547      | -84.302700      |
| 11        | Bellevue, KY           | 502.20                  | Cross-section obstructed by island                             | 502.25                         | 38.991792      | -84.837647      |
| 12        | Brooksburg, IN         | 551.25                  | No change  | 551.25                         | 38.736139      | -85.261681      |
| 13        | Jeffersonville, IN     | 600.30                  | Initial site obstructed by boat docks                          | 600.48                         | 38.284083      | -85.702078      |
| 14        | Mauckport, IN          | 649.35                  | No change  | 649.35                         | 38.028136      | -86.221511      |
| 15        | Rome, IN               | 698.40                  | No change  | 698.40                         | 37.944417      | -86.508119      |
| 16        | Rockport, IN           | 747.45                  | No change  | 747.45                         | 37.880942      | -87.040939      |
| 17        | Evansville, IN         | 796.50                  | No change  | 796.50                         | 37.932656      | -87.618878      |
| 18        | Uniontown, KY          | 845.55                  | Initial site too close to dam; must move for safety            | 845.31                         | 37.788361      | -87.982083      |
| 19        | Carrsville, KY         | 894.60                  | No change  | 894.60                         | 37.409914      | -88.380736      |
| 20        | Metropolis, IL         | 943.65                  | Initial site in barge fleeting area                            | 943.90                         | 37.142917      | -88.739022      |
| 21        | Allegheny River        | N/A                     | Not Randomized   | 8.20                           | 40.48369       | -79.88589       |
| 22        | Monongahela River      | N/A                     | Not Randomized   | 11.90                          | 40.38322       | -79.84635       |

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**Figure 1. Ohio River PFAS Ambient Monitoring Locations; Allegheny and Monongahela Rivers Locations**

## Sample Collection – Equal Discharge Increment Sampling (EDI)

Two rounds of sampling were conducted at the 20 Ohio River and two tributary locations listed in Table 1. EDI samples provide for a more average representation of a given cross-section and minimizes the chances of sampling an anomaly that could be more likely to occur with a single point grab sample at any given sampling location. Typically only one site was sampled per day; however up to two sites were sampled per day if conditions permitted. Samples were collected using the EDI method, modified for PFAS sampling, and consisted of a representative composite of five vertical water column samples at a given cross-sectional sampling point. The EDI method was reliant on flow measured by an Acoustic Doppler Current Profiler (ADCP) which provided for an accurate calculation of the equal discharge increment and their exact locations. Samples were collected at the mid-point for each of the five flow quintiles along the cross-sectional line. Sampling was conducted using a D96-A1 sampler along with a VSR reel drive and US-SS1 churn splitter. Each of the five vertical water column samples were representative of each flow quintile and was combined in the churn splitter and homogenized. The homogenized sample was then decanted into two 250ml HDPE containers and shipped to the laboratory for analysis. The second 250ml sample

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served as a backup in the event the primary sample was compromised or was otherwise deemed unusable. Following sample collection, all associated equipment was decontaminated using 0.2% phosphate free detergent and rinsed with PFAS free water. Complete details of the sample collection method are described in *Standard Operating Procedure for the Collection of Equal Discharge Increment Samples for PFAS Compounds in the Ohio River* (ORSANCO, 2020).

## **Sample Collection – Discrete Sample Collection**

The purpose of the discrete sampling was to investigate how PFAS are distributed throughout the water column. Discrete water samples were collected at three EDI sampling locations in the first round and at five sites in the second round of sampling. At each location, discrete samples were collected at three depths (surface, mid-depth, and bottom) and at three points laterally along the cross-sectional line. These lateral points correspond to the first, third, and fifth flow quintile points established for the EDI sampling. Surface samples were collected immediately below the water surface, as near to the surface as possible without drawing air into the system. This was challenging as the river surface was rarely calm and flat. Mid-depth samples were collected at the midpoint between the surface and bottom, while bottom samples were collected approximately one meter off bottom so as not to collect any bottom sediment. This produced nine river samples for each cross-sectional location (3 points laterally x 3 points vertically).

Discrete cross-sectional samples were collected using a peristaltic pump with HDPE/silicone tubing. The tubing was lowered to the desired depth at each sampling point. The pump (non-contact) was then engaged to draw water through the tubing and directly into the PFAS sample containers. Two 250 ml bottles were collected for each sample. The second 250ml sample served as a backup in the event the primary sample was compromised or was otherwise deemed unusable. New tubing was used at each sampling location and decontaminated (using EDI decontamination procedures), prior to use in the field. Used HDPE/silicone tubing was discarded after use.

