Benthic Phosphorus Fluxes in the Lower Great Miami River

Chad R. Hammerschmidt and Kortney R. Mullen
Department of Earth & Environmental Sciences, Wright State University, Dayton, OH

Introduction

We evaluated riverbed sediment as either a potential source or sink of phosphorus in the Lower Great Miami River. Excessive amounts of phosphorus in water of the Lower Great Miami River during low river flows in summer and early fall degrade aquatic ecosystems and prevent the Lower Great Miami River from being a high-quality warmwater stream. Regulators concluded that point-source discharges of nitrogen and phosphorus from municipal wastewater treatment plants are the principal cause of impairment year-round, and particularly during low river flow. However, previous studies have not examined riverbed sediment as a potential source and sink of phosphorus during low-flow conditions. Failure to examine this potential source of phosphorus could lead to incorrect conclusions about the cause of river impairment and investment in expensive nutrient-removal technologies that fail to achieve desired improvements in aquatic ecosystem health. The purpose of this research was to evaluate riverbed sediment as either a potential source or sink of phosphorus in the water column of the Great Miami River. This was accomplished by measuring geochemical conditions and phosphorus flux from riverbed sediment at 11 locations in the Lower Great Miami River.

Background

More than 70 percent of the runoff that drains into the Great Miami River is from agricultural land used primarily for production of corn, soybeans, and wheat. Most of this agricultural land drains into the Great Miami River and its tributaries upstream of Dayton, Ohio, with the Lower downstream drainage basin being more urbanized. The Lower Great Miami River extends from river mile 81.5 in Dayton to its confluence with the Ohio River in western Hamilton County, Ohio. The Lower Great Miami River drainage system includes extensive hydraulically connected sand and gravel aquifers that provide nearly all of the region's potable water supply. In recent years, the Lower Great Miami River has become an important recreational venue for fishing and boating. Concerns over nutrient enrichment in the Lower Great Miami River led to a pilot water-quality trading program that allows nonpoint sources of nutrients from agricultural runoff, which are more economically mitigated than point sources from municipal wastewater treatment plants, to trade with point sources in order to reduce total nutrient loading to the river. However, regulators have concluded that impairment of Lower Great Miami River biological communities in the summer and early fall is largely a result of nutrient dynamics during lower river flows, and therefore not directly influenced by recent nutrient loading from watershed runoff.

All organisms require nutrients to sustain life and growth. Nitrogen (N) and phosphorus (P) are primary nutrients for algal and macrophyte production and are essential to the functioning of healthy aquatic ecosystems. However, overabundance of nutrients, including P in freshwater systems (Schindler, 1977; Hecky and Kilham, 1988), can exert negative ecosystem effects, including alteration of trophic dynamics by increasing algal and macrophyte production,

increasing turbidity (through algal abundance), decreasing concentrations of dissolved oxygen, and increasing the magnitude of diel fluctuations of dissolved oxygen and pH. These symptoms of eutrophication shift species composition away from those typical of high-quality warmwater streams towards less desirable species compositions of degraded warmwater systems (OEPA, 1999).

Human activities over the last century have increased the amount of N and P loadings to aquatic ecosystems. This increase is due to municipal and industrial wastewater discharges, fertilizer use, and atmospheric inputs (Puckett, 1995). Despite improvements in water quality due to better treatment of wastewater discharges, an overabundance of nutrients still exists in the Great Miami River watershed (OEPA, 2001; 2011; 2012). Algal blooms in the Great Miami River were observed by the Ohio Environmental Protection Agency (OEPA) in 1995 (OEPA, 1997) and again in 2011 (Smith, 2011). Nutrient enrichment is listed by OEPA as one of the most pervasive causes of impairment in the Upper Great Miami River watershed in a recent study of biological and water quality (OEPA, 2011).

Nutrients in the Great Miami River are eventually transported to the Gulf of Mexico, where they contribute to hypoxia in coastal waters of Louisiana and Texas. The Great Miami River Watershed has some of the largest P yields in the entire Mississippi-Atchafalaya River (i.e., Gulf of Mexico) watershed (Goolsby et al., 1999). Moreover, and among the eight Ohio watersheds in Heidelberg University's Ohio Tributary Monitoring Program, the Great Miami River has the highest concentrations and unit area loads of total and dissolved P (Loftus, 2004). Transport of nutrients in spring runoff to the Gulf of Mexico is thought to be responsible for increased algal growth leading to seasonal hypoxic conditions in the Gulf (Rabalais et al., 2002; Scavia et al., 2004).

