Water Quality in Ohio Rivers and Streams

Project Study Plan

Version 2.0 November 9, 2022

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1. OBJECTIVES

This Study Plan, implemented by the National Center for Water Quality Research (NCWQR), pertains to the on-going monitoring of stream water quality that has been in operation since 1975. The project's objectives are to gather chemical water quality data for rivers and streams in Ohio, to evaluate data in order to calculate the load of various chemical species entering Lake Erie and the Ohio River, to detect trends in water quality, and to interpret the effect of land use patterns on water quality. The chemical data to be collected include nitrate (NO3⁻), nitrite (NO2⁻), total Kjeldahl nitrogen (TKN), total phosphorus (TP), and orthophosphate (SRP or DRP). Findings from these objectives are shared with local, state, and federal agencies along with other scientists. Much of the data is made available at the NCWQR's Ohio Tributary Loading Data website (https://ncwqr.org/monitoring/). In general, the NCWQR samples frequently enough to resolve important environmental patterns, establishes method detection limits that are not more than 10% of the lowest concentrations of interest, and attain the analytical accuracy and precision stated in each method's standard operation procedure (SOP).

2. ISSUES

This Study Plan is motivated by the NCWQR's interest in understanding the impacts of land use of all types on surface water quality whether in lakes, rivers, or streams. The NCWQR's Heidelberg Tributary Loading Program locates sampling stations near the mouth of a river or near some physiographic transition. When possible, stations are located at United States Geological Survey (USGS) gaging stations to capitalize on flow data available for the same point for load calculations. Lake Erie tributaries are located as close to the lake as possible while avoiding reversals of flow due to lake level rises during seiche events. On the other hand, the Scioto River station is located at a boundary of glaciation where topography and land use changes.

Data from this monitoring program has aided in identifying the importance of non-point source pollution. The data document typical patterns of water quality response to runoff events that increase the flow of the river or stream. Patterns are observed for the studied chemical species in the leading front of sediment, the zone that contains sediment-attached species, and to the trailing zone attributed to the discharge from tile systems. The data also document the differences in concentration distributions as a function of flow that characterize systems dominated by point sources (high concentrations under ambient flow conditions) in contrast to those contaminated by non-point sources (high concentration during runoff events when most of the load is delivered in a short period of time). All of these patterns are important in understanding the ecology of these rivers and addressing causes of impairment.

The major long-term issue addressed by this Study Plan is the eutrophication of Lake Erie and its control by reduction of phosphorus concentration in the lake. This continuing study has helped to document achievement of the phosphorus target load of 11,000 metric tons of phosphorus (P)

into Lake Erie starting in the 1980s. Also, this study has documented decreases in total phosphorus in the Maumee and Sandusky Rivers of approximately 40% between 1975 to 1995, and decreases in dissolved reactive phosphorus (DRP or orthophosphate) of more than 80%. More recently, the NCWQR has documented substantial increases (170%) in DRP concentrations and loads, at the same time that Lake Erie is exhibiting increased phosphorus concentrations and related hypoxia and harmful algal blooms (HAB). In other watersheds, this Study Plan will address topics such as eutrophication of Grand Lake St. Marys as well as nitrate exports from Ohio River tributaries that can contribute to the Gulf of Mexico hypoxic zone.

Data from this project find use in many aspects of environmental management. The NCWQR data have been used by the Annex 4 working group formed following the Great Lakes Water Quality Agreement in 2012 to establish new target loads and concentrations for Lake Erie. Data from the NCWQR will also be used in the future to help quantify success at achieving these targets and will play a major role in the Ohio Environmental Protection Agency (OEPA) Western Lake Erie Basin collaborative plan to meet those target loads. The OEPA also uses NCWQR data in several Total Maximum Daily Load (TMDL) studies. Finally, the NCWQR data have been used by OEPA to conduct watershed mass balances throughout Ohio. Throughout the region and the nation, the data are used in the development, calibration and validation of land-use/water quality models.

