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## Upstream Sources Inhibit Benthic Phosphorus Fluxes in the Lower Great Miami River, Southwest Ohio

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UPSTREAM SOURCES INHIBIT BENTHIC PHOSPHORUS FLUXES IN THE  
LOWER GREAT MIAMI RIVER, SOUTHWEST OHIO

A thesis submitted in partial fulfillment of the  
requirements for the degree of  
Master of Science

By

KORTNEY MULLEN  
B.S., Wright State University, 2015

WRIGHT STATE UNIVERSITY

2017

WRIGHT STATE UNIVERSITY  
GRADUATE SCHOOL

May 11, 2017

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY Kortney Mullen ENTITLED Upstream Sources Inhibit Benthic  
Phosphorus Fluxes in the Lower Great Miami River, southwest Ohio BE ACCEPTED IN  
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF  
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## ABSTRACT

Mullen, Kortney. M.S. Department of Earth and Environmental Sciences, Wright State University, 2017. Upstream sources inhibit benthic phosphorus fluxes in the Lower Great Miami River, southwest Ohio.

Human activities have increased nutrient loadings to aquatic ecosystems during the past century. During low river flow in late summer and early fall, excessive concentrations of phosphorus (P) are present in the Lower Great Miami River (LGMR) and contribute to its eutrophication. Although wastewater treatment plants are suspected of being major point sources of P to the LGMR during low river flow, riverbed sediment has not been examined as an additional potential source of P. Benthic P fluxes were measured at 11 representative locations along the LGMR during late summer and early fall of 2015. Sediment and overlying water sampled from the LGMR were incubated in laboratory flux chambers, and total and filtered P were measured over time in overlying water to estimate fluxes. Concentrations of P in river water and benthic fluxes of filtered total P (range from  $-50$  to  $390 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) varied considerably among sites and sampling periods. Benthic fluxes of filtered total P were inversely related to filtered total P concentrations in overlying river water ( $p = 0.002$ ,  $r = -0.60$ ). This relationship suggests that elevated concentrations in river water inhibit mobilization of P from sediment, likely by minimizing the concentration gradient between pore and overlying water. Accordingly, upstream sources that increase concentrations of P in river water,

including wastewater treatment plants, could inhibit the potential for P to be remobilized from, as opposed to temporarily stored in, downstream sediment.

## TABLE OF CONTENTS

	Page
I. INTRODUCTION.....	1
II. METHODS.....	9
a. Sampling.....	9
b. Measuring benthic fluxes.....	18
i. Benthic flux chamber.....	18
ii. Incubations.....	20
c. Sample analysis.....	27
III. RESULTS AND DISCUSSION.....	29
a. River conditions.....	29
b. Sediment.....	33
c. Benthic fluxes.....	39
d. Benthic flux scaled.....	47
e. Conclusion.....	50
REFERENCES.....	52
APPENDIX.....	56

## LIST OF FIGURES

Figure	Page
1. Cycling and retention processes that influence phosphorus concentrations in river water (from Withers et al., 2008).....	3
2. Great Miami River watershed in southwest Ohio. The Great Miami River flows from north of Dayton to the Ohio River in western Hamilton County, Ohio. River sediment and water sampling locations are between the cities of Dayton and Hamilton.....	6
3. Lower Great Miami River sampling locations in Island Park pool (Sites 1, 1b) and above and below the Tait Station dam (Sites 2, 3).....	11
4. Lower Great Miami River sampling locations in West Carrollton pool (Sites 4, 4b) and above and below Hutchings Station dam (Sites 5, 6).....	12
5. Lower Great Miami River sampling locations above (Sites 7, 7b) and below (Site 8) the Black Street Dam in Hamilton, Ohio.....	13
6. Sediment coring at Island Park (Site 1) in the Lower Great Miami River.....	16
7. Water column profiles of physicochemical parameters in the pool above Black Street dam (near Site 7) in Hamilton, OH.....	17
8. Components of the benthic flux chambers used to examine sediment-water exchange of phosphorus in the Lower Great Miami River (Hammerschmidt and Fitzgerald, 2008), and a photograph of multiple chambers in operation inside a darkened, water-filled incubation chamber.....	19
9. Linear regression analysis of filtered total P concentration versus incubation time for three sediment cores from Island Park pool (Site 1b) during the late-Sept sampling period.....	26
10. Concentrations of unfiltered total, filtered total, and orthophosphate in Lower Great Miami River water during the three sampling periods. Site 1 is farthest upstream and Site 8 is downstream. Diamond symbols indicate the relative location of point source discharges to the river.....	32

11. Total extractable Fe related to the organic content of surface sediment (0–2 cm) in the Lower Great Miami River.....	38
12. Benthic flux of filtered P among all sampling periods and sites in the Lower Great Miami River. Bars are the mean ( $\pm$ SD) flux of three replicate cores. Locations during each period that were not sampled are labeled as N/S (denoting not sampled).....	42
13. Relationship between benthic filtered P flux (average among replicate cores at each location) and filtered total P concentration in river water of the Lower Great Miami River.....	44
14. Relationship between benthic filtered P flux and total P in surface sediment (0–2 cm) of individual cores from the Lower Great Miami River.....	45
15. Estimated mass balance of total P ( $\text{kg P d}^{-1}$ ) in the Lower Great Miami River during low-flow conditions in August and September.....	48



## LIST OF TABLES

Table	Page
1. Sediment sampling locations and water depths in the Lower Great Miami River.....	10
2. Ambient water temperatures in the Lower Great Miami River during sampling and temperature ranges of sediment flux chambers during incubations.....	21
3. Ambient dissolved oxygen concentrations in the Lower Great Miami River during sampling and dissolved oxygen ranges of sediment flux chambers during incubations.....	23
4. Ambient pH of water in the Lower Great Miami River at the time of sampling and ranges of pH in water of sediment flux chambers during incubations.....	24
5. Total unfiltered and filtered (0.22- $\mu$ m) P and orthophosphate concentrations and form of total P (%) in water of the Lower Great Miami river.....	31
6. Concentrations of organic matter content, water content, total P, and total extractable Fe in surface sediment in each core among the sampling locations and periods. Values are the average of 0–1 and 1–2 cm sediment horizons.....	34
7. Benthic fluxes of filtered total P from sediment in the Lower Great Miami River. Fluxes in each core were determined from the incubation periods.....	40

## LIST OF APPENDED FIGURES

A1. Relationship between total P and organic matter dry-weight concentrations in sediments of the Lower Great Miami River .....	56
A2. Relationship between total P and extractable Fe dry-weight concentrations in sediments of the Lower Great Miami River.....	57

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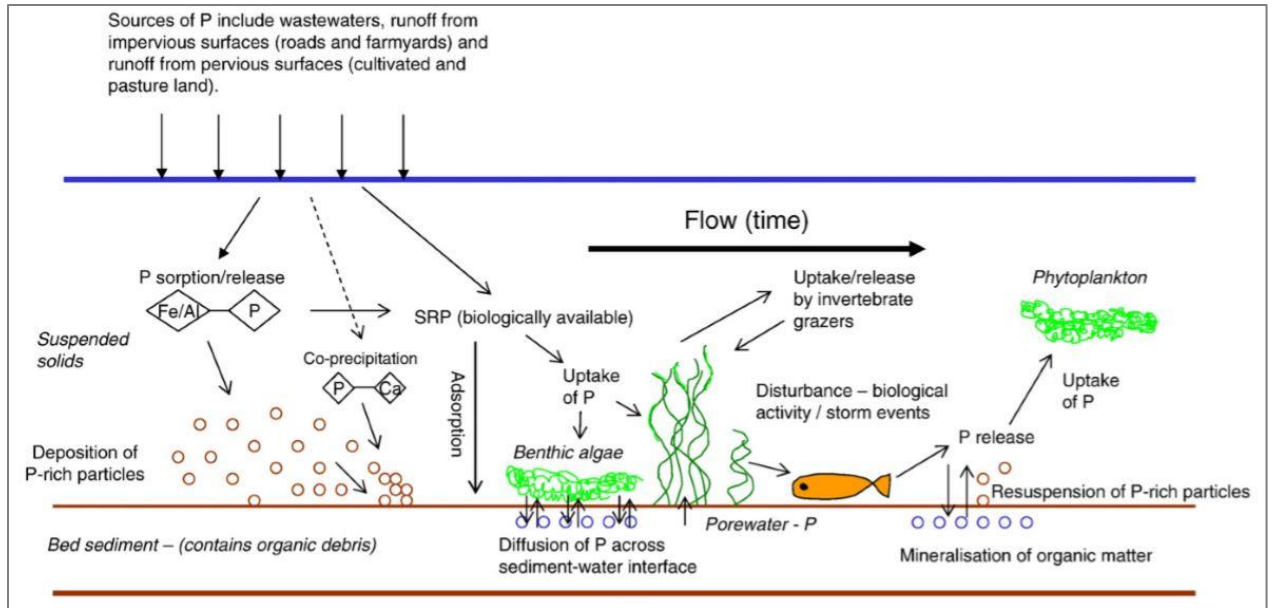
I would also like to thank my family and friends for their endless love and support through this journey. I couldn't have done it without you.

## **I. INTRODUCTION**

During the last century, human activities have increased the amounts of phosphorus (P) and nitrogen in many aquatic ecosystems. The increase of nutrient loadings is mainly due to fertilizer use and industrial and municipal wastewater discharges to receiving waters (Puckett, 1995). Phosphorus and nitrogen are essential nutrients; however, excessive concentrations can have negative ecological consequences, including increased algal production and turbidity, decreased concentrations of dissolved oxygen, and exacerbated diel fluctuations of dissolved oxygen and pH (Schindler, 1977; Hecky and Kilham, 1988). These symptoms of eutrophication often shift aquatic organism species composition away from those typical of high-quality surface waters and towards less diverse and desirable species compositions of degraded ecosystems.

Once P is introduced to a river, it cycles between particulate and dissolved phases in bottom sediment and the water column (Figure 1; Mainstone et al., 2002; Withers et al., 2008). Microbes in river sediment can assimilate nutrients from the water column as they are cycled within the river system. Biotic and physicochemical processes transform P between organic and inorganic forms and affect its partitioning between soluble and particulate phases (Jarvie, 2005). Phosphorus is transferred from the water column to sediments predominantly by either biological uptake and eventual deposition of biomass, scavenging by minerals, or precipitation (Holtan, 1961; Holtan et al., 1988; House et al., 1995a). Burial of P in river sediment removes potentially bioavailable P from the water column and it contributes to a benthic reservoir that may be a potential source of

either soluble or particulate P to river water should river flow and redox conditions change. Burial of P in the riverbed is expected to be greatest under low-flow conditions that allow for more particle deposition; however, mobilization of P from sediment to overlying water also may be greatest under low-flow conditions if the sediment becomes anoxic.