## **Quality Control Sample Collection**

Quality control samples were collected as part of this effort which included equipment blanks, field blanks, trip blanks, and field replicates. These quality control samples were handled and treated in the same manner as the river water samples.

An equipment blank was prepared at each sampling location for each sampling method employed at a given location (i.e. EDI and peristaltic pump methods). The equipment blank was a rinsate, which used PFAS-free water that was passed over all equipment surfaces that came into direct contact with sample water during the normal collection process.

One field blank was collected for each week of sampling. The field blank consisted of PFAS-free deionized water collected in an HDPE sample container. The lid of the field blank container was removed just prior to the river sample collection process. The field blank lid was reattached promptly after the river sample collection was complete. The field blank served to determine if a sample had been compromised by atmospheric conditions and/or sampling handling practices.

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One trip blank was collected and analyzed for each week of sampling. A trip blank consisted of an HDPE sample container filled with PFAS free deionized water prior to deployment to the field. The trip blank container was transported in a sample cooler and remained closed for the entire week of sampling.

An EDI field replicate sample was collected at each of the three discrete sample collection sites referenced in the previous section. Collection of the EDI field replicates at the discrete sampling locations was done in an effort to maximize the data available in order to evaluate the different sampling methods employed in this project. A field replicate consisted of a second homogenized river water sample aliquot decanted from the churn splitter from which the primary EDI sample was drawn. Both the primary sample and the field replicate sample were analyzed and compared as a measure of variability within the homogenized volume of water in the churn splitter.

## Sample Analysis

US EPA Office of Research and Development Site Characterization and Monitoring Technical Support Center (EPA ORD SCMTC) provided contracting support through Battelle Laboratories for the laboratory analyses of all PFAS samples collected as part of this effort. Analysis for target PFAS was performed using liquid chromatography tandem mass spectrometry (LC-MS/MS) as detailed in the Quality Assurance Project Plan: PFAS Source Characterization on the Ohio River (EPA ORD SCMTC, 2020). Analytical results were generated for the select 28 PFAS target analytes listed in Table 2.

**Table 2. PFAS Analyte List**

|    | <b>Analyte Name</b>                           | <b>Acronym</b>    | <b>CAS Number</b> |
|----|---|-------------------|-------------------|
| 1  | Perfluorobutanoic acid                        | PFBA              | 375-22-4          |
| 2  | Perfluoropentanoic acid                       | PFPeA             | 2706-90-3         |
| 3  | Perfluorohexanoic acid                        | PFHxA             | 307-24-4          |
| 4  | Perfluoroheptanoic acid                       | PFHpA             | 375-85-9          |
| 5  | Perfluorooctanoic acid                        | PFOA              | 335-67-1          |
| 6  | Perfluorononanoic acid                        | PFNA              | 375-95-1          |
| 7  | Perfluorodecanoic acid                        | PFDA              | 335-76-2          |
| 8  | Perfluoroundecanoic acid                      | PFUnA             | 2058-94-8         |
| 9  | Perfluorododecanoic acid                      | PFDoA             | 307-55-1          |
| 10 | Perfluorotridecanoic acid                     | PFTrA             | 72629-94-8        |
| 11 | Perfluorotetradecanoic acid                   | PFTeDA<br>(PFTeA) | 376-06-7          |
| 12 | N-methylperfluorooctanesulfonamidoacetic acid | NMeFOSAA          | 2355-31-9         |
| 13 | N-ethylperfluorooctanesulfonamidoacetic acid  | NEtFOSAA          | 2991-50-6         |
| 14 | Perfluorooctanesulfonamide                    | PFOSA             | 754-91-6          |
| 15 | Perfluorobutanesulfonic acid <sup>a</sup>     | PFBS              | 375-73-5          |
| 16 | Perfluoropentanesulfonic acid                 | PFPeS             | 2706-91-4         |
| 17 | Perfluorohexanesulfonic acid                  | PFHxS             | 355-46-4          |