3. PARAMETER COVERAGE

The parameters that are measured in this project are shown in Table 3.1. Detection limits can be found in the Standard Operating Procedures (SOPs) for each chemical parameter.

		Method
Chemical Parameter	Instrument	Reference
Total Phosphorus (TP)	Seal Analaytical AAIII	EPA Method 365.1
Orthophosphate (SRP)	Seal Analaytical AAIII	EPA Method 365.1
Total Kjeldahl nitrogen (TKN)	Seal Analaytical AAIII	EPA Method 351.2
Nitrate as N (NO ₃ -N)	Thermo Scientific IC	EPA Method 300.1
Chloride (Cl ⁻)	Thermo Scientific IC	EPA Method 300.1
Sulfate (SO ₄ ²⁻)	Thermo Scientific IC	EPA Method 300.1
Total Suspended Solids (SS)	Mettler Balance	EPA Method 160.2

Table 3.1 Chemical Parameters, Instruments, and Methods of the Heidelberg Tributary Loading Program

4. SAMPLING METHODS

At all monitoring stations, nutrient samples are taken three times per day using automated refrigerated ISCO samplers. Stream water is delivered to a receiving basin within a stream-side structure using a submersible pump. The peristaltic pumping system for the autosampler is used to move water from the receiving basin to the adjacent autosampler. The submersible pump also supports more dependable winter collections. Timers that control the submersible pumps allow hourly back flushing of the sampling lines and receiving basin. Sample bases are collected and changed once per week. OEPA approval for variances from published preservation methods is detailed in the letter dated January 29, 2016, Appendix A. During low-flow periods, a minimum of one sample per day is analyzed for the parameters listed in Section 3. For periods of high flow (e.g., storm runoff events), all samples are analyzed.

Analytical methods are listed in Table 3.1 in the previous section and detailed in Standard Operating Procedures (SOPs). SOPs are updated routinely and include method detection limits (MDLs).

5. STREAM FLOW MEASUREMENTS

Stream flow measurements are taken from the USGS's Groundwater and Streamflow Information Program (<u>www.usgs.gov</u>). Sampling location information is presented in Section 6, Appendix B.

6. SAMPLING LOCATIONS

Sampling locations with latitude and longitude, and U.S. Geological Survey HUC 8 and HUC 15 numbers are shown in table 6.1. Locations indicated with an "*" are sites where samples are taken at a different place than the stream gauge. Further details for each location can be found in Appendix B.

	USGS Gage		
River	Number	Latitude	Longitude
Maumee River at Waterville*	04193500	41.500000	-83.712778
Sandusky River near Fremont	04198000	41.307778	-83.158889
Honey Creek at Melmore*	04197100	41.022222	-83.109722
Rock Creek at Tiffin	04197170	41.113611	-83.168333
Portage River at Woodville	04195500	41.449444	-83.361389
Cuyahoga River at Independence	04208000	41.395278	-81.630000
Blanchard River near Findlay	04189000	41.055833	-83.688056
Tiffin River at Stryker	04185000	41.504444	-84.429722
Unnamed Tributary to Lost Creek	04185440	41.361667	-84.691111
Scioto River at Chillicothe	03231500	39.341389	-82.971111
Great Miami River at Miamisburg*	03271500	39.606667	-84.286944
Chickasaw Creek at St. Marys	402913084285400	40.486944	-84.481667

Coldwater Creek at Coldwater	402958084363300	40.499444	-84.481667
Muskingum River at McConnelsville	03150000	39.645000	-81.850000
Huron River at Milan	04199000	41.300833	-82.608333
South Turkeyfoot near Shunk	04192599	41.356389	-84.050833
West Creek near Hamler*	04192574	41.261944	-84.036667
Wolf Creek at Holland	04193999	41.609444	-83.684167
Potato Run near Wharton	04188324	40.865711	-83.491379
Unnamed Tributary to Blanchard	04188252	40.761368	-83.595360
River near Dunkirk			

Table 6.1 Rivers and Location of Sampling Sites of the Heidelberg Tributary Loading Program

7. SAMPLING SCHEDULE

At each sampling station, samples are taken three times per day (04:00, 12:00 and 20:00 hours). Sample bases are changed once per week. A minimum of one sample per day is analyzed for samples taken during low flow periods and up to three samples per day are analyzed during storm runoff events.