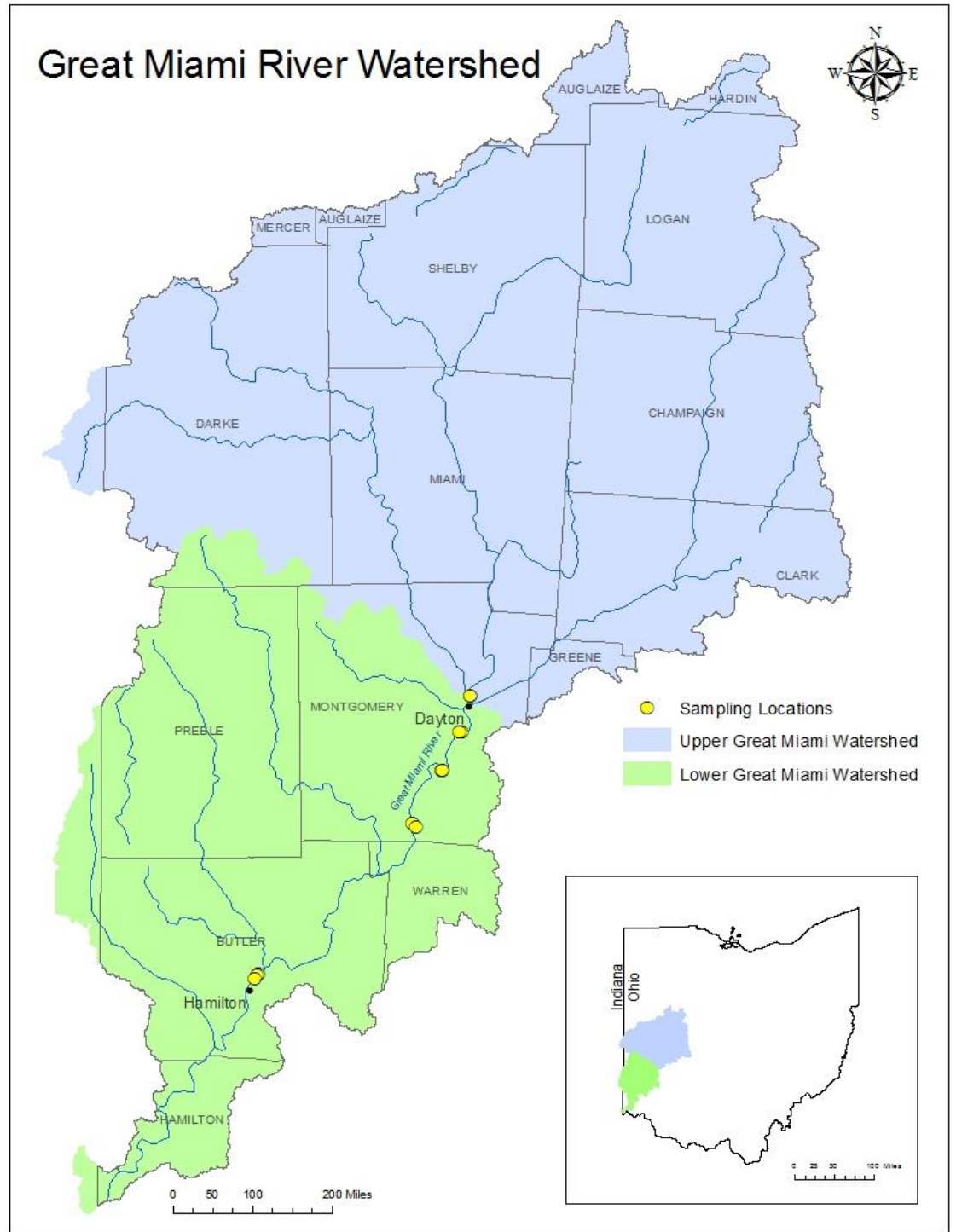
**Figure 1.** Cycling and retention processes that influence phosphorus concentrations in river water (from Withers et al., 2008).

Soluble P is released from sediment as a result of microbial remineralization of organic matter and redox-sensitive dissolution of phosphate-bearing minerals (Boström et al., 1988). Phosphate has a high affinity for trivalent metals and can form  $\text{FePO}_4(\text{s})$  with Fe(III) under oxic conditions, which are common in most river waters. However, surface sediment in rivers can become anoxic, particularly under low-flow conditions and in reaches upstream of impoundments, where water flow and vertical mixing can be impeded and organic matter deposition may be increased. Anoxia, and associated lowering of the reduction-oxidation potential in surface sediments, can result in microbial Fe(III) reduction and subsequent solubilization and remobilization of phosphate from  $\text{FePO}_4(\text{s})$  in sediment (Boström et al., 1988). Therefore, sediments can be both sinks and sources of P to river water, but the degree to which sediment-water exchange influences P cycling in rivers, including the Great Miami River, is not well understood.

The Great Miami River is a warm-water river that drains 9800 km<sup>2</sup> of land in western Ohio southward to the Ohio River, west of Cincinnati (Figure 2). North of the city of Dayton, the watershed is divided into multiple sub-catchments, including the upper and middle reaches of the Great Miami River and the Stillwater and Mad Rivers, the three of which have confluence in Dayton. Agriculture, including cultivated crops and animal feeding operations, is the primary land use (~75%) in the watershed north of Dayton (<http://www.epa.state.oh.us/dsw/tmdl/greatmiamiriver.aspx#116712980-great-miami-river-upper>). The Lower Great Miami River extends from river mile (RM) 81.5 in Dayton to its confluence with the Ohio River. In contrast to the upper watershed, land use in the Lower Great Miami watershed is mostly developed urban and residential land (~40%), agricultural fields (28%), and forest (19%)

(<http://www.epa.state.oh.us/dsw/tmdl/greatmiamiriver.aspx#116712980-great-miami-river-upper>). Accordingly, nutrients in river water upstream of Dayton are suspected of mostly being from agricultural runoff, while the Lower Great Miami River is influenced to a greater extent by urban and residential runoff, as well as wastewater inputs from treatment plants. There are several municipal wastewater treatment plants that discharge into the Lower Great Miami River between the cities of Dayton and Hamilton, OH, including the City of Dayton Water Reclamation Facility (average discharge is about  $1.7 \times 10^8 \text{ L d}^{-1}$ , Montgomery County Western Regional Wastewater Treatment Plant ( $\sim 5.4 \times 10^7 \text{ L d}^{-1}$ , and the Miamisburg Water Reclamation Facility (about  $1.1 \times 10^7 \text{ L d}^{-1}$ ; OEPA, 2012). For context, the Lower Greater Miami River at Dayton, upstream of the wastewater outfalls, has a discharge of about  $2 \times 10^9 \text{ L d}^{-1}$  during low flow conditions in late summer (USGS 03270500 Great Miami River at Dayton, Ohio).





**Figure 2.** Great Miami River watershed in southwest Ohio. The Great Miami River flows from north of Dayton to the Ohio River in western Hamilton County, Ohio. River sediment and water sampling locations are between the cities of Dayton and Hamilton.

Nutrient loading is considered one of the most pervasive causes of impairment in the Great Miami River watershed (OEPA, 2011). Despite improvements in water quality due to better treatment of wastewater discharges, an overabundance of nutrients still exists in the Great Miami River (OEPA, 2001; 2011; 2012). Algal blooms in the Great Miami River were observed by the Ohio Environmental Protection Agency in summer of 1995 (OEPA, 1997) and again in summer of 2011 (Smith, 2011). Recent evaluations of nutrient loadings in the Great Miami River watershed suggest that nonpoint sources (e.g., agriculture) contribute most of the annual P load carried by the river (Reutter, 2003). However, most evaluations of biological community productivity and diversity (e.g., Index of Biological Integrity, Invertebrate Community Index, Modified Index of Well Being) in the Great Miami River and its tributaries are conducted during summer and early fall, when low-flow conditions prevail and runoff of nutrients from nonpoint sources is also lower. These evaluations show a decline in biological community performance in the Lower Great Miami River and strong evidence of excess nutrients (OEPA, 2012). For example, the evaluations documented elevated concentrations of soluble P forms in the water column as well as increased periphyton biomass and large diel swings of dissolved P concentrations. Regulators of municipal wastewater treatment plants have concluded that point sources of nutrients are the primary driver of trophic dynamics during low-flow conditions in summer and fall (OEPA, 2012). Therefore, degradation of biological communities due to nutrient enrichment may best be ameliorated by lowering permitted nutrient concentrations in effluent. However, the significance nutrient inputs from point sources relative to known and unknown nonpoint sources, including benthic remobilization, is not well defined in the river.

Inputs of P from point sources (i.e., treated wastewater) to the Lower Great Miami River do not vary considerably throughout the year, but the significance of point sources relative to nonpoint sources are likely to vary as a function of precipitation, runoff, and river flow. During low-flow conditions in late summer and early fall, the period when water quality impairments have been documented in the Lower Great Miami River (OEPS, 1997; Smith, 2011), runoff of nutrients from agricultural nonpoint sources is not substantial. Alternative, natural nonpoint sources of P could include weathering of soil material (Holtan et al., 1988), decay of riparian vegetation (Meyer and Likens, 1979), and river bank erosion (Walling et al., 2008). These nonpoint sources of P are usually in particulate form, and fluxes are relatively small for most rivers ( $<10 \text{ mg m}^{-2} \text{ yr}^{-1}$ ; Withers et al., 2008). Benthic remobilization is another potential source of P to the Lower Great Miami River, but sediment-water exchange of P has not been quantified in either this or most other rivers. Lack of information about benthic P fluxes prevented OEPA (2012) from concluding that nutrient point sources (i.e., wastewater treatment plants) are the main cause of eutrophication during low-flow conditions in the summer and fall in the Lower Great Miami River. Excluding a potential benthic source could lead to inaccurate conclusions and investments on expensive methods to remediate poor water quality.

In this study, I investigated riverbed sediment as a potential source of P to the water column of the Lower Great Miami River during low-flow conditions in late summer and early fall of 2015. This study was accomplished by quantifying benthic fluxes of P from sediment at 11 representative locations. Based on P fluxes measured from eutrophic lakes, which can range from 0.1 to  $2.7 \text{ mg P m}^{-2} \text{ d}^{-1}$  in the midwestern United States (Cooke et al., 1977; Cooke et al., 1993; Chowdhury and Al Bakri, 2006), I

hypothesized that benthic P remobilization is a significant source of P to the Lower Great Miami River during low river discharge in late summer and early fall.