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|    |  |              |             |
|----|--|--------------|-------------|
| 18 | Perfluoroheptanesulfonic acid                        | PFHpS        | 375-92-8    |
| 19 | Perfluorooctanesulfonic acid                         | PFOS         | 1763-23-1   |
| 20 | Perfluorononanesulfonic acid                         | PFNS         | 68259-12-1  |
| 21 | Perfluorodecanesulfonic acid                         | PFDS         | 335-77-3    |
| 22 | 1H,1H,2H,2H-Perfluorohexane sulfonate                | 4:2 FTS      | 757124-24-4 |
| 23 | 1H,1H,2H,2H-Perfluorooctane sulfonate                | 6:2 FTS      | 27619-97-2  |
| 24 | 1H,1H,2H,2H-Perfluorodecane sulfonate                | 8:2 FTS      | 39108-34-4  |
| 25 | Hexafluoropropylene oxide dimer acid <sup>b, c</sup> | HFPO-DA      | 13252-13-6  |
| 26 | 4,8-dioxa-3H-perfluorononanoic acid <sup>c</sup>     | ADONA        | 919005-14-4 |
| 27 | 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid  | 11Cl-PF3OUdS | 763051-92-9 |
| 28 | 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid     | 9Cl-PF3ONS   | 756426-58-1 |

a – Replacement compound for PFOS

b – Commonly known as Gen X

c – Replacement compound for PFOA

## Sample Collection Schedule

Two rounds of PFAS sampling were completed at 20 Ohio River and two tributary sites. Each round of sampling took five to six weeks to complete. The first round of sampling was completed in June-July, 2021, and the second round in September-October 2021. Sample collection dates have been provided in the data tables. River flows were almost always higher during the first round of sampling, in the summer 2021, than the second round of sampling completed in the fall 2021.

## Results

Project results represent ambient conditions for PFAS in the Ohio River at the time of sample collection. Characterization or generalization of river conditions based on these PFAS analytical results should not be extended to any other time frame beyond the scope of this project. Additional analyses of the data are not planned at this time.

The Appendix contains a list and detailed explanation for acronyms and commonly used terms used in this report.

### EDI Cross-Section Sampling

Table 3. includes the EDI cross-sectional results for 28 PFAS analytes for two rounds of sampling. Numeric values in ng/L (parts per trillion) are provided for data above the laboratory limit of quantitation (LOQ). Samples that were detected, but below the LOQ, have been marked by the laboratory with a J-flag qualifier. The J-flag qualifier indicated the presence of the PFAS analyte, but the result did not have the statistical confidence at the level detected. Samples that had results below the detection level or did not show the presence of the analyte were marked by the laboratory with a U-flag qualifier.

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Table A-1. in the Appendix contains the EDI results, and, additionally shows numeric values for data below the LOQ, and the laboratory established criteria for the detection limit (DL), level of detection (LOD), and limit of quantitation (LOQ).

Results from both rounds of sampling indicated the presence of select PFAS analytes at trace levels. The first round of sampling generally had more detections and more detections above the limit of quantitation than the second round of sampling. Broad observations from the first round of sampling include:

- Every site had detections of multiple PFAS (majority of which were J-flagged, very low levels).
- Twelve of twenty eight PFAS were detected; nine were detected frequently.
- Five of twenty eight PFAS were detected above the laboratory LOQ.
- PFOA and HFPO-DA were detected above the LOQ most frequently.
- HFPO-DA had the highest concentration at 32.2 ng/L.
- PFOA was detected at nineteen sites with a range from 4.88 ng/L to 12.90 ng/L.
- HFPO-DA (GenX) was detected at nine sites with a range from 5.63 ng/L to 32.20 ng/L.
- PFOS was detected below the LOQ at every site.
- PFBA was detected at one site at 5.31 ng/L.
- PFBS was detected at three sites with a range from 5.01 ng/L to 6.05 ng/L.
- PFPeA was detected at five sites with a range from 5.76 ng/L to 26.60 ng/l.

Broad observations from the second round of sampling include:

- Every site had detections of one or more PFAS (majority of which were J-flagged, very low levels).
- Nine of twenty eight PFAS were detected; eight were detected frequently.
- Six of twenty eight PFAS were detected above the LOQ.
- PFOA and PFBA were detected above the LOQ most frequently, followed by HFPO-DA.
- 6:2FTS had the highest concentration at 28.2 ng/L (re-analysis underway), followed by HFPO-DA at 12.0 ng/L.
- PFOS was detected at one site at 7.73 ng/L.
- PFOA was detected at seven sites with a range from 5.00 ng/L to 6.82 ng/L.
- HFPO-DA (GenX) was detected at four sites with a range from 5.43 ng/L to 12.0 ng/L. PFBA was detected at eight sites with a range from 5.53 ng/L to 10.30 ng/L.