Evaluations of nutrient loading in the Great Miami River watershed suggest that nonpoint sources contribute most of the annual P load carried by the river (Reutter, 2003). Often a significant amount of the annual nutrient load can be attributed to just a few large runoff events that typically occur between late winter and early summer. Thus, management programs directed at preventing export of nutrients downstream should focus primarily on preventing nutrients from being exported from agricultural land and entering streams and aquifers. 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 significant runoff events carrying large nutrient loads from nonpoint sources are not occurring. These evaluations show a decline in biological community performance in the Lower Great Miami River, downstream of Dayton (OEPA, 2012). Results from these evaluations also show strong evidence of excess nutrients. For example, the studies have documented elevated concentrations of soluble forms of P in water as well as increased periphyton biomass and large diel changes of dissolved oxygen 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 in biological communities due to nutrient enrichment may best be

ameliorated by lowering permit nutrient concentrations in effluent. But, is this conclusion correct?

Rivers and streams have an ability to assimilate nutrients. Phosphorus assimilation in lotic systems is often controlled by characteristics of bottom sediment and P concentration in the water column. Vegetation and periphyton provide short-term retention of P and facilitate long-term retention through accrual of organic matter, but long-term retention is thought to be determined by sediment geochemistry and other site characteristics (Reddy et al., 1996). Trivalent metals, particularly ferric iron, can scavenge phosphate from water and retain it in a biologically unavailable form in sediment until the Fe(III) is reduced and phosphate released under conditions of low dissolved oxygen and Eh (Boström et al., 1988). Thus, sediment can be both a source and sink of P, and its contribution to trophic dynamics in the Great Miami River is not well understood. One study found riverbed sediment to be a net source of soluble reactive P (SRP), a biologically active form of P, under three circumstances, where: (1) there was minimal point source influence (headwater streams), (2) point source inputs were subject to dilution by water containing low concentrations of SRP, and (3) equilibrium phosphorus concentration of riverbed sediment was relatively high, as a result of deposition of particulates with high exchangeable P concentrations (e.g., $FePO_4(s)$) from diffuse sources (Jarvie et al., 2004). Although iron and P concentrations in sediment of the Great Miami River are unknown, it is possible that sediment is a source of P to the river, particularly under low-flow conditions that may allow surface sediment to become anoxic, $FePO_4$ minerals to dissolve, and P to be released to overlying water. In addition, P can be released from sediment during the decomposition of organic material, the rate of which would be expected to be greatest when water and sediment temperatures are highest in summer and early fall (i.e., period of greatest water quality impairment in the Great Miami River). The conclusion of OEPA (2012) that point sources of nutrients are the primary driver of trophic dynamics during low-flow conditions in summer and fall in the Lower Great Miami River is tenuous because internal P fluxes and cycling, including P fluxes from sediment into the river, have not been measured.

Objective

We hypothesized that benthic remobilization is a significant source of P to the Lower Great Miami River during low-flow conditions in late summer and early fall. The objective of the study was to quantify fluxes of P from sediment at representative locations along the Lower Great Miami River.

Methods

Field sampling. Sediment was sampled for benthic flux chambers and geochemical analyses from 11 representative locations along the main stem of the Lower Great Miami River during relatively low-flow conditions in 2015 (Table 1, Figure 1). Eight of the sampling sites were in pools upstream of low-head dams and the other three were in free-flowing reaches, within 300 m of an upstream dam. Selection of sampling sites was biased toward pools because it was expected that sediment in pools would have greater enrichment of fine material, including organic debris and associated P, and therefore potentially have the greatest input of P to overlying water. To examine temporal variability, sediment was sampled during each of three

expedities that occurred over about week-long periods in August (Aug 18–24), mid-September (Sept 10–18), and late September/early October (Sept 28–Oct 2); hereafter, we refer to these sampling periods as Aug, mid-Sept, and late-Sept. During the three sampling periods, river discharge at Hamilton (USGS gauge 03274000) averaged 1400 (Aug), 825 (mid-Sept), and 710 ft^3 s^{-1} (late-Sept). These discharges were representative of low-flow conditions during the late summer and early fall of 2015.