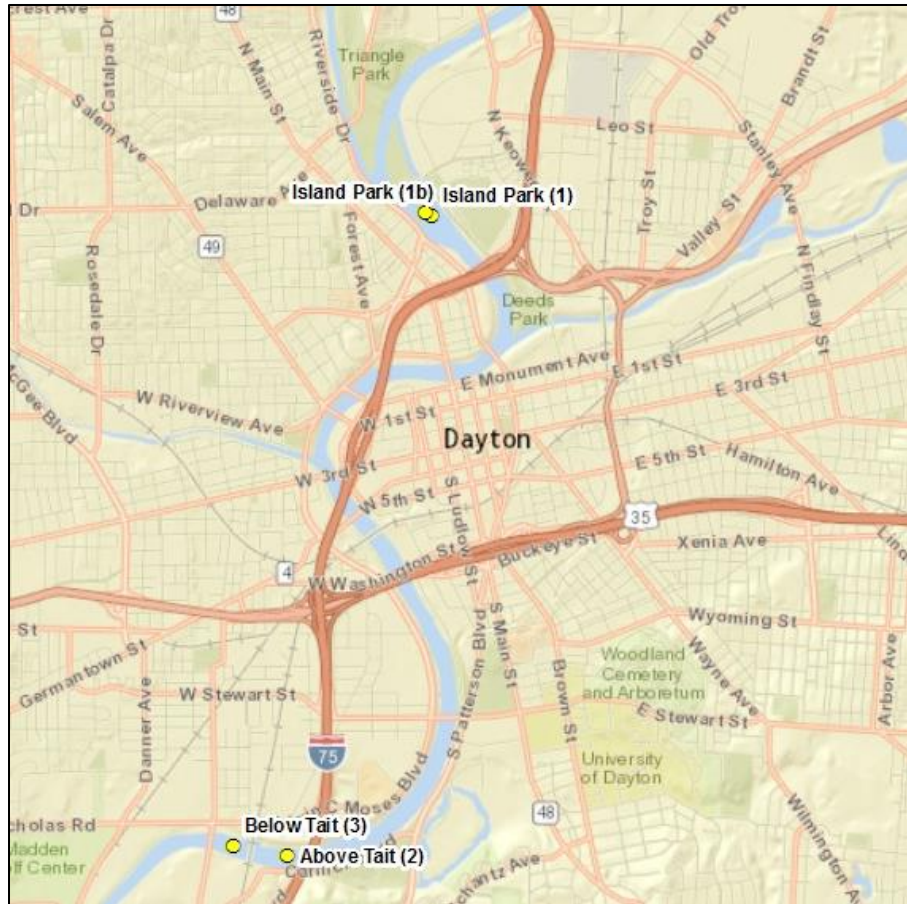
## II. METHODS

### *Sampling*

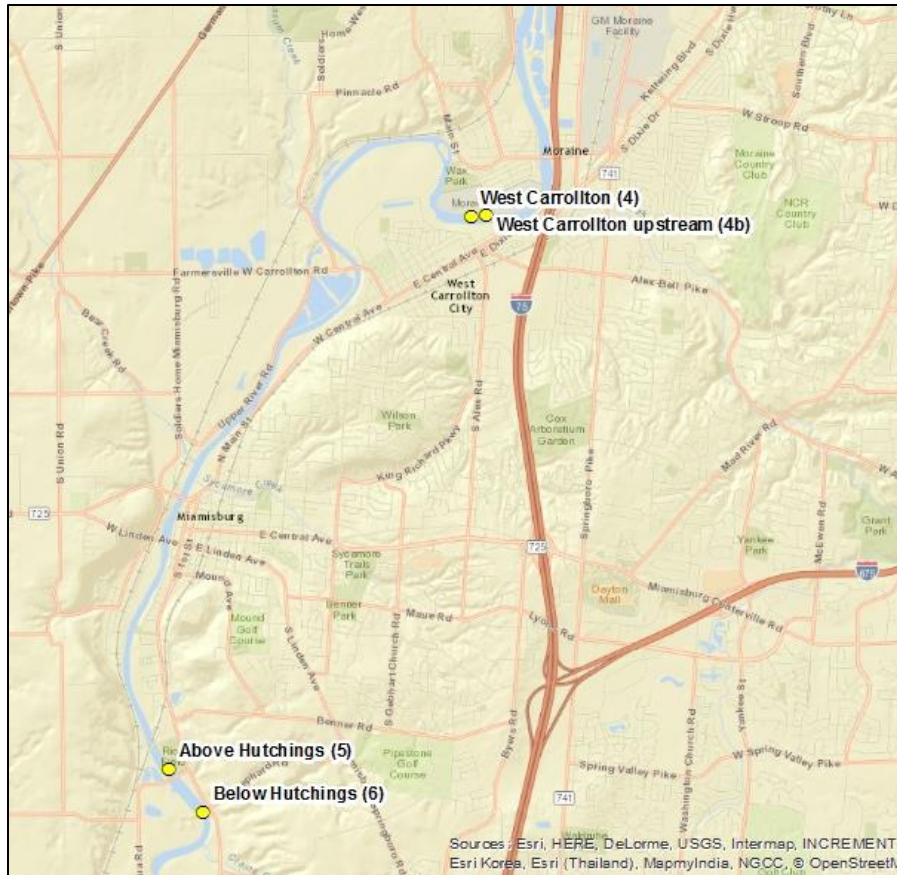
A benthic flux chamber method (Hammerschmidt and Fitzgerald, 2008) was used to quantify fluxes of P from sediment of the Lower Great Miami River at multiple locations. Sediment for flux chamber incubations were sampled from 11 locations in the Lower Great Miami River during low-flow conditions in late summer and early fall of 2015 (Figure 2, Table 1). Sampling occurred over a period of days in August (Aug 18–24), September (Sept 10–18), and late September/early October (Sept 28–Oct 2), which are referred to as Aug, mid-Sept, and late-Sept. Eight of the sampling sites were in low-head dam pools, and three were below dams in free-flowing river sections. Dam pools were selected for sampling due to the potential for greater organic content and fine sediments associated with P, where there could be a greater flux of P to overlying water. Samples were collected above and below the Tait Station Dam (Figure 3), Hutchings Station Dam (Figure 4), and the Black Street Dam in Hamilton (Figure 5). The Island Park (Figure 3) and West Carrollton (Figure 4) sampling locations were both relatively large pools above low-head dams.

**Table 1.** Sediment sampling locations and water depths in the Lower Great Miami River.

Site	Latitude (N)	Longitude (W)	River mile	Sampling periods	Water depth (m)	Site description
1	39°46'33.81"	84°11'41.43"	85.3	mid-Sept	1.0	Island Park pool
1b	39°46'35.09"	84°11'45.53"	85.3	late-Sept	2.0	Island Park pool
2	39°43'48.88"	84°12'30.59"	76.7	Aug, mid-Sept, late-Sept	0.5	Tait Station pool
3	39°43'51.10"	84°12'49.20"	76.5	Aug, mid-Sept, late-Sept	0.5	Below Tait Station dam
4	39°40'49.68"	84°14'34.97"	72.0	mid-Sept, late-Sept	1.5	West Carrollton pool
4b	39°40'49.85"	84°14'25.91"	71.9	mid-Sept	1.0	West Carrollton pool
5	39°36'44.54"	84°17'29.53"	63.9	Aug, mid-Sept, late-Sept	2.0	Hutchings pool
6	39°36'25.05"	84°17'09.26"	63.5	Aug, mid-Sept, late-Sept	0.5	Below Hutchings dam
7	39°25'00.51"	84°33'03.09"	36.8	Aug	0.5	Black Street dam pool
7b	39°24'56.92"	84°33'09.38"	36.7	mid-Sept, late-Sept	0.5	Black Street dam pool
8	39°24'37.89"	84°33'25.05"	36.2	Aug, mid-Sept, late-Sept	0.5	Below Black Street dam

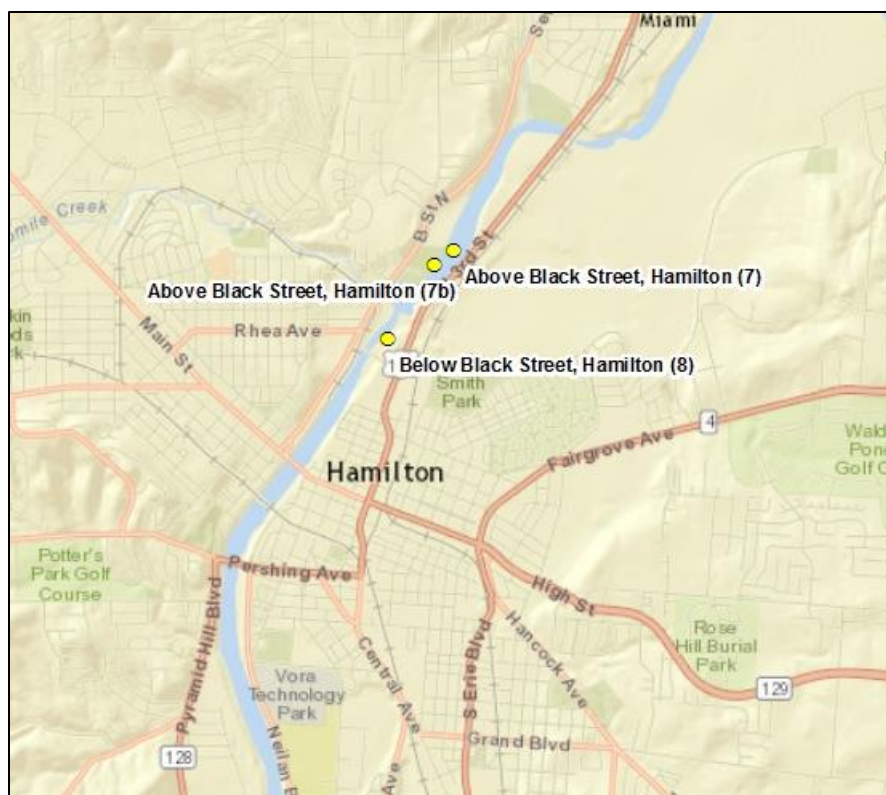


**Figure 3.** Lower Great Miami River sampling locations in Island Park pool (Sites 1, 1b) and above and below the Tait Station dam (Sites 2, 3).



**Figure 4.** Lower Great Miami River sampling locations in West Carrollton pool (Sites 4, 4b) and above and below Hutchings Station dam (Sites 5, 6).





**Figure 5.** Lower Great Miami River sampling locations above (Sites 7, 7b) and below (Site 8) the Black Street Dam in Hamilton, Ohio.



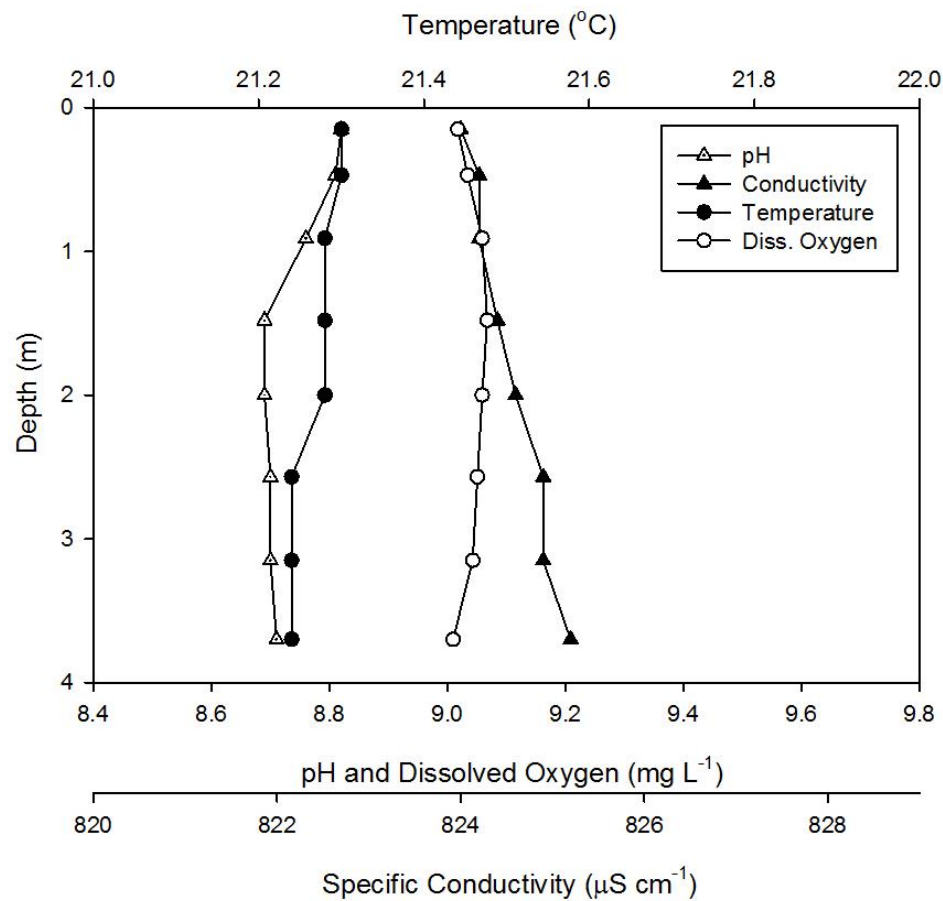
Sampling locations were selected to be representative of the diverse habitats of the Lower Great Miami River, including areas previously found to have impaired water quality during low-flow conditions (OEPA, 2012). Timing of sampling was in response to observed flow conditions during 2015. Sampling periods were determined by observing the United States Geological Survey (USGS) current water data for Ohio, which measures daily streamflow conditions at numerous locations along the Great Miami River. Great Miami River discharge less than  $42 \text{ m}^3 \text{ s}^{-1}$  at Hamilton, OH, (USGS gauge 03274000) was considered a low-flow condition. During each sampling period, river discharges were representative of low-flow conditions. River discharges at Hamilton during each of the sampling periods averaged 40 (Aug), 23 (mid-Sept), and 20  $\text{m}^3 \text{ s}^{-1}$  (late-Sept).

Three sediment cores were collected from each site by push coring from either a boat or by wading into the river (Figure 6). The corer consisted of a 3-m PVC pipe (5 cm OD) with a one-way valve and point of attachment for a polycarbonate coring tube. The coring tube (6.35 cm ID, 7 cm OD, 30 cm length) had a bevel on the penetrating end of the tube. About 10 cm of intact sediment was collected in each core tube, with the remaining volume comprised of overlying water. Core tubes were sealed with a sponge (to later aid with extrusion of sediment) and a water-tight cap on the bottom and an additional watertight cap on the top. Each core was carefully handled to prevent disturbance of the sediment-water interface and were placed upright in a covered cooler. This method preserves the sediment-water interface and any in situ geochemical gradients. After core tubes were transferred to Wright State University, they were fitted with a stirring head and motor before incubation (described below). River water also was

sampled at each location with a 2-L polycarbonate bottle by hand facing into the flow from upstream. The polycarbonate bottles were thoroughly cleaned for trace-level water sampling (Hammerschmidt et al., 2011). Surface water was inferred to be representative of water at the sediment-water interface due to the water column being well mixed, as indicated by conservative-type vertical distributions of dissolved oxygen and pH at all locations, including, for example, in a relatively deep pool above Black Street dam in Hamilton (near Site 7, Figure 7). Water was subsampled from each 2-L bottle for analysis of unfiltered total P, filtered total P, and orthophosphate (ortho-P). Water for analysis of filtered total P was acidified with 2% high-purity  $\text{HNO}_3$  (Instra-Analyzed, J.T. Baker), and water for ortho-P determination was stored at  $-20\text{ }^{\circ}\text{C}$  until analysis. Remaining bottled water from each location was stored in the dark at *in situ* temperature and used to refill the flux chambers between incubation test periods. Ambient temperature, dissolved oxygen, conductivity, and pH of water above the sediment-water interface were measured with either a YSI ProPlus, YSI ProDO (Yellow Springs Instruments), or Manta2 (Eureka Water Probes), which were calibrated before each use.