Replicate EDI cross-sectional samples were collected at three Ohio River stations for each round of sampling and generally showed good agreement. All samples with replicate data above the limit of quantification (LOQ) met the goal for precision of less than thirty percent relative percent difference (%RPD).

## Discrete Sampling

Table 4. includes discrete sampling results. Discrete sampling was completed at three EDI cross-sectional sampling locations during the first round of sampling, and at five EDI cross-sectional sampling locations during the second round of sampling. The goal of the discrete sampling was to identify if there was any



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systematic distribution of select PFAS analytes in the water column. Results of discrete sampling did not identify any patterns of distribution of PFAS in the water column from the two rounds of sampling. In addition, discrete samples generally showed good agreement with the EDI cross-section sample results at each individual sample location. Since the discrete data shows relatively uniform results throughout the Ohio River water column, this might suggest, based on these two rounds of sampling, that future sample collection efforts could be completed with grab sampling which can be accomplished with one sampler, instead of three samplers and a boat to complete EDI cross-section sampling.

Table A-2. in the Appendix contains the discrete data, and additionally presents numeric values for data below the LOQ, as well as the laboratory established criteria for the detection limit (DL), level of detection (LOD), and limit of quantitation (LOQ).

## Quality Assurance Results

ORSANCO requested the laboratory to re-analyze several samples for the 6:2FTS analyte due to unexpected results and potential contamination issues with this PFAS analyte in both Rounds 1 and 2. In Round 1, re-analysis for the 6:2 FTS analyte indicated levels below detection, but the holding time was exceeded. These results have been qualified by the laboratory with a T-flag. ORSANCO also requested one sample to be re-analyzed for PFOS due to a laboratory flag (Q) in Round 2. The Q flag indicated a QAQC parameter did not meet or exceeded one of established criteria for analyte identification (more than one parameter is used for identification). Samples in round 2 that have been requested to be rerun are flagged with an (R).

Results of equipment blanks, field blanks, and trip blanks can be found in Table A-3. in the Appendix. Acceptance criteria for blanks require them to be below the laboratory limit of quantitation (LOQ). All project blank results were below the LOQ, indicating acceptable quality assurance results, with the exception of blanks at ORM 551.3 for 6:2FTS (Round 2) which have been scheduled to be re-analyzed by the laboratory. Acceptance criteria for replicate samples was based on a relative percent difference of <30%. All replicate samples for which there were PFAS analyte detections above the LOQ met the acceptance criteria.

The data tables and report will be updated after analytical results have been reviewed and approved for release by USEPA.

## Project Definitions

Project definitions and acronyms can be found in the Appendix.

## APPENDIX

### PFAS PROJECT DEFINITIONS AND ACRONYMS

**ACOUSTIC DOPPLER CURRENT PROFILER (ADCP):** The ADCP measures stream (river) channel measurement that uses the Doppler Principle to detect specific velocities in many segments (or bins) of the depth and total width of the stream channel.



**CHURN SPLITTER:** A device used to ensure that the combination of samples added to the churn are equally mixed. The churn functions to homogenize the mixture of subsamples so that any sediment and particulates are evenly distributed in the matrix. The churn splitter contains a paddle used to move the water. The churn can simultaneously dispense into sampling containers. For PFAS sample compositing, the Churn Splitter must be made of PFAS free materials.



**CROSS-SECTION:** For the purposes of PFAS sample collection efforts, cross-section refers to three equidistant points across the width of the river representing the left side bank, midpoint or center, and the right side when facing downstream.

**DISCRETE SAMPLE:** An individual aliquot taken from a larger matrix (liquid, solid, air, etc.). Commonly referred to as a “grab” sample. Represents a portion collected at a specific point in time and may or may not be representative sampling of the entire matrix for given a given analyte or parameter. For the PFAS project, discrete samples may be used to describe individual samples collected that are to be composited.

**DETECTION LIMIT (DL):** This is the lowest level at which the entire analytical system can achieve a recognizable signal and acceptable calibration point for a given analyte. This is a calculated variable determined by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5 x

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10<sub>n</sub>) (where n = integer). It may be the concentration of the lowest calibration standard taking into consideration specified sample weights, volumes and clean up procedures. Some USEPA methods may use ML instead of DL. The DL is established by the analytical laboratory and is verified (and adjusted as appropriate) quarterly.

**DPPS:** Discrete peristaltic pump sampling. This is a sample collection method that uses a peristaltic pump to acquire a liquid aliquot at a given depth. Movement of the sample is achieved using a squeezing and releasing motion that mimics the peristaltic action in the human gut.