Table 1. Sediment sampling locations in the Lower Great Miami River. Water depths are to the nearest 0.5 m.

| Site	Latitude (39 °N)	Longitude (84 °W)	Sampling periods	Water depth (m)	Site description
1	46'33.81"	11'41.43"	mid-Sept	1.0	Island Park pool
1b	46'35.09"	11'45.53"	late-Sept	2.0	Island Park pool
2	43'48.88"	12'30.59"	Aug, mid-Sept, late-Sept	0.5	Tait Station pool
3	43'51.10"	12'49.20"	Aug, mid-Sept, late-Sept	0.5	Below Tait Station dam
4	40'49.68"	14'34.97"	mid-Sept, late-Sept	1.5	West Carrollton pool
4b	40'49.85"	14'25.91"	mid-Sept	1.0	West Carrollton pool
5	36'44.54"	17'29.53"	Aug, mid-Sept, late-Sept	2.0	Hutchings pool
6	36'25.05"	17'09.26"	Aug, mid-Sept, late-Sept	0.5	Below Hutchings dam
7	25'00.51"	33'03.09"	Aug	0.5	Black Street dam pool
7b	24'56.92"	33'09.38"	mid-Sept, late-Sept	0.5	Black Street dam pool
8	24'37.89"	33'25.05"	Aug, mid-Sept, late-Sept	0.5	Below Black Street dam
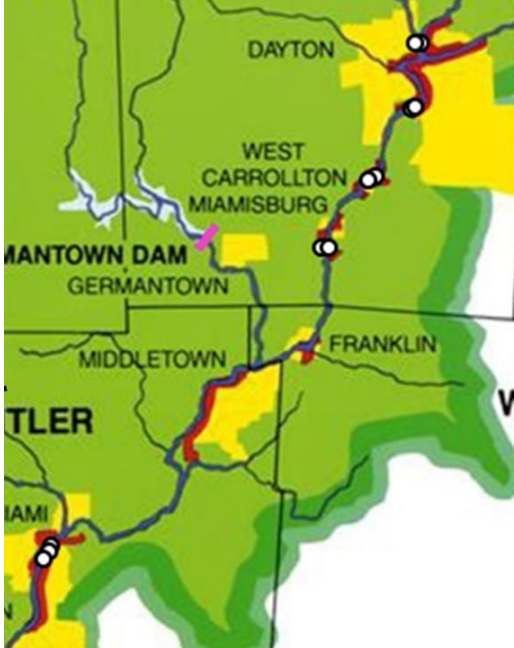
Figure 1. Sediment sampling locations (white circles) in the Great Miami River between Dayton and Hamilton, OH. Adapted from the Miami Conservancy District.

Figure 2. Sediment coring at Sites 8 (panel A), 2 (panel B), and 4b (panel C) in the Lower Great Miami River.

Three cylindrical, intact cores of surface sediment and overlying water (6.35 cm ID, 7 cm OD, 30 cm length) were obtained from each sampling site with a push corer, either by wading or from either a 16-ft Jon boat or 10-ft Zodiac inflatable boat (Figure 2). Particular care was taken to not disturb the sediment-water interface during either sampling or transport back to the research laboratory for incubation. About 10–15 cm of sediment was collected in each tube, with overlying water comprising the remaining volume. Tubes were sealed on the sediment end with a water-tight plastic cap, wrapped with electrical tape, held in an upright position inside a water-filled cooler (for temperature control and darkness), and transported to Wright State University where they were fitted with a stirring head and motor prior to incubation (described below). River water also was sampled at each location by hand collection into acid-cleaned 2-L

polycarbonate bottles facing upstream of sampling personnel. Hand collection of surface water was presumed to be representative of water near the sediment-water interface because physicochemical profiling indicated that the water column was well mixed at all locations, including, for example, in a relatively deep pool above the Black Street dam in Hamilton (Figure 3). Within 3 h of sampling, water was subsampled from each bottle for analysis of unfiltered total P, filtered total P, and soluble reactive P (SRP); the latter two being filtered through 0.2-μm membranes. Samples for analysis of total P were acidified to 2% with high-purity HNO_3 and those for determination of SRP were stored at −20 °C until analysis. The remaining water in each 2-L bottle was stored in the dark, at