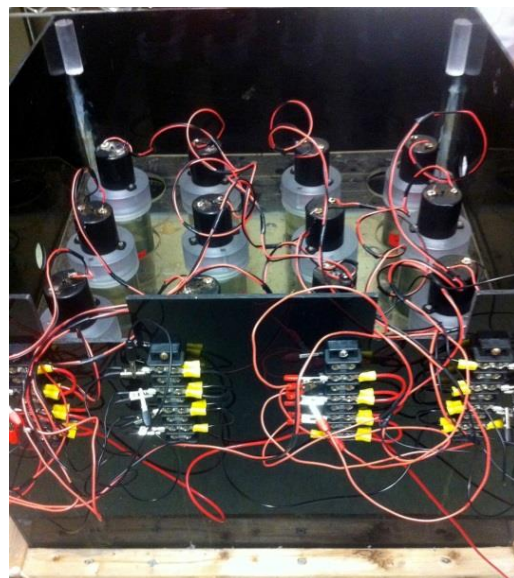
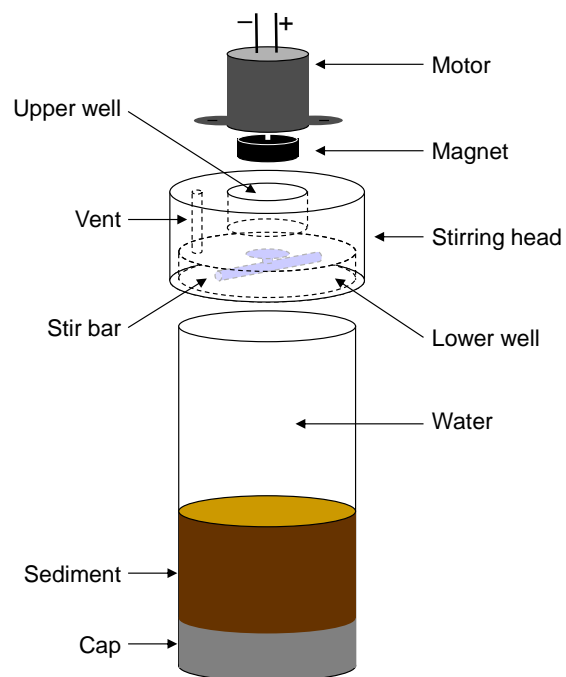
**Figure 6.** Sediment coring at Island Park (Site 1) in the Lower Great Miami River.



**Figure 7.** Water column profiles of physicochemical parameters in the pool above Black Street dam (near Site 7) in Hamilton, OH.

### ***Measuring benthic fluxes***

*Benthic flux chambers.* Fluxes of P from sediment were measured with benthic flux chambers of river sediment and water. Benthic flux chambers consisted of three main parts (Figure 8): the flux chamber, stirring head, and a direct current motor with button magnet, as described in detail by Hammerschmidt and Fitzgerald (2008). Briefly, the flux chamber was a polycarbonate sediment coring tube used originally to collect sediment and overlying water from the river. The stirring head was a polycarbonate tube cap with a lower and upper well. The lower well fit tightly over the outside of the core and contained a Teflon-coated “floating” magnetic stir bar (5.4 cm length). The upper well housed a button magnet attached to a 25 RPM DC motor. An atmospheric vent (0.5 cm diameter) in the stirring head minimized dissolved oxygen depletion in overlying water during incubation, which would be unnatural for a well-mixed river water column. Benthic flux chambers were incubated in a darkened, water-filled (to moderate temperature fluctuation) incubation container holding multiple cores simultaneously. This technique was developed initially for quantifying mercury fluxes from coastal sediments (Hammerschmidt and Fitzgerald, 2008) and later modified for benthic P fluxes in freshwater (Taylor, 2012).



**Figure 8.** Components of the benthic flux chambers used to examine sediment-water exchange of phosphorus in the Lower Great Miami River (Hammerschmidt and Fitzgerald, 2008), and a photograph of multiple chambers in operation inside a darkened, water-filled incubation chamber.

*Incubation.* Each flux chamber was used to quantify sediment-water fluxes of P during an incubation period under *in situ* conditions. For all sampling locations and periods, the range of incubation temperatures was representative of the ambient water temperature at the time of sediment and water sampling (Table 2). Based on a previous benthic P-flux study (Taylor, 2012), each chamber was incubated for 96 h, and a water sample was removed after about 0, 12, 24, 48, and 96 h. Incubation periods were sufficient to result in measurable changes of P concentrations in overlying water, in most chambers, in order to quantify a flux between sediment and water.

**Table 2.** Ambient water temperatures in the Lower Great Miami River during sampling and temperature ranges of sediment flux chambers during incubations.

Site	Temperature (°C)					
	August		mid-Sept		late-Sept	
	Ambient	Incubation	Ambient	Incubation	Ambient	Incubation
1	--	--	23.6	21.2–23.3	--	--
1b	--	--	--	--	21.0	20.7–21.6
2	23.1	22.5–23.8	25.6	21.6–24.6	21.4	20.7–21.6
3	22.8	22.5–23.8	24.5	21.6–24.6	22.3	20.7–21.6
4	--	--	24.2	21.2–23.3	--	--
4b	--	--	--	--	21.5	20.7–21.6
5	24.6	22.7–23.8	21.5	20.8–21.6	16.4	18.9–21.6
6	25.1	22.7–23.8	22.2	20.8–21.6	17.0	18.9–21.6
7	23.7	21.6–23.4	--	--	--	--
7b	--	--	21.3	20.8–21.6	17.0	18.9–21.6
8	24.6	21.6–23.4	22.4	20.8–21.6	17.5	18.9–21.6



During the incubations, water overlying the sediment was continuously stirred to prevent formation of a benthic boundary layer. A motor speed of 25 RPM was used because it was the fastest speed that did not disturb or resuspend fine sediment particles during preliminary tests (Hammerschmidt and Fitzgerald, 2008). At each time water was sampled, electrochemical measurements of pH, temperature, and dissolved oxygen were made in each incubation chamber, and 60 mL of water were collected into acid-cleaned, polyethylene syringes. Water samples were filtered through pre-rinsed 0.22- $\mu$ m capsule filters (Millipore) and transferred to acid-cleaned plastic tubes. A volume of river water equal to that removed for analysis and from the same location where sediment was collected was added back into the core without disturbing the sediment. Water removed from the core was analyzed to determine the flux of filtered total P and the fraction as ortho-P. Water in the chambers remained oxic during incubations, however, dissolved oxygen concentrations in chambers were often less than those in river water at the time of sampling (Table 3). Measurements of dissolved oxygen in ambient river water were made between 10 a.m. and 3 p.m., when solar irradiation of the river and photosynthesis were maximum, potentially temporally biasing ambient concentration measurements. Although oxygen concentrations in incubation chambers were less than ambient, oxygen levels during incubation were comparable to those in a study with constant oxygen flow through the cores (Slone, 2016). The pH of water in incubation chambers also was less than values measured in the river (Table 4).

**Table 3.** Ambient dissolved oxygen concentrations in the Lower Great Miami River during sampling and dissolved oxygen ranges of sediment flux chambers during incubations.

Site	Dissolved oxygen (mg L <sup>-1</sup> )					
	August		mid-Sept		late-Sept	
	Ambient	Incubation	Ambient	Incubation	Ambient	Incubation
1	--	--	7.90	7.53–7.68	--	--
1b	--	--	--	--	9.55	6.82–7.92
2	9.10	7.35–7.92	12.6	7.61–8.15	11.7	6.75–7.59
3	7.82	7.23–7.49	11.5	5.76–6.37	12.7	5.21–5.43
4	--	--	9.30	6.76–7.12	--	--
4b	--	--	--	--	9.70	6.00–7.41
5	8.40	6.81–7.29	8.38	7.22–7.48	9.40	7.60–7.92
6	9.50	7.58–7.76	10.90	7.21–7.39	11.0	8.14–8.20
7	8.60	6.68–7.10	--	--	--	--
7b	--	--	8.94	6.99–7.10	10.7	6.14–7.70
8	11.4	7.01–7.78	8.85	7.63–7.68	10.8	7.91–8.00

**Table 4.** Ambient pH of water in the Lower Great Miami River at the time of sampling and ranges of pH in water of sediment flux chambers during incubations.

Site	pH					
	August		mid-Sept		late-Sept	
	Ambient	Incubation	Ambient	Incubation	Ambient	Incubation
1	--	--	8.41	8.21–8.24	--	--
1b	--	--	--	--	8.28	7.99–8.19
2	8.43	8.20–8.32	8.46	8.11–8.22	8.51	7.92–8.11
3	8.34	8.15–8.23	8.42	7.66–8.09	8.52	7.56–7.69
4	--	--	8.45	8.03–8.13	--	--
4b	--	--	--	--	8.30	7.61–7.95
5	8.44	8.19–8.29	8.33	8.06–8.16	8.37	8.08–8.11
6	8.55	8.38–8.44	8.44	8.14–8.20	8.42	8.15–8.19
7	8.30	7.97–8.03	--	--	--	--
7b	--	--	8.42	8.23–8.25	8.61	8.14–8.22
8	8.49	8.16–8.25	8.54	8.50–8.51	8.66	8.19–8.27

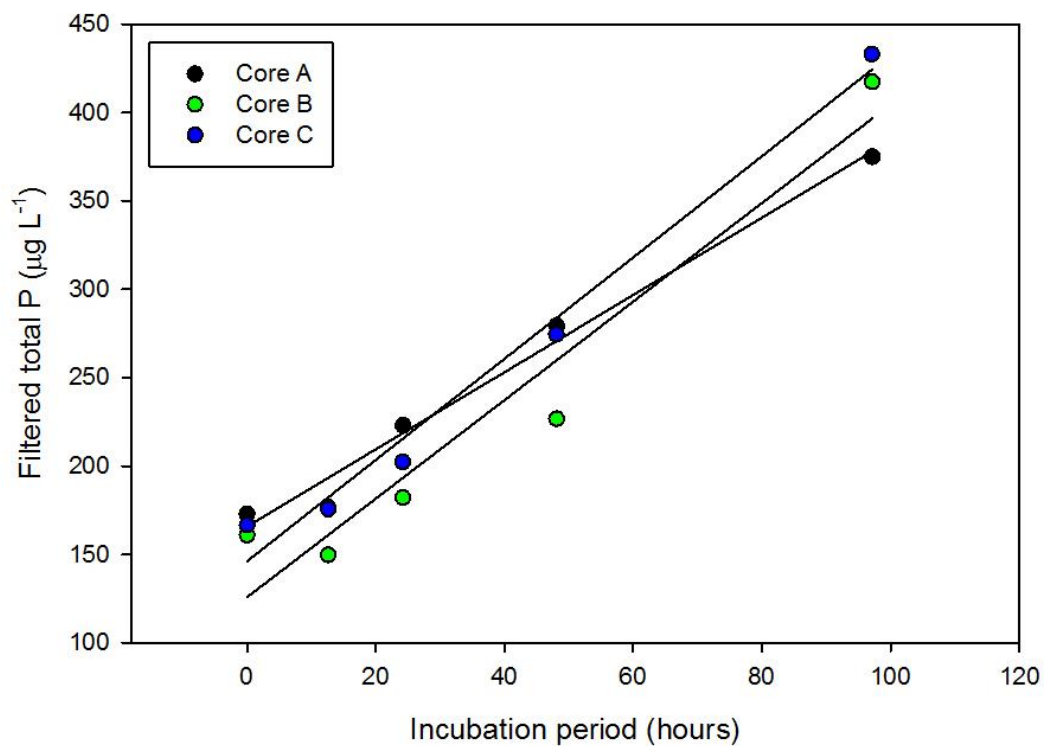
At the end of the 96-h incubation period, overlying water was removed from the flux chambers, and sediment was extruded and sectioned to remove the upper 0–1 and 1–2 cm of sediment. Sections of sediment were transferred to acid-cleaned, 50-mL centrifuge tubes, frozen at  $-20^{\circ}\text{C}$ , and freeze dried to measure water content prior to analysis of total P, total extractable iron (Fe), and organic matter concentrations in dried solids.

The flux ( $F$ ,  $\text{mg m}^{-2} \text{d}^{-1}$ ) of filtered P from river sediment in each chamber was estimated from the slope of a linear regression analysis of measured concentration in overlying water versus incubation time (Hammerschmidt and Fitzgerald, 2008):

$$F = \frac{dC}{dt} \times \frac{V}{A}$$

where  $C$  was the concentration of filtered total P at time  $t$ ,  $V$  was the volume of water in the core (determined),  $A$  was the surface area of the core ( $0.0032 \text{ m}^2$ ), and  $dC/dt$  was the slope of a linear regression analysis of filtered total P concentration versus time.