8. QA/QC PLAN

The NCWQR maintains a Quality Assurance Plan (QAP) consistent with Ohio EPA's "Manual of Surveillance Methods and Quality Assurance Practices." The QAP and corresponding SOPs are maintained as separate documents as they are routinely reviewed and updated.

9. WORK PRODUCTS

Work products, specifically chemical parameter concentrations and stream flow data, will be submitted to Ohio EPA on an annual basis. Data can be submitted more frequently upon request from Ohio EPA.

10. QUALIFIED DATA COLLECTORS AND OTHER PERSONNEL

A list of QDCs for this project can be found in Table 10.1. The procedures for training and supervising personnel that are not qualified as Level 3 data collectors are found in the QAP.

Name	Address*	QDC Number	Phone	Email
Laura Johnson#	NCWQR	01106	419-448-2056	ljohnson@heidelberg.edu
Jakob Boehler	NCWQR	00926	419-448-2056	jboehler@heidelberg.edu
Aaron Roerdink	NCWQR	00057	419-448-2250	aroerdin@heidelberg.edu

Lead Project Manager

*310 East Market St, Tiffin, OH 44883

11. CONTRACT LABORATORY INFORMATION

No contract laboratory will be used for the project. All analysis will be completed within the NCWQR and by NCWQR personnel.

12. SCIENTIFIC COLLECTOR'S PERMIT

The NCWQR believes that this requirement is not applicable for this Study Plan or the type of sampling undertaken in this study.

13. DIGITAL PHOTO CATALOG OF SAMPLING LOCATIONS

The NCWQR believes that this requirement is not applicable for this Study Plan or the type of sampling undertaken in this study. Please see Section 6 and Appendix B for detailed information on each sampling location. The NCWQR will maintain the photographic catalog if requested by the Director.

14. VOUCHER SPECIMENS

Biological sampling is not being completed under this Study Plan, and this requirement is not applicable.

15. LEAD PROJECT MANAGER STATEMENT ON SAMPLE LOCATIONS

Dr. Laura Johnson, lead project manager, will maintain and make available to the Director the name of the water body sampled, the sample location latitude and longitude, and the USGS HUC 8 number and name for each sampling location. Support for this statement can be found in Section 6 and Appendix A.

16. QUALIFIED DATA COLLECTION

All data collection will be conducted under the direct supervision of the QDCs listed in Section 10. These QDCs are approved for all data collection under this Study Plan. No QDC that is not approved for the type of collections detailed in this Study Plan will be used.

17. STATEMENT FROM QUALIFIED DATA COLLECTORS

I hereby certify that I have not been convicted of or pleaded guilty to a violation of section 2911.21 of the Revised Code (criminal trespass) of a substantially similar municipal ordinance within the previous five years.

Laura Johnson (Printed Name)

Jakob Boehler (Printed Name)

Aaron R. Roerdink (Printed Name)

(Signature) (Signature)

(Signature)

(Date)

9/2022

(Date)

20221110 (Date)

APPENDIX A



John R. Kasich, Governor Mary Taylor, Lt. Governor Craig W. Butler, Director

January 29, 2016

Dr. Laura Johnson National Center for Water Quality Research Heidelberg University 310 E. Market St. Tiffin, OH 44883

Dear Dr. Johnson:

The National Center for Water Quality Research (NCWQR) and the Division of Surface Water (DSW) have been discussing our different approaches to sample collection, preservation, and analysis since the Credible Data Rules were introduced in 2006. Ohio EPA frequently used NCWQR data prior to 2006 and has great interest in doing so again. However, differences in sample preservation have limited our ability to do so in the past ten years. The Credible Data Law (ORC 6111.52) and rules specify that we can only use level 3 data, the highest data level, for various purposes including development of Total Maximum Daily Loads. Methods to attain level 3 data are listed in the Credible Data rules.