**EQUAL DISCHARGE INCREMENT (EDI):** the division of a waterway into segments based on an equal portion of flow (water discharge). This is often different from divisions of a water way by equal distances or widths across the river channel. For EDI PFAS sampling, a minimum of five quintile segments, each representing 20% of total discharge flow from one bank to the other, will be used.

**EQUIPMENT BLANK:** (aka rinsate blank) PFAS free water is taken through the equipment sampling process and may be poured through equipment, withdrawn/siphoned from a PFAS free container by equipment or equipment is soaked or surrounded by an aliquot of PFAS free water in a PFAS free sampling container over a period of time (ie., monitoring probes). Equipment blanks are used to indicate whether equipment may be a source of contamination and ensures that any decontamination and cleaning processes are adequate for sample collection of intended analytes. For PFAS analysis, Equipment blanks are run daily, prior to any sample collection during each round of sampling.

**FIELD BLANK:** The field blank is a PFAS free sampling container filled with PFAS free reagent water that is brought to and resides with the samplers during the entire sample collection process. If contaminants from air deposition are a concern, the field sampling container is left open to the elements during the sample collection event and then capped prior to preservation, storage, and shipping. The field blank is used to assess whether or not conditions at the point in time sampling occurred may have contaminated the sample. For the PFAS sampling project, one field blank shall be collected per each field sampling event (weekly) during each round of sampling.

**“FISH”:** The nickname ORSANCO uses to reference the US D-96-A1 sampler used in the EDI method. For PFAS sampling, all components of the FISH are modified such that any materials coming in direct contact with the surface water are comprised of PFAS free materials.



**HOLDING TIME:** This is the amount of time from when the sample has been collected to when the sample should undergo pre-treatment, extraction and/or analysis. Results may or may not be affected. When samples exceed the holding time, they have been flagged with a “T”.

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**LABORATORY CONTROL SPIKE (LCS)/LABORATORY CONTROL SPIKE DUPLICATE (LCSD):** An LCS/LCSD are samples are reagent water (PFAS free) samples that are spiked with a known amount of certified reference standard and then taken through the entire analytical process. The spike amount of certified reference standard should be near the mid-level concentration of the calibration range. LCS/LCSD is used to assess the accuracy of the method without matrix interferences. Percent recovery and relative percent difference are two statistics used in LCS/LCSD assessments.

**LEVEL OF DETECTION (LOD):** The level of Detection is determined through the detection limit (DL), using a factor between 2-4 times the DL as a spiking concentration with a signal to noise ratio (S/N) greater than or equal to 3 with all analyte identification method requirements satisfied. In establishing the LOD for a project, the sample aliquot size (mass, volume, dilution, % solid) should be taken into account and adjusted for. The LOD is used as the minimum estimated concentration and where the Type II (false negative rate) is 1% as below the LOD, the Type II error rate is >50%. LOD is calculated typically 3.18 times the MDL and then rounded up to 1, 2, 5 or 10 and based on the specified volume. Actual volumes processed through the analytical method may see +/- deviation from the 1, 2, 5, 10 LOD. The LOD has been established by the analytical laboratory and is verified (and adjusted as appropriate) quarterly.

**LIMIT OF QUANTITATION (LOQ):** The limit of quantitation is the smallest concentration that produces a quantitative result with a known and recorded precision and bias. For DOD/DOE projects, the LOQ is set at or above the concentration of the lowest initial calibration standard within the analyte concentration range. The LOQ should be at least (LOD<sup>2</sup>). The LOQ is the lowest level in the calibration curve that is used for quantitation. Results that fall below the LOQ and above the DL are flagged with a "J" to indicate the value is an estimated value. <LOQ is used to indicate any values that fall below the DL and are flagged with a "U". The LOQ is used (rather than DL) since type II error rate is 1% at LOQ (vs >50% at DL). Sometimes the LOQ may be referred to as the minimum reporting level (MRL) or Practical quantitation level (PQL). In establishing the LOQ for a project, the sample aliquot size (mass, volume, dilution, % solid) should be taken into account and adjusted for. The LOQ has been established by the analytical laboratory and is verified (and adjusted as appropriate) quarterly.