Phosphorus concentrations in overlying water increased over time during the core incubations, as illustrated for the Island Park pool (Site 1b) in late-Sept (Figure 9). Each core had a flux uncertainty determined as the product of  $V/A \times$  standard error of the slope of the linear regression. The P flux either out of or into sediment was determined to be significant if the  $p$ -value of the regression slope was  $<0.05$ . A mean ( $\pm$  SD) flux was calculated for each site and sampling period from three replicate flux chambers (labeled A, B, C) to account for heterogeneity within each site, including if either the chambers had a significant negative flux, inferring sediment uptake, or fluxes were statistically insignificant as indicated by the  $p$ -value of the linear regression slope.



**Figure 9.** Linear regression analysis of filtered total P concentration versus incubation time for three sediment cores from Island Park pool (Site 1b) during the late-Sept sampling period.

### *Sample Analysis*

Total unfiltered and filtered P were measured by quadrupole inductively coupled plasma mass spectrometry (ICP-MS, U.S. EPA 6020a). Orthophosphate was measured with an automated, colorimetric Lachat Quikchem 8500 flow injection analysis system (Standard Method 4500-P F, APHA et al. 1995; Lachat Applications Group, 2008). Sediment masses were measured with a balance calibrated with ASTM Class 1 reference weights. Sediment organic content was measured as loss-on-ignition (LOI) after heating at 550 °C for 4 h (Heiri et al., 2001). Total P in sediment was extracted by digestion with H<sub>2</sub>SO<sub>4</sub> and ammonium persulfate (U.S. EPA, 2004), and total extractable Fe was solubilized by digestion with concentrated, high-purity HNO<sub>3</sub> (Standard Method 3030E, APHA et al., 1995); digestions for both analytes were conducted in a hot block at the prescribed temperature and duration. Total P and extractable Fe in sediment were quantified by ICP-MS.

Quality control analyses included procedural blanks, replicates, calibration standards traceable to U.S. National Institute of Standards and Technology, and certified reference materials. Precision of P determinations in water averaged ( $\pm$  SD)  $4.5 \pm 3.6\%$  ( $n = 36$  triplicate sets) relative standard deviation (RSD) for total P and  $1.0 \pm 1.5\%$  RSD for ortho-P ( $n = 357$  triplicates). Imprecision among procedurally replicated preparations and determinations of analytes in sediment averaged  $10.5 \pm 6.7\%$  RSD for total P ( $n = 13$  triplicates),  $12.1 \pm 9.1\%$  RSD for organic matter content ( $n = 27$  triplicates), and  $10.1 \pm 6.8\%$  RSD for total extractable Fe ( $n = 6$  triplicates). The similar degree of imprecision among the three sediment-associated analytes likely reflects heterogeneity within the sediment, in addition to error introduced by sample preparation and analysis. Recovery of

total P from certified reference material MESS-4 (marine estuarine sediment, National Research Council Canada) averaged  $0.98 \pm 0.14 \text{ mg g}^{-1}$  ( $n = 15$ ), which was within the certified range ( $1.04 \pm 0.16 \text{ mg g}^{-1}$ ). Recovery was also determined for total extractable Fe from certified reference material MESS-3 ( $73 \pm 2\%$  of certified mean,  $n = 9$ ) and MESS-4 ( $82 \pm 5\%$ ,  $n = 3$ ). Full recovery of Fe from sediment was not expected because hydrofluoric acid was not used for acid digestions, but quality of analysis is suggested by the consistency of Fe recovery among replicates and digestion batches.

### III. RESULTS AND DISCUSSION

#### *River conditions*

Lower Great Miami River discharges during the sampling periods ranged from 20 to 40 m<sup>3</sup> s<sup>-1</sup> at Hamilton, OH (USGS gauge 03274000), during the sampling periods and were representative of typical low-flow conditions in the river during late summer and early fall. Ambient water temperatures ranged from 16.4 to 25.6 °C (Table 2), with cooler temperatures in late September. Ambient dissolved oxygen ranged from 7.82 to 12.7 mg L<sup>-1</sup> (Table 3), and river-water pH was between 8.28 and 8.66 (Table 4).

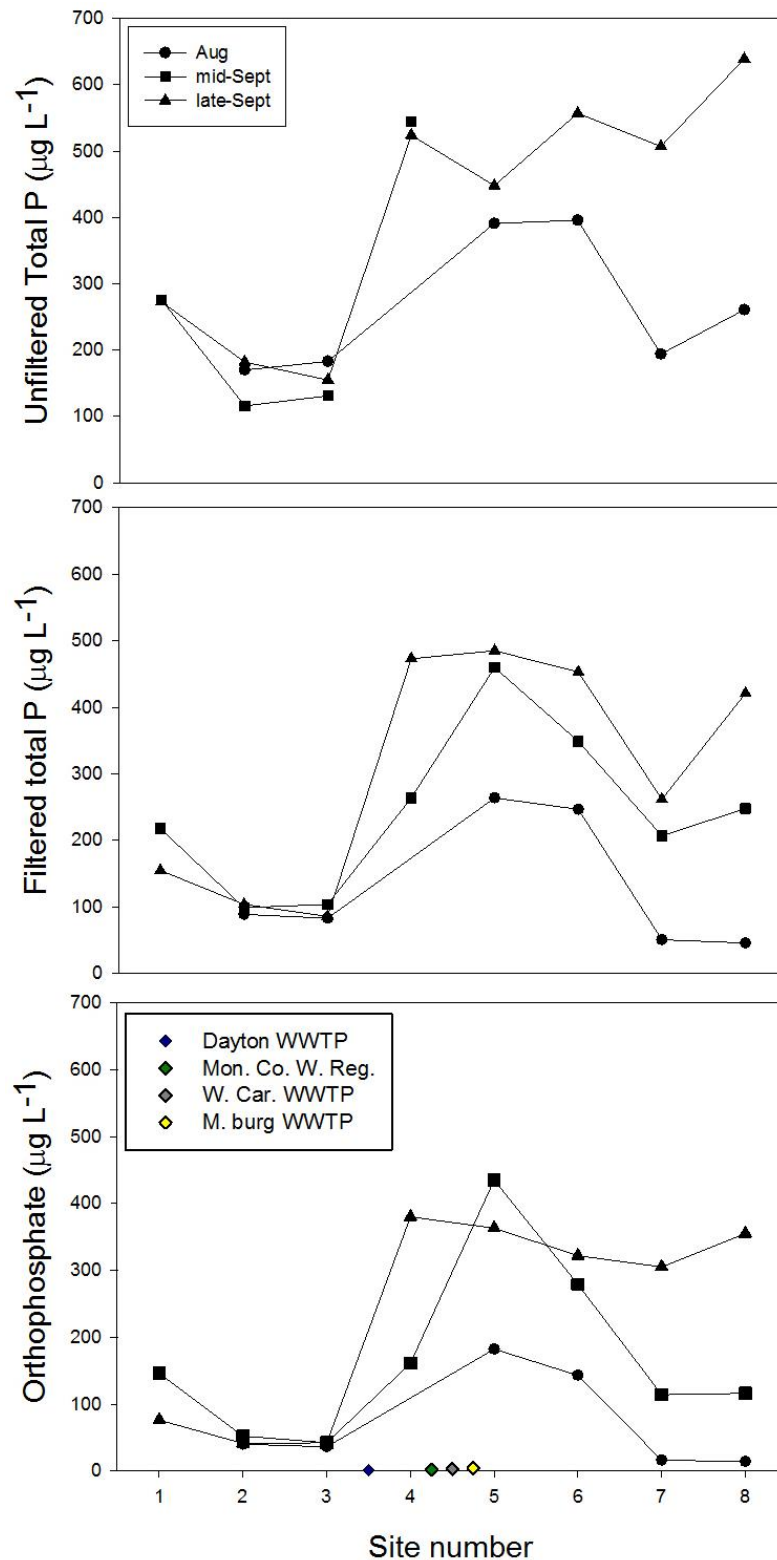
Ambient concentrations of P in river water varied among sampling locations in the Lower Great Miami River (Table 5; Figure 10). Sites 2 and 3, located upstream of major point source discharges to the river, had relatively low concentrations of P in all forms among each of the three sampling periods. Consistent among all sampling periods, concentrations of P increased markedly downstream of Site 3, especially during mid-Sept and late-Sept. Concentrations of unfiltered and filtered total P and ortho-P in river water were significantly higher at Sites 4–8 than at Sites 1–3 among all sampling periods (Mann–Whitney,  $p < 0.05$ ). These latitudinal distributions of P indicate that concentrations are relatively low near downtown Dayton and suggest a significant source of P to the river downstream of Site 3, particularly between the Tait Station dam and the West Carrollton pool. The significant increase of P likely results from inputs from either benthic remobilization or point-source discharges to the river. Effluent from Dayton Water Reclamation Facility is discharged to the river between Sites 3 and 4. Similar downstream patterns of total P, with a marked increase downstream of Site 3, were observed by the Ohio EPA in surveys conducted during late summer in 2010 (OEPA,



2015). Montgomery County Western Regional Wastewater Treatment Plant, West Carrollton Wastewater Treatment Plant and Miamisburg Water Reclamation Facility Downstream discharge effluent to the river between Sites 4 and 5. Downstream of Site 5, concentrations of P decreased in August and mid-September, but elevated concentrations persisted downstream in late-September. Filtered total P averaged ( $\pm$  SD)  $68 \pm 19\%$  of unfiltered total P, and ortho-P accounted for  $62 \pm 21\%$  of filtered total P among all river water samples.

**Table 5.** Total unfiltered and filtered (0.22  $\mu\text{m}$ ) P and orthophosphate (ortho-P) concentrations and relative distributions of the different P fractions in water of the Lower Great Miami River.

Site	Period	Concentration in river water ( $\mu\text{g L}^{-1}$ )				
		Unfiltered total P	Filtered total P	Ortho-P	Filtered/ unfiltered P (%)	Ortho-P/ filtered P (%)
1	Aug	--	--	--	--	--
	Mid-Sept	276	218	146	79	67
	Late-Sept	273	155	76	57	49
2	Aug	170	89	40	52	45
	Mid-Sept	116	99	52	85	53
	Late-Sept	182	104	41	57	40
3	Aug	183	83	36	45	43
	Mid-Sept	131	104	42	79	41
	Late-Sept	155	86	42	55	48
4	Aug	--	--	--	--	--
	Mid-Sept	365	264	161	72	61
	Late-Sept	524	473	380	90	80
5	Aug	391	264	182	68	69
	Mid-Sept	544	460	435	85	94
	Late-Sept	448	485	363	108	75
6	Aug	396	247	143	62	58
	Mid-Sept	478	349	279	73	80
	Late-Sept	557	453	322	81	71
7	Aug	194	51	16	26	31
	Mid-Sept	324	207	114	64	55
	Late-Sept	507	262	305	52	116
8	Aug	261	46	14	18	30
	Mid-Sept	382	248	116	65	47
	Late-Sept	639	421	355	66	84



**Figure 10.** Concentrations of unfiltered total, filtered total, and orthophosphate in Lower Great Miami River water during the three sampling periods. Site 1 is farthest upstream and Site 8 is downstream. Diamond symbols indicate the relative location of point source discharges to the river.

### ***Sediment***

Organic and water contents and concentrations of total P and total extractable Fe in surface sediment (0–2 cm) varied considerably among sampling locations (Table 6). Total P concentrations in surface sediment ranged from 0.87 to 5.92 mg g<sup>-1</sup> dry weight, with a mean of  $1.96 \pm 1.10$  mg g<sup>-1</sup> dry weight among all samples ( $n = 131$ ). Total P in sediment was consistently elevated at Hutchings pool (Site 5) compared to other locations during all three sampling periods. In the three pools where replicate cores were collected from different locations in the pool, sediment P concentrations did not differ between locations in either Island Park (Sites 1 and 1b;  $t$ -test,  $p = 0.33$ ) or West Carrollton (Sites 4 and 4b; Mann-Whitney,  $p = 0.86$ ) pools, but concentrations were different between locations in the Black Street pool (Sites 7 and 7b;  $t$ -test,  $p = 0.003$ ). At the four sites that were sampled during each of the three sampling periods (Sites 2, 3, 5, and 6), concentrations of total P in sediment were not different among sampling events (ANOVA,  $p > 0.05$ ), with the exception of Site 5, where sediment concentrations were greater in late-Sept than in Aug (Tukey,  $p = 0.03$ ). The temporal increase of P in sediment at Site 5 is consistent with measurements of P flux into the sediment during early and late-Sept sampling periods (discussed below). Overall, these results suggest that sediment P concentrations in the Lower Great Miami River during low-flow conditions are (1) relatively consistent in space within particular pools, (2) consistent over time, and (3) variable among different reaches of the river.