NCWQR uses refrigerated autosamplers that collect daily or more frequent water samples over the course of seven days. Once a week the samples are collected from the autosamplers and taken to the NCWQR lab for analysis. Conventional level 3 methods for most parameters require the prompt filtration and acid preservation of samples. However, the Credible Data rules do provide us with a means to consider alternate methods.

The director may approve other level 3 methods as part of a project study plan approval. Any level 3 methods must have a degree of accuracy commensurate with the purpose for which the data will be used. (OAC 3745-4-06(C))

NCWQR has completed two comparison studies to evaluate differences between parameters analyzed on Day 0 and those analyzed on Day 7 (samples stored in the refrigerated autosampler for a week). We also jointly conducted a lab comparison study to evaluate the comparability of analytical results for split samples analyzed by the NCWQR lab and our Division of Environmental Services lab.

You provided a report summarizing the results of the NCWQR 2014 comparison, "A comparison of the effects of preservation and storage on nutrient concentrations from several Lake Erie tributaries," by L. Johnson and A. Roerdink. This report concluded there were statistical differences among samples (fresh vs. stored) for two parameters – DRP (dissolved reactive phosphorus, also known as ortho phosphorus) and chloride. Your report also noted that most DRP differences were at lower level concentrations and "that the small, consistent increase in DRP concentrations has no detectable effect on loading estimates."

50 West Town Street • Suite 700 • P.O. Box 1049 • Columbus, OH 43216-1049 epa.ohio.gov • (614) 644-3020 • (614) 644-3184 (fax) Dr. Laura Johnson National Center for Water Quality Research Heidelberg University Page 2

Based on your report and the laboratory comparison study, DSW approved a Miami Conservancy District (MCD) Project Study Plan (PSP). MCD uses NCWQR's methods to collect their samples. In this approval, nitrate, TKN, total phosphorus, orthophosphate (a.k.a. SRP), and total suspended solids were considered to be level 3 "J" data. The "J" signifies estimated and is recognition that there are some differences between your sample preservation methods and those of Ohio EPA. Also, the approval considered nitrite and ammonia to be level 2 data. This level 2 data would have less utility but would still be useable for nitrogen loading calculations (for the Ohio River Basin as well as the Lake Erie Basin).

In 2007, NCWQR submitted a draft PSP and a laboratory Quality Assurance Project Plan (QAPP) to DSW. At the time we had inadequate information to be able to approve the PSP. In the intervening years, as described above, we have resolved the issues preventing approval. In order to move forward from here, we would appreciate if you could submit a new PSP and current QAPP. This would provide us a path through the Credible Data process so we can again make use of the large volume of quality data produced by NCWQR. Now that we have verified the comparability of your results to our own, we intend to apply this forthcoming approval to both future and past data from NCWQR.

The PSP must be submitted by a current Qualified Data Collector (QDC). Eight different people from NCWQR have been approved as QDCs in the past. Three of those (Dorothy Ewing, Jack Kramer, and Barbara Merryfield) are currently QDCs but all expire in March 2016, with a three month grace period. Since the qualifications to become a QDC don't expire (only the status does), any of these eight could easily re-activate their QDC status by submitting a copy of their QDC application with a new signature page (new attachments aren't necessary, we have the supporting documentation on file).

Chemistry samples for an approved PSP can be collected by non-QDCs as long as those people have been trained by a QDC (who exercises periodic oversight over techniques and quality control). The rules and guidelines for the preparation of PSPs and QAPPs are found in OAC Rule 3745-4-06 and its appendices.

Following implementation of the PSP and QAPP, annual submission of data would provide for automatic renewal of any QDCs that are part of the PSP implementation, sampling, and oversight. Let us know if we can clarify anything in this letter or facilitate your submittal of QDC applications, a PSP, or resulting data. Contact Jeff Reynolds at (614) 705-1011 with any questions about the Credible Data Program.