**METHOD DETECTION LIMIT (MDL):** This is a statistically calculated value (t-value) that represents the lowest measureable level that is reported with 99% confidence that the analyte concentration is value is greater than 0. Calculating an MDL with 99% confidence indicates that there is a 1% probability of a false positive when the sample yields a result at the MDL. MDL's are usually performed annually (and may be verified quarterly or as needed) and dependent on analytical and laboratory functions. The MDL is an approximation of the detection limit (DL). Refer to 40 CFR Part 136 for guidance on how to perform and MDL procedure. The MDL is established by the analytical laboratory and is verified (and adjusted as appropriate) quarterly.

**NON-DETECT (ND):** Used in lab reports to indicate that the target analyte was not found using the current analytical procedure and method parameters.

**PERISTALTIC PUMP:** A device used to draw or pull a volume of sample from its original location to another point for collection through tubing via mechanical squeezing and releasing of flexible tubing from a small drive motor. A peristaltic pump is commonly used to draw water up from depths below the surface. A typical peristaltic pump can draw water up from depths of about 25 feet.

**PFAS:** A group of man-made (synthetic) per- and polyfluoroalkyl substances that are used in manufacturing and industry due to their water resistant and stable properties. There are in excess of over

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5,000 PFAS compounds that are produced globally; commonly known PFAS chemicals include PFOA, PFOS, GenX, and ADONA. Because PFAS compounds are stable, they are persistent (don't break down) in the environment and exposure to certain PFAS may produce adverse health effects. Chemically, PFAS chemicals have a carbon chain backbone with fluorides, alkyl, or other functional groups attached in a straight or branched chain.

**QUALIFIER FLAG:** This is an indicator to denote that either a situation occurred from sample receipt, pre-treatment, extraction, or analysis that may have affected results or that results have been determined to fall outside established QAQC levels such that an exact concentration may not be calculated and an estimate value has been provided.

**REPLICATE SAMPLE (FIELD REPLICATE):** Samples taken from the same population under the same conditions. An aliquot or sub-sample is taken from the original collected event. Replicate samples will be collected in the exact manner of the primary sample. Replicates, for the purposes of this PFAS project, are defined as an additional and separate aliquot of water taken from the churn splitter containing the primary river sample. The primary sample is decanted first, then, an additional PFAS free sample container is filled from the churn splitter. Replicates will be collected at the rate of not less than one per 10 EDI events. This number can be increased to meet specific quality control measures if necessary. A replicate sample can be used to assess method variance in sample collection and analysis.

**RELATIVE PERCENT DIFFERENCE (RPD%):** The relative percent difference is a statistical assessment of the variability between two samples. For PFAS analytes the formula is:

where  $C_s$  = Sample PFAS analyte concentration  
 $C_R$  = Replicate sample PFAS analyte concentration

$$RPD = \frac{|C_s - C_R|}{(C_s + C_R) / 2} \times 100$$

**REPORTING LIMIT:** The reporting limit is a *project specific, method sensitive analyte criterion that is established by the end user and their quantitative data needs*. The RL should be the lowest concentration for a specific analyte to generate quantitative data with known precision and bias for a given matrix. An RL can be established at or above the LOQ. Data may be reported below the RL, however, that data should be qualified as an estimated concentration and proper qualifier flags should be used.

**TRANSECT:** A horizontal transect is a delineation across the width of the Ohio river where samples are collected equi-distant at the left descending bank, mid-point of the river and the right descending bank. A vertical transect extends from the surface of the water down to the bottom of the river bed. A sample just below the surface, mid depth and at the bottom is collected. For the PFAS project, the vertical transects are collected at the loci of the horizontal transect.

**TRIP BLANK:** A trip blank is transported through the entire start to finish process of the PFAS sampling event. If the laboratory is providing sampling containers, the trip blank is filled at the laboratory (Battelle Norwell Laboratory) using PFAS free reagent water into a PFAS free sampling container, sealed and

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transported with sample containers. Trip blanks are frequently associated with the collection of volatiles samples. For this PFAS sampling project, there will be one trip blank per sampling event.

**US-D-96-A1:** A depth integrating collapsible bag sampler used for collecting suspended particles and sediment samples. Also referred to as the "FISH". This device is capable of collecting a maximum volume of 3 liters (3L) and weighs about 80 lbs when full. This bag sampler is appropriate for collection of surface water in moving water conditions where the velocity is between 2-6 ft/sec. For PFAS sample collection, the collapsible bag and nozzle (components in direct contact with flowing surface water matrix) must be made of PFAS free materials such as HDPE or polypropylene. Teflon and other fluoropolymers **MUST NOT** be used in PFAS sampling.