**Table 6.** Water content and dry-weight concentrations of organic matter, total P, and total extractable Fe in surface sediment in each core among the sampling sites and periods. Values are the average of 0–1 and 1–2 cm sediment horizons.

Site	Core	August				mid-September				late-September			
		OM (%)	Water (%)	Total P (mg g <sup>-1</sup> )	Fe (mg g <sup>-1</sup> )	OM (%)	Water (%)	Total P (mg g <sup>-1</sup> )	Fe (mg g <sup>-1</sup> )	OM (%)	Water (%)	Total P (mg g <sup>-1</sup> )	Fe (mg g <sup>-1</sup> )
1	A	--	--	--	--	1.53	6.7*	1.56	6.9	--	--	--	--
	B	--	--	--	--	0.82	7.1*	2.08	6.4	--	--	--	--
	C	--	--	--	--	0.67	6.1*	1.56	6.7	--	--	--	--
1b	A	--	--	--	--	--	--	--	--	3.67	38.7	1.35	14.6
	B	--	--	--	--	--	--	--	--	4.77	31.7	1.82	10.2
	C	--	--	--	--	--	--	--	--	7.12	43.5	1.17	18.8
2	A	1.20	17.5	1.23	7.0	0.94	13.6	1.35	8.4	1.02	7.6	1.51	10.3
	B	1.17	10.6	1.41	7.3	0.97	5.4*	2.00	7.5	1.10	8.5	1.43	9.0
	C	1.08	10.4	1.21	6.0	1.55	8.4	1.69	6.5	1.44	11.9	1.85	7.6
3	A	0.95	7.1*	1.59	6.1	1.04	10.3	1.62	8.9	0.96	10.2	1.59	7.4
	B	1.63	8.8*	1.86	6.6	0.93	9.0	1.64	6.5	0.95	9.5	1.54	7.2
	C	0.88	8.5*	1.85	6.5	1.69	25.6	1.87	7.4	0.75	7.5	1.52	7.8
4	A	--	--	--	--	1.22	13.2	2.45	6.9	3.36	33.0	1.00	9.2
	B	--	--	--	--	0.86	9.2	0.88	6.5	4.21	37.3	0.97	6.1
	C	--	--	--	--	--	--	--	--	4.61	42.3	1.29	9.0
4b	A	--	--	--	--	5.40	41.1	1.20	15.9	--	--	--	--
	B	--	--	--	--	4.57	41.9	0.93	15.2	--	--	--	--
5	A	1.96	17.8	3.41	7.9	3.32	33.2	4.32	10.2	2.56	32.1	4.17	8.0
	B	2.82	20.6	3.39	7.8	2.52	31.0	4.35	8.7	4.45	33.5	5.92	8.0
	C	1.18	20.6	1.99	6.2	2.64	32.5	4.19	9.2	2.51	34.4	4.92	7.8
6	A	0.84	14.5	1.41	6.4	0.85	8.20	1.86	3.5	0.99	8.4	1.50	6.2
	B	0.92	8.5	1.34	6.2	0.76	13.3	1.99	4.3	0.73	9.0	1.55	5.2
	C	0.79	6.3*	1.66	7.3	0.68	7.5	1.27	6.0	1.10	7.2*	1.90	7.3
7	A	1.67	10.1*	1.49	7.4	--	--	--	--	--	--	--	--
	B	1.03	11.3*	1.84	7.3	--	--	--	--	--	--	--	--

7b	C	1.09	12.1*	1.67	6.2	--	--	--	--	--	--	--	--
	A	--	--	--	--	4.05	35.1	0.95	11.0	6.49	39.4	1.15	15.5
	B	--	--	--	--	3.94	34.0	1.32	10.8	4.44	32.8	0.97	9.9
	C	--	--	--	--	4.44	34.7	1.29	12.2	3.14	29.1	0.87	7.8
8	A	0.80	16.5	3.37	5.6	1.33	17.5	2.33	9.0	1.09	19.3	0.91	6.6
	B	1.29	17.9	2.80	6.8	1.00	20.1	3.92	7.1	1.50	26.7	1.06	7.2
	C	0.93	18.4	2.39	6.5	1.05	18.6	3.80	7.3	1.60	21.2	1.15	6.8

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\*Observed water loss in the process of sediment extrusion and sectioning.

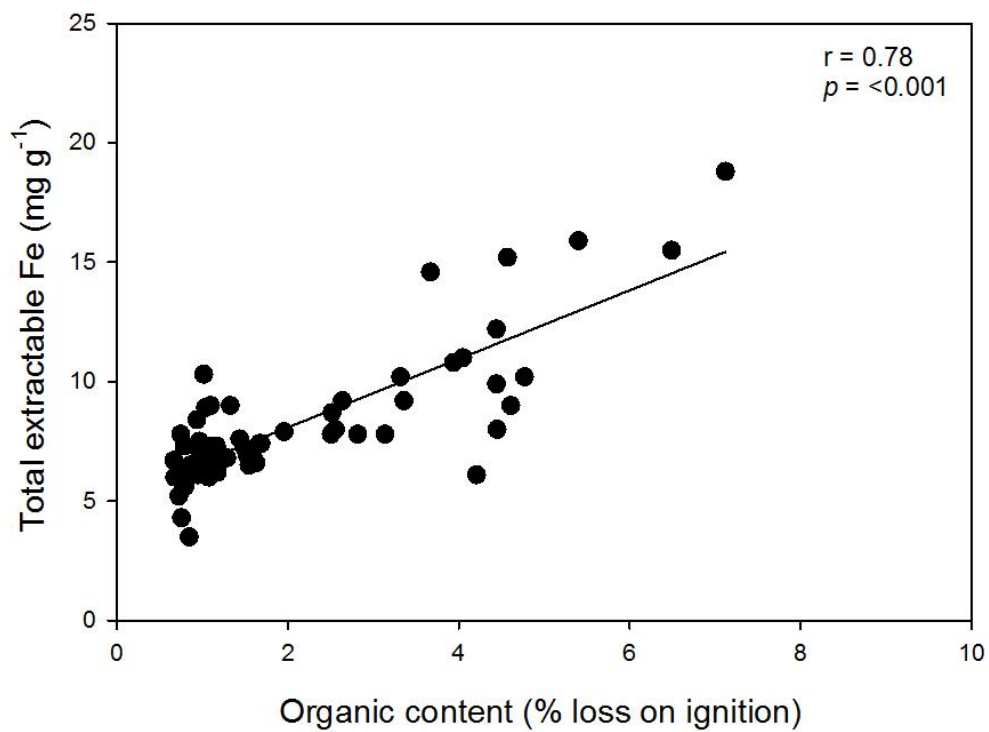
Concentrations of total extractable Fe ranged 3.5–18.8 mg g<sup>-1</sup> dry weight with a mean of  $8.11 \pm 2.8$  mg g<sup>-1</sup>. Extractable total Fe in sediment was greatest at Site 1b in late-Sept and Site 4b in mid-Sept, with an average of the three cores from each site being 14.5 mg g<sup>-1</sup> dry weight and 13.8 mg g<sup>-1</sup> dry weight. At the four sites that were sampled during each of the three sampling periods (Sites 2, 3, 5, and 6), concentrations of total extractable Fe in sediment were not different among sampling events, with the exception of Site 5, where Fe sediment concentrations were greater in mid-Sept than in either Aug or late-Sept.

Organic content of the 0–2 cm surface sediment ranged from 0.67% to 7.12% and averaged  $2.02 \pm 1.56\%$ . Organic content of surface sediment was greatest at Site 1b in late-Sept and Site 4b in mid-Sept, consistent with elevated concentrations of Fe. Organic content of surface sediment was not different among sampling events at the four sites that were sampled during each of the three sampling periods (Sites 2, 3, and 5), with the exception of Site 6, where the organic content of the sediment was less than at the other three sites.

Surprisingly, total P in sediment was unrelated to either organic matter ( $p = 0.95$ , Figure A1) or total extractable Fe ( $p = 0.16$ , Figure A2). Total extractable Fe was positively correlated with organic matter in surface sediment ( $p = <0.0001$ ,  $r = 0.78$ , Figure 11). A positive relationship between P and either organic matter or Fe in surface sediment is often observed in lakes (Søndergaard et al., 2003). An absence of a relationship between total P in sediment and either organic matter or extractable Fe might have resulted from variable sorting of the sediment collected within the cores. Sampled sediment consisted mainly of sand and gravel while only a few of the locations had silty

material. Although total P in the sediment was unrelated to either organic matter or total extractable Fe, other studies show that organic matter and Fe can be related through different physico-chemical and biological controls that influence P cycling of uptake and release in rivers. Physico-chemical controls, such as metal oxides, predominantly Fe and aluminum (Lijklemam 1980, Zhang and Huang, 2007), interact strongly with dissolved P through sorption and desorption reactions (Withers and Jarvie, 2008). Similarly, mineral precipitation reactions under anaerobic conditions in eutrophic waters with high P pore water concentrations, such as Fe(II) phosphate, can fix P in sediment and regulate P concentrations in the water column (House, 2003). Biological controls, such as microorganisms, can contribute to P cycling through the decomposition of organic matter and can affect the flux of P at the sediment-water interface by uptake, redox alterations, or burial of P (Gachter and Meyer, 1993; McDowell, 2003). Microbial activity related to high organic matter inputs can cause sediment to become anoxic through oxygen consumption during microbial respiration. These changing conditions can result in the reductive dissolution of Fe(III) phosphates, which release bioavailable orthophosphate into the pore water (House, 2003). Therefore, these reducing conditions by the microbial processing of organic matter can drive the biogeochemical cycling of P in the river bed sediment (House, 2003).





**Figure 11.** Total extractable Fe related to the organic content of surface sediment (0–2 cm) in the Lower Great Miami River. Both concentrations are on a dry-weight basis.

### ***Benthic Flux***

Measured benthic fluxes of filtered P averaged  $2.9 \pm 3.3 \text{ mg m}^{-2} \text{ d}^{-1}$  among all sites and sampling periods during low-flow conditions in late summer of 2015. Fluxes of filtered total P varied considerably among individual cores, sites, and sampling period (Table 7, Figure 12). River-bed sediment were a net source of P to the river at most locations. In late-Sept, mean benthic fluxes of P ranged from  $-1.6$  to  $12 \text{ mg m}^{-2} \text{ d}^{-1}$  at Sites 5 and 1b, respectively, indicating substantial variability of fluxes among locations. Negative fluxes indicate net uptake of P from the water column to sediment.