Sincerely,

Tiffani Kavalec, Chief Division of Surface Water

cc: Brian Hall, DSW Cathy Alexander, DSW Jeff Reynolds, DSW

Appendix B

Tributary Sampling Stations of The National Center for Water Quality Research At Heidelberg University

Station: Maumee River at Waterville, Ohio (MBG)

Dates of Operation: 1-1-1975 to 9-30-1978, 10-13-1982 to present

Location of USGS gage: 41.500000, -83.712778 Location of sampling station: 41.477723, -83.712777 ()

Parameters: suspended solids, nutrients, major ions and pesticides

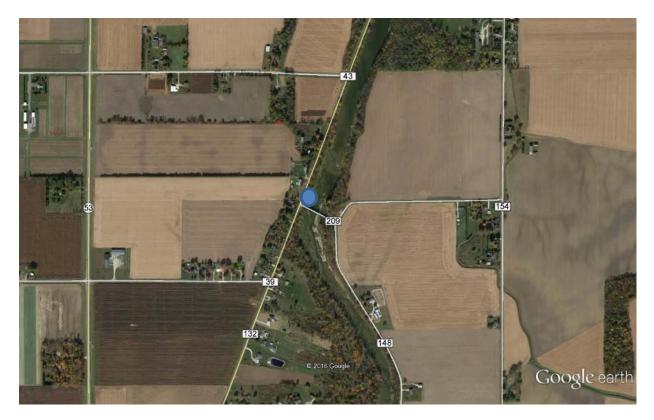


Station: Sandusky River near Fremont, Ohio (S10)

Dates of Operation: 1-1-1975 to present

Location of sampling station: 41.307778, -83.158889 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS

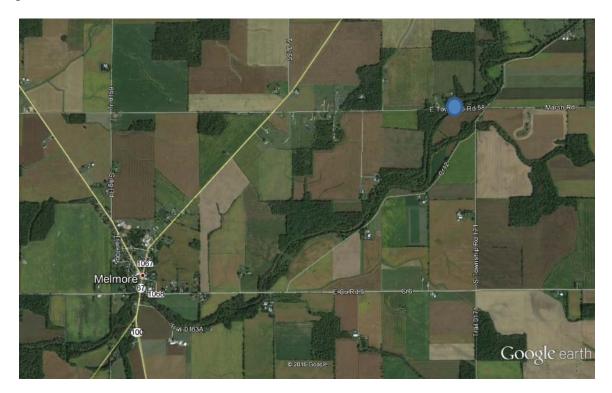


Station: Honey Creek at Melmore, Ohio (MLM)

Dates of Operation: 1-28-1976 to present

Location of USGS gage: 41.022222, -83.109722 Location of sampling station: 41.037222, -83.076628 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS



Station: Rock Creek at Tiffin, Ohio (ROC)

Dates of Operation: 10-11-1982 to present

Location of sampling station: 41.113611, -83.168333 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS



Station: Portage River at Woodville, Ohio (POR)

Dates of Operation: 8-30-2012 to present

Location of sampling station: 41.449444, -83.361389 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS

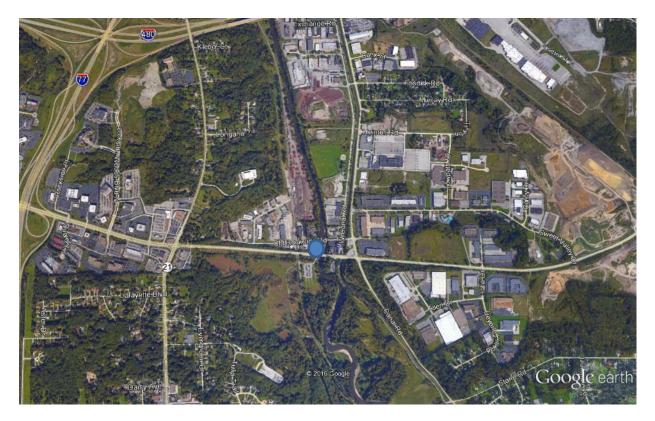


Station: Cuyahoga River at Independence, Ohio (CUY)