Figure 3. Physicochemical profiles in the pool upstream of the Black Street dam in Hamilton, OH. Note the narrow scale of units.

room temperature, until some of it was used to replenish the flux chambers. Ambient dissolved oxygen, temperature, conductivity, and pH of river water were measured *in situ* with an optode, thermocouple, and electrodes (Standard Method 4500-H^{+} B and 2510 B, APHA et al., 1995), respectively. The thermocouple was traceable to the U.S. National Institute of Standards and Technology (NIST). The optode and electrodes were calibrated before each use according to manufacturer's specifications, either by air-saturation or with NIST-traceable solutions.
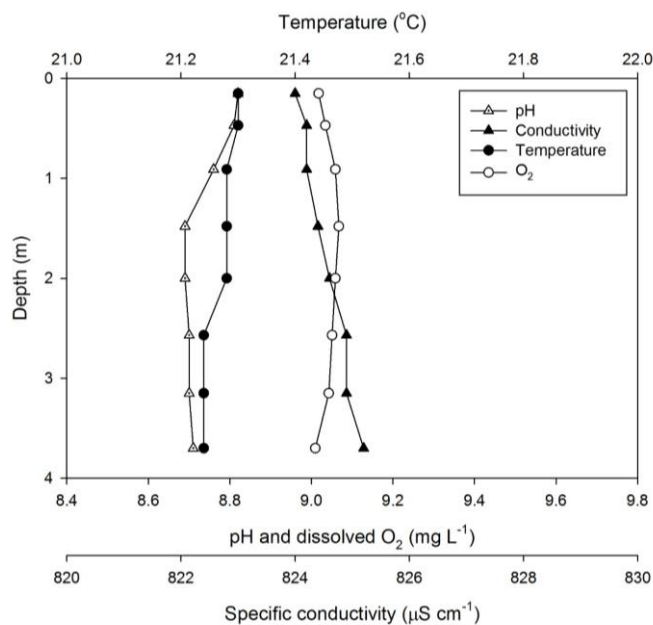
Measured benthic fluxes. Fluxes of P from sediment of the Lower Great Miami River were quantified with benthic flux chambers of river sediment and overlying water (Figure 4), a technique we initially developed for quantifying benthic fluxes of mercury (Hammerschmidt and Fitzgerald, 2008) and have since adapted for measuring sediment-water exchange of P (Taylor, 2012). The benthic flux chambers consisted of undisturbed cores of sediment and overlying

water that were incubated at *in situ* benthic conditions with constant stirring of overlying water to prevent accumulation of dissolved P in a benthic boundary layer.