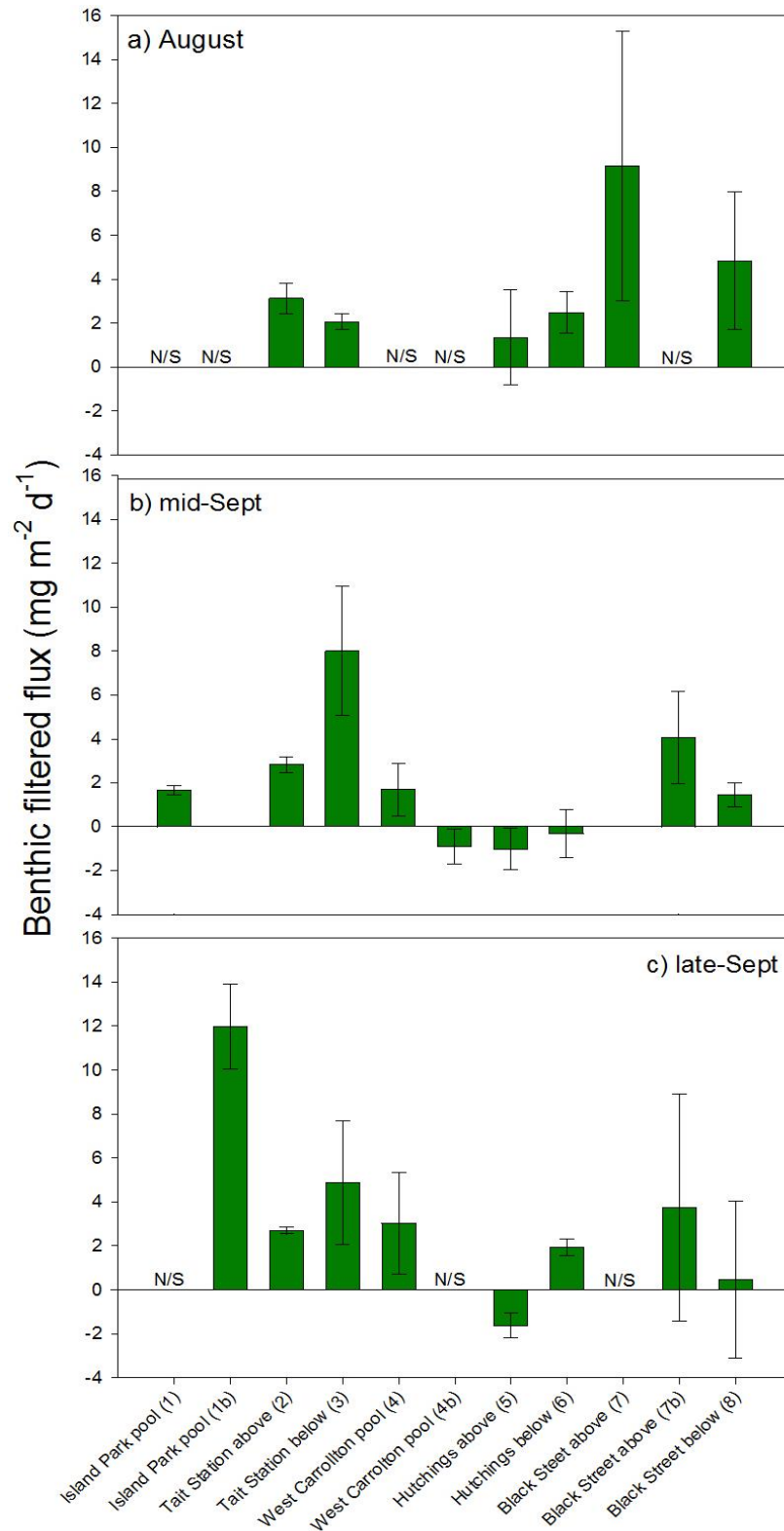
**Table 7.** Benthic fluxes of filtered total P from sediment in the Lower Great Miami River. Fluxes in each core were determined from the incubation periods.

Site	Core	August flux (mg P m <sup>-2</sup> d <sup>-1</sup> )		mid-Sept flux (mg P m <sup>-2</sup> d <sup>-1</sup> )		late-Sept flux (mg P m <sup>-2</sup> d <sup>-1</sup> )	
		Core (± SE)	Site mean (± SD)	Core (± SE)	Site mean (± SD)	Core (± SE)	Site mean (± SD)
1	A	--	--	1.4 ± 0.8*	1.7 ± 0.2	--	--
	B	--		1.8 ± 0.5		--	
	C	--		1.8 ± 0.7*		--	
1b	A	--	--	--	--	9.8 ± 0.7	12.0 ± 1.9
	B	--		--		13.4 ± 2.0	
	C	--		--		12.8 ± 0.9	
2	A	2.3 ± 0.5	3.1 ± 0.7	2.7 ± 0.3	2.8 ± 0.4	2.9 ± 0.7	2.7 ± 0.2
	B	3.7 ± 0.4		2.6 ± 0.3		2.7 ± 0.3	
	C	3.4 ± 0.2		3.2 ± 0.7		2.6 ± 0.4	
3	A	2.5 ± 0.4	2.1 ± 0.4	9.5 ± 0.6	8.0 ± 3.0	7.9 ± 2.1	4.9 ± 2.8
	B	2.0 ± 0.2		4.6 ± 0.9		2.4 ± 0.4	
	C	1.7 ± 0.2		10.0 ± 0.8		4.3 ± 0.8	
4	A	--	--	0.9 ± 0.6*	1.7 ± 1.2	2.7 ± 1.3*	3.0 ± 2.3
	B	--		2.5 ± 0.3		0.9 ± 0.5*	
	C	--				5.5 ± 1.4	
4b	A	--	--	-1.5 ± 0.2	-0.9 ± 0.8	--	--
	B	--		-0.3 ± 0.6*		--	
5	A	0.2 ± 0.2*	1.3 ± 2.2	-1.0 ± 1.5*	-1.0 ± 0.9	-1.9 ± 1.1*	-1.6 ± 0.6
	B	3.8 ± 0.9		-2.0 ± 0.6*		-2.0 ± 1.2*	
	C	0.0 ± 0.7*		-0.1 ± 0.4*		-1.0 ± 0.5*	
6	A	2.7 ± 0.6	2.5 ± 1.0	0.8 ± 1.0*	-0.3 ± 1.1	2.1 ± 1.1	1.9 ± 0.4
	B	3.4 ± 0.8		-0.4 ± 0.6*		1.5 ± 0.2	

	C	$1.5 \pm 1.1^*$		$-1.4 \pm 1.4^*$		$2.2 \pm 0.7^*$	
7	A	$15.3 \pm 1.2^*$	$9.2 \pm 6.1$	--	--	--	--
	B	$9.1 \pm 0.9$		--		--	
	C	$3.1 \pm 0.6$		--		--	
7b	A	--	--	$3.6 \pm 1.4^*$	$4.1 \pm 2.1$	$9.5 \pm 4.9^*$	$3.7 \pm 5.2$
	B	--		$2.2 \pm 0.3$		$-0.4 \pm 0.8$	
	C	--		$6.4 \pm 0.7$		$2.0 \pm 0.7$	
8	A	$3.2 \pm 0.3$	$4.8 \pm 3.1$	$1.5 \pm 0.2$	$1.5 \pm 0.5$	$-3.6 \pm 0.6$	$0.5 \pm 3.6$
	B	$8.4 \pm 1.4$		$2.0 \pm 1.4^*$		$2.5 \pm 0.2$	
	C	$2.9 \pm 0.1$		$0.9 \pm 1.0^*$		$2.5 \pm 0.4$	

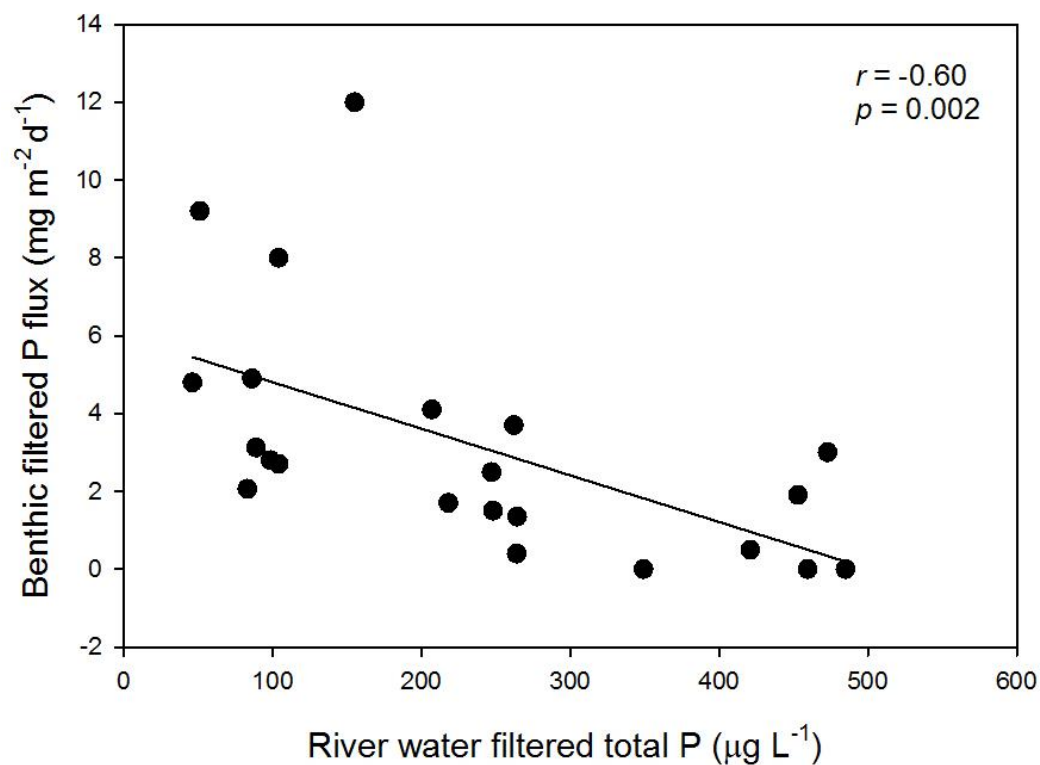
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\*Regression slopes > 0.05 indicate that the flux was not statistically different from 0.

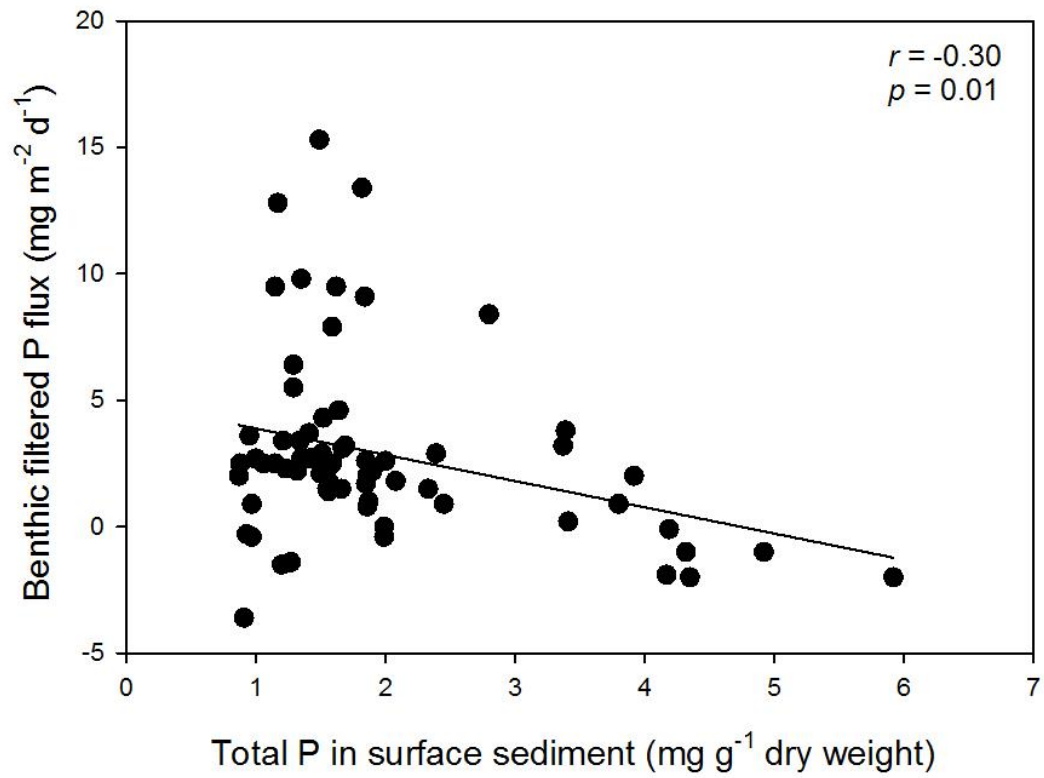


**Figure 12.** Benthic flux of filtered P among all sampling periods and sites in the Lower Great Miami River. Bars are the mean ( $\pm$  SD) flux of three replicate cores. Locations during each period that were not sampled are labeled as N/S (denoting not sampled).

Benthic fluxes of filtered P were related inversely to the concentration of filtered total P in river water ( $p = 0.002$ ,  $r = -0.60$ , Figure 13). This relationship suggests that elevated concentrations in river water inhibit mobilization of P from sediment, likely by minimizing the concentration gradient between pore fluid and overlying water. When concentrations in the water column were increased, fluxes from sediment were either relatively small or there was net uptake of P into sediment. Net uptake of P into sediment at Site 5 was supported by a significant increase of sediment P concentrations over time. Accordingly, upstream sources of P to river water inhibit its remobilization from sediment and potentially contribute to its storage in sediment. Benthic fluxes of filtered total P from sediment also were related inversely to concentrations of total P in surface sediment ( $p = 0.01$ ,  $r = -0.30$ , Figure 14). This relationship implies that the flux of P from sediment decreases as the sediment reservoir increases, which seems counterintuitive because one might expect the flux to increase with a greater reservoir in sediment. However, when the relationships in Figures 13 and 14 are considered in tandem, they suggest that the concentration of P in the water column is the main driver of P exchange across the sediment-water interface. When concentrations of P in the water column are elevated, flux from the sediments is inhibited and P concentrations in sediment may increase as a result of net uptake. All together, these observations suggest that reducing water column concentrations of P by reducing external loadings could have the unintended consequence of increasing P fluxes from sediment.