Dates of Operation: 11-4-1981 to present

Location of gage: 41.395278, -81.630000 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS



Station: Blanchard River near Findlay, Ohio (BCH)

Dates of Operation: 7-9-2007 to present

Location of sampling station: 41.055833, -83.688056 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS

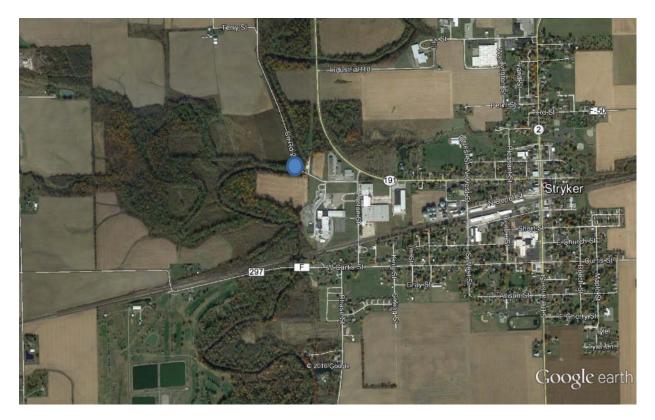


Station: Tiffin River at Stryker, Ohio (STR)

Dates of Operation: 7-9-2007 to present

Location of sampling station: 41.504444, -84.429722 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS

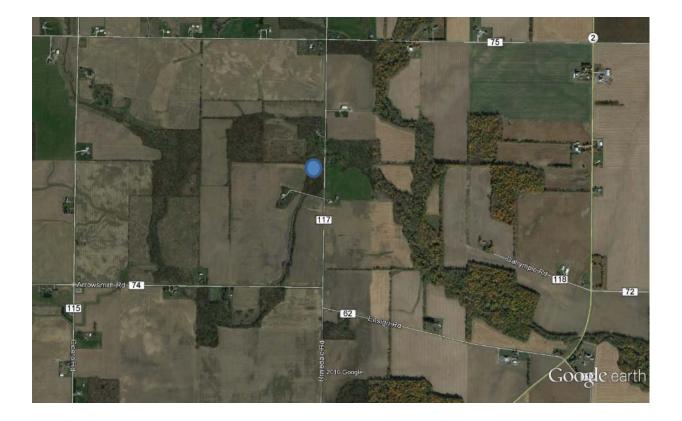


Station: Unnamed Tributary to Lost Creek near Farmer, Ohio (DEF)

Dates of Operation: 8-6-2007 to present

Location of sampling station: 41.361667, -84.691111 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS

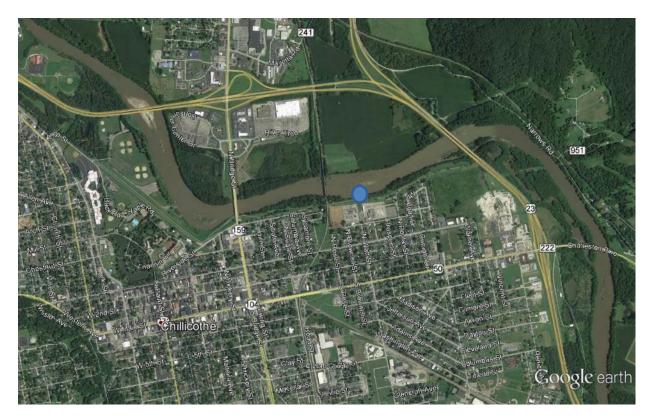


Station: Scioto River at Chillicothe, Ohio (SCI)

Dates of Operation: 10-23-1996 to present

Location of sampling station: 39.341389, -82.971111 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS

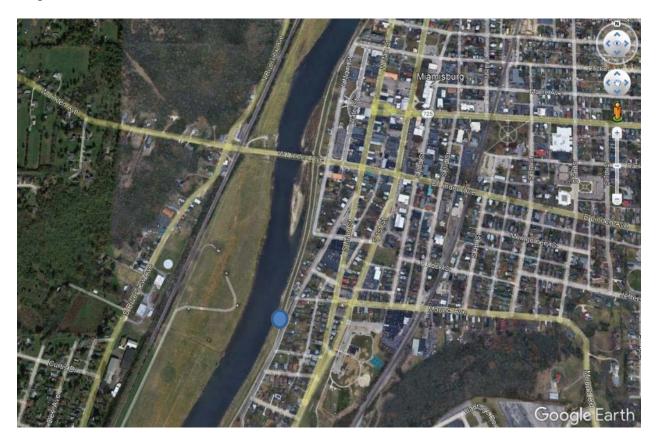


Station: Great Miami River below Miamisburg, Ohio (MIA)

Dates of Operation: 4-22-1996 to present

Location of USGS gage: 39.644444, -84.289722 Location of sampling station: 39.636411,-84.292423 (

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS

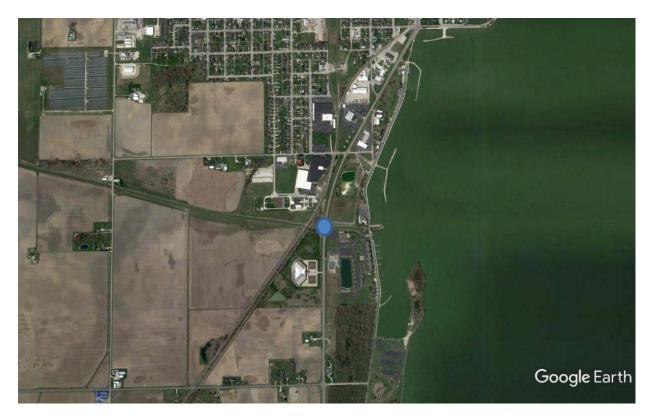


Station: Beaver Creek near Celina, Ohio (CEL)

Dates of Operation: 10-2-2013 to present

Location of sampling station: 40.534565, -84.574557 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS



Station: Chickasaw Creek at St. Marys, Ohio (CHI)

Dates of Operation: 9-22-2008 to present

Location of sampling station: 40.486944, -84.481667 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS

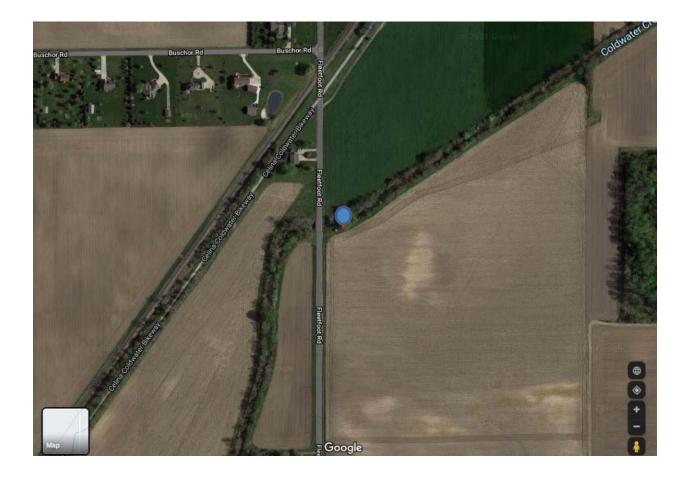


Station: Coldwater Creek at Coldwater, Ohio (CHI)

Dates of Operation: 11-8-2010 to present

Location of sampling station: 40.499444, -84.609167 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS



Station: Muskingum River at McConnelsville, Ohio (MUS)

Dates of Operation: 4-11-1994 to present

Location of sampling station: 39.645000, -81.850000 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS



Station: Huron River at Milan, Ohio

Dates of Operation: 01-26-2018 to present

Location of sampling station: 41.300833, -82.608333 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS



Station: South Turkeyfoot Creek near Shunk, Ohio

Dates of Operation: 01-08-2018 to present

Location of sampling station: 41.356388, -84.050833 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS

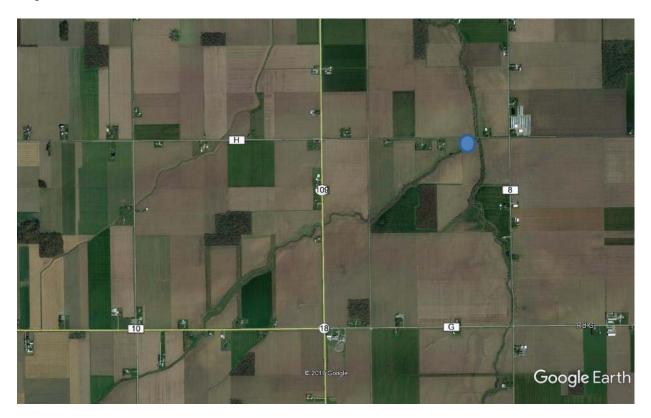


Station: West Creek near Hamler, Ohio

Dates of Operation: 01-15-2018 to present

Location of USGS gage: 41.261944, -84.036666 Location of sampling station: 41.268508, -84.021050 ()

Parameters: TP, SRP, TKN, NO₃⁻-N, Cl⁻, SO₄²⁻, and SS

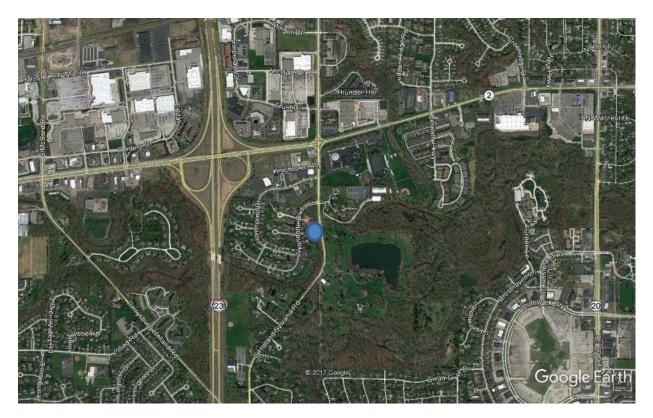


Station: Wolf Creek at Holland, Ohio

Dates of Operation: 03-01-2018 to present

Location of sampling station: 41.609444, -83.684166 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS

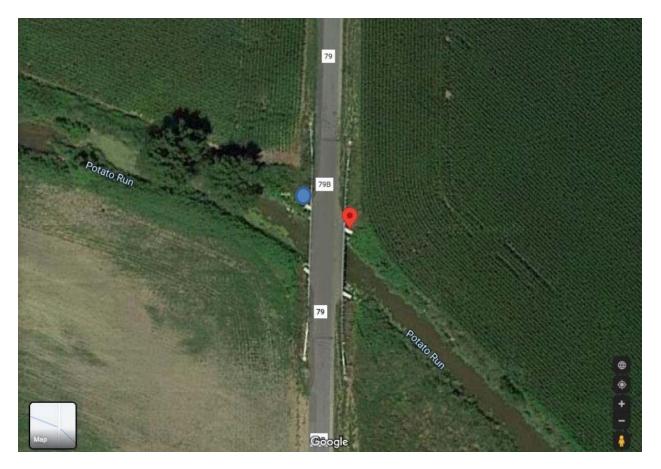


Station: Potato Run near Wharton, Ohio

Dates of Operation: 05-14-2018 to present

Location of sampling station: 41.300833, -82.608333 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS



Station: Unnamed Tributary to Blanchard near Dunkirk, Ohio

Dates of Operation: 05-14-2018 to present

Location of sampling station: 41.300833, -82.608333 ()

Parameters: TP, SRP, TKN, NO3⁻-N, Cl⁻, SO4²⁻, and SS