Benthic flux chambers were composed of three main parts (Figure 4): 1) the "flux chamber," a polycarbonate sediment coring tube containing undisturbed sediment and overlying water, 2) the "stirring head," a polycarbonate tube cap with Teflon-coated magnetic stir bar, and 3) a direct current motor with button magnet. The coring tube was made of polycarbonate with a bevel on one end for easier sediment penetration. The stirring head was positioned atop the flux chamber when in use and has a lower and upper well. The lower well was positioned snuggly over the outside of the chamber tube and contained a Teflon-coated, "floating" magnetic stir bar (5.4 cm length). The upper well housed the button magnet that was attached to a 25 RPM motor that rotated the stir bar inductively. A 0.5-cm diameter atmospheric vent in the stirring head minimized depletion of dissolved oxygen in water overlying sediment during incubation, which would be unnatural for most locations in the Lower Great Miami River (e.g., Figure 3). All equipment in contact with water and sediment in the chambers was made of either polycarbonate or Teflon, cleaned rigorously with acid, and rinsed with reagent-grade water (nominal resistivity > 18 MΩ-cm) prior to use.
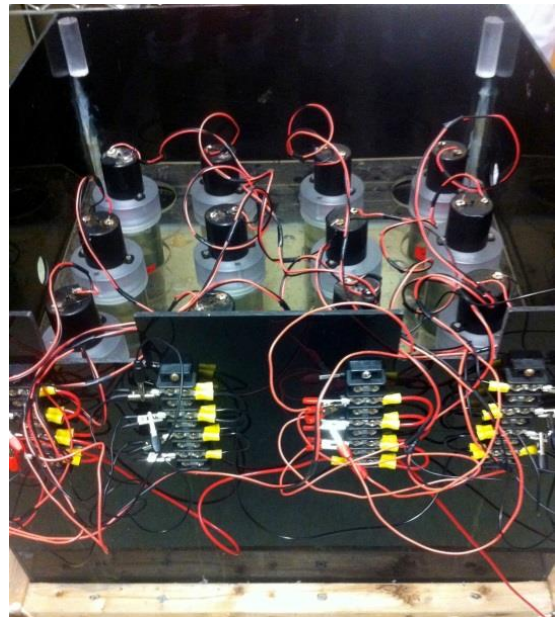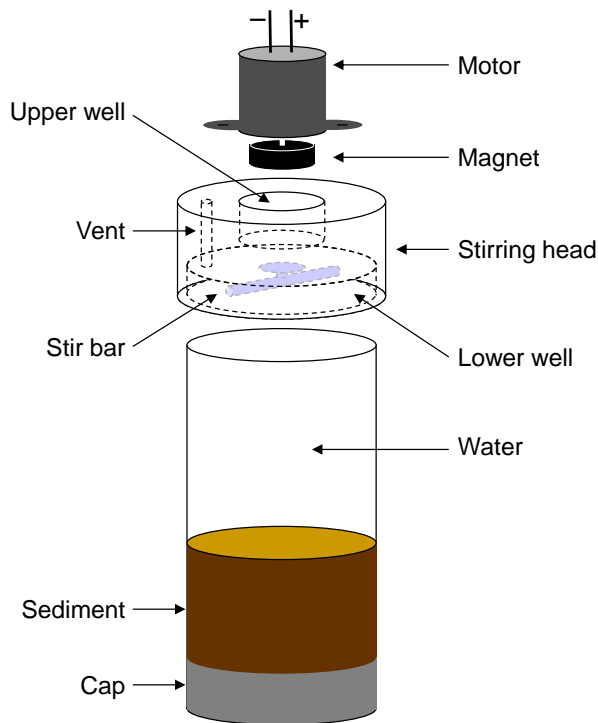

Figure 4. Components of benthic flux chambers used on examine sediment-water exchange of phosphorus in the Lower Great Miami River (Hammerschmidt and Fitzgerald, 2008), and a photograph of multiple chambers in operation inside a darkened, water-filled incubation chamber (covered with black, opaque polycarbonate sheet when in use).

Sediment-water fluxes of P were assessed for each flux chamber over a range of incubation periods under *in situ* conditions (dark, *in situ* temperature ± 3 °C; Table 2). Each chamber was used for four sequential incubation periods, the durations of which nominally were 12, 24, 48, and 96 h, based on our previous benthic P-flux study in Grand Lake Saint Marys (Taylor, 2012). Such incubation periods were sufficient to yield measureable changes of P concentration in overlying water. Water overlying the sediment was stirred continuously during the tests to prevent formation of a benthic boundary layer. A motor speed of 25 RPM was used because it is greatest speed that did not disturb fine sediment particles in a previous study (Hammerschmidt and Fitzgerald, 2008). At the end of each incubation period, water (~60 mL) was sampled from each chamber and an equal volume of river water, from the same site, was added gently back into the chamber so as not to disturb sediments. Water removed from the chamber was analyzed chemically to determine the flux of filtered P (< 0.2 µm), as well as pH and dissolved oxygen. The pH in chambers remained alkaline during incubations, although incubation pH was slightly less than measured ambient conditions, likely as a result of active photosynthesis during daytime field measurements (Table 3). Water in the chambers also remained oxic during incubations (Table 4).

Table 2. Ambient water temperatures in the Lower Great Miami River at time of sediment sampling and ranges of temperatures that sediment flux chambers were exposed to during incubations.

| | Temperature (°C) | | | | | |
| | August | | mid-Sept | | late-Sept | |
Site	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 and 4b	--	--	24.2	21.2–23.3	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

After the 96-h incubation period, all overlying water was removed from the chamber, and the upper 0–1 and 1–2 cm horizons of sediment were sectioned from the core and transferred to acid-cleaned 50-mL centrifuge tubes. When pore fluids were not lost due to draining from the core during sectioning, sediment was centrifuged to separate solids from pore water, which were then filtered with acid-cleaned syringes through