**Figure 13.** Relationship between benthic filtered P flux (average among replicate cores at each location) and filtered total P concentration in river water of the Lower Great Miami River.



**Figure 14.** Relationship between benthic filtered P flux and total P concentration of surface sediment (0–2 cm) of individual cores from the Lower Great Miami River.

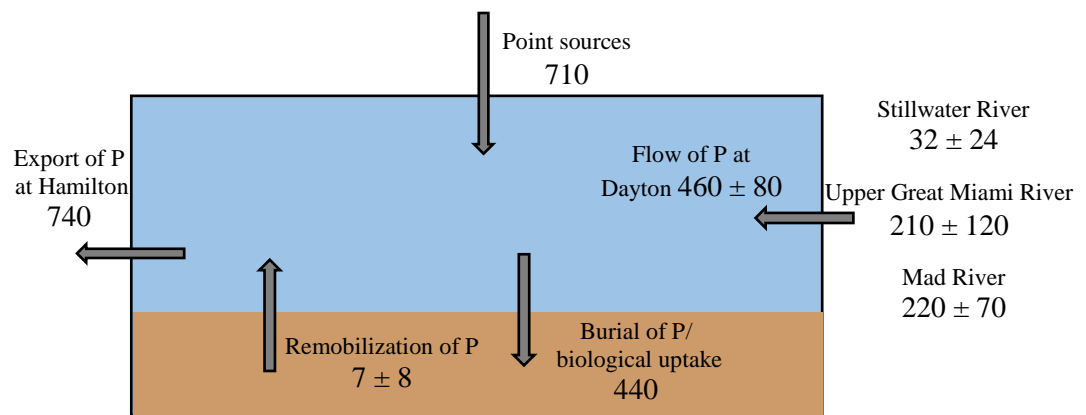


The results of this study are consistent with the findings of Jarvie and colleagues (2005), who examined P remobilization from two eutrophic river basins in the United Kingdom. They observed that remobilization of ortho-P from river sediment was dependent on a diffusion gradient between the sediment-water interface and river water, and that sediments were a source when concentrations of ortho-P were greater in pore water than in river water. They also observed that sediments were net sinks of ortho-P at river locations influenced by sewage inputs where water column concentrations were greater than those in pore fluids (Jarvie et al., 2005). As I have concluded, and as suggested by others (Haggard et al., 2005; House and Denison, 2000; Jarvie et al., 2005, 2006), decreases of P loadings to river water, such as a reduction of point-source inputs, could result in an increased release of P from sediment.

### ***Benthic flux scaled***

The average benthic P flux among all sites and sampling periods was  $2.9 \pm 3.3 \text{ mg m}^{-2} \text{ d}^{-1}$  during low-flow conditions in late summer 2015. This flux estimate is based on incubations of sediments were obtained with a push corer (e.g., silt, sand, pebbles), which are representative of only about 20% of the Lower Great Miami River bottom, with the other ~80% composed on cobble, boulders and bedrock (OEPA, 2015). Phosphorus partitioning with the larger size classes of particles is presumably small compared to the finer particles. When scaled to about 20% of a total area of about  $1.2 (\pm 0.4) \times 10^7 \text{ m}^2$  for the Lower Great Miami River (130 km long  $\times$   $95 \pm 32 \text{ m}$  average width), the benthic flux is estimated to be about  $7 \pm 8 \text{ kg P d}^{-1}$ .

Benthic fluxes of P are not a large source of P to the Lower Great Miami River relative to other known sources (Figure 15). The Upper Great Miami River ( $210 \pm 120 \text{ kg P d}^{-1}$ ), Stillwater River ( $32 \pm 24 \text{ kg P d}^{-1}$ ), and Mad River ( $220 \pm 70 \text{ kg P d}^{-1}$ ) contribute around ( $460 \pm 80 \text{ kg P d}^{-1}$ ) to the Lower Great Miami River. The fluvial sources to the Great Miami River were estimated from gauged water flows and concentrations of total P in each river during low-flow in August and September of 2013 (MCD, 2013). Point sources are estimated to contribute about  $710 \text{ kg P d}^{-1}$ , based on well-constrained discharge and concentration measurements from regulatory monitoring of wastewater facilities. Phosphorus discharge at Hamilton is estimated to be about  $740 \text{ kg P d}^{-1}$  based on river flow and water column concentrations. Sedimentation and biological uptake of P were not quantified in this study. Accordingly, these two losses of P from river water, among potential other losses, were estimated to be about  $440 \text{ kg P d}^{-1}$  as the closing term of the budget, if steady-state conditions are assumed during the low-flow period in late



**Figure 15.** Estimated mass balance of total P (kg P d<sup>-1</sup>) in the Lower Great Miami River during low-flow conditions in August and September.

summer during times of greater river discharge, it is likely that significance of upstream nonpoint sources increases relative to point sources and that burial and biological uptake are much less than the export flux to downstream. Indeed, scouring of particulate P from the benthos during high-flow conditions could further exacerbate export. These estimates suggest that P remobilization from sediment is a minor source to the river compared to other sources.

Benthic fluxes of filtered P were inversely related to concentrations in river water (Figure 13), and it is inferred that point sources were a dominant source of P to the river during low-flow conditions in summer 2015 (Figure 15). The Ohio EPA has recommended reducing NPDES permit limits for P to  $1 \text{ mg L}^{-1}$  for publicly owned waste water treatment plants that discharge to the Lower Great Miami River, which would essentially halve point source inputs based on current effluent concentrations. If the proposed permitting were implemented, then point source loadings could be reduced to about  $350 \text{ kg d}^{-1}$ , and total external loadings to the Lower Great Miami River could decrease from about  $1170 \text{ kg d}^{-1}$  currently to  $810 \text{ kg d}^{-1}$  during low flow in later summer. Such a reduced loading could result in a lowering of water-column P concentrations by about 30%, assuming upstream sources remain constant and sinks for P remain proportional to inputs. Lowered P concentrations in river water may exacerbate its efflux from sediment, perhaps by as much as doubling, depending on existing ambient P concentrations in the water (Figure 13). However, an increase of benthic P remobilization from about  $7 \pm 8 \text{ kg d}^{-1}$  (Figure 15) to as much as  $14 \text{ kg d}^{-1}$  will remain a minor, if not trivial, source to the river during low flow, even when external loadings are lowered to about  $810 \text{ kg d}^{-1}$ , as proposed. The reservoir of P in only the upper 2 cm of

sediment in the Lower Great Miami River is estimated to be about 80,000 kg, based on the mean measured concentration, estimated river area, 20% of the river bottom being composed to silty-to-gravelly material, and assuming a dry sediment density of  $1.4 \text{ g cm}^{-3}$ . This suggests that there is a substantial reservoir of P in sediment that will need to be decreased, either by efflux of soluble forms to overlying water or scouring of particles, before recovery of the river is complete.

### *Conclusions*

During low river flow in late summer and early fall, excessive concentrations of P are present in the Lower Great Miami River (LGMR) and contribute to its eutrophication. Wastewater treatment plants are suspected of being major point sources of P to the Lower Great Miami River during low river flow. In this study, riverbed sediment was examined as an additional potential source of P and was found to be only a minor source of P to the Lower Great Miami River relative to external point and nonpoint sources. Benthic fluxes of filtered total P were inversely related to filtered total P concentrations in overlying river water, and there is a large reservoir of P in the river's sediment. These observations suggest that, while benthic remobilization is not leading major source of P to the river, nutrient abatement strategies could increase P fluxes from sediment. A better understanding of remobilization of legacy P and the best way to manage water quality improvements is needed. The potential lag time for re-equilibrium states between the sediment-water interface should be applied when changes in watershed management are made, such as reducing external P loadings. It is also important to address the complexity

of the different physico-chemical and biological controls that influence P cycling of uptake and release in rivers to help sustain improvements in water conditions.

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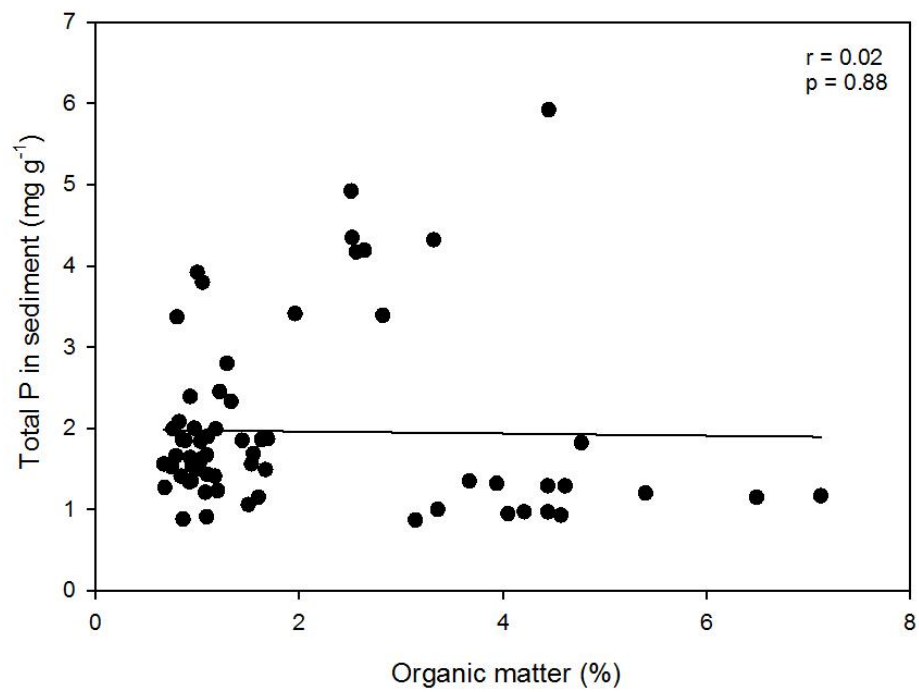
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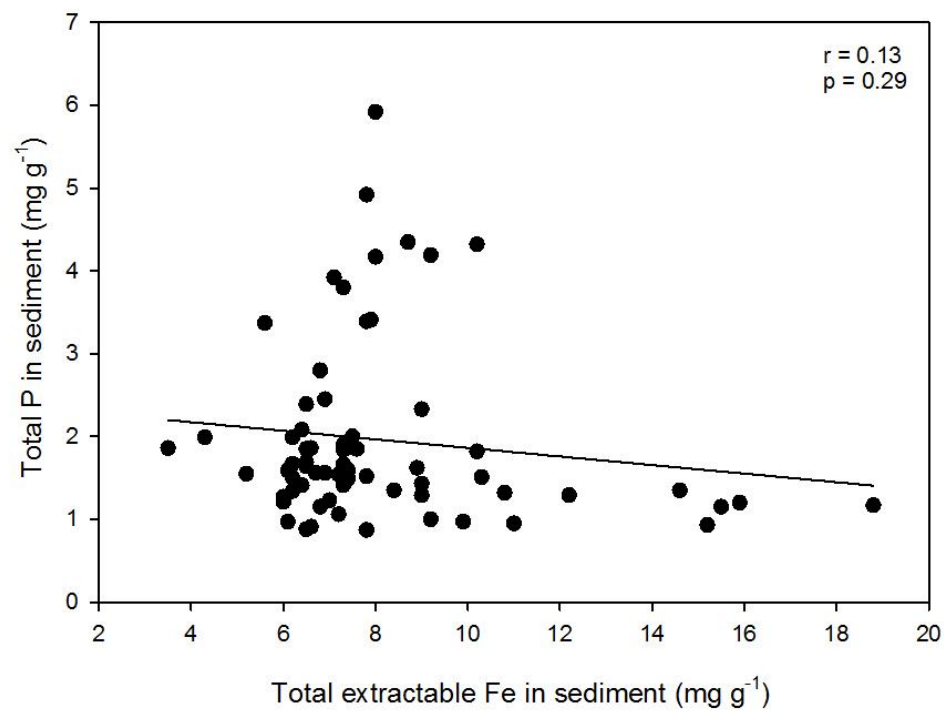
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## Appendix



**Figure A1.** Relationship between total P and organic matter dry-weight concentrations in sediments of the Lower Great Miami River.



**Figure A2.** Relationship between total P and extractable Fe dry-weight concentrations in sediments of the Lower Great Miami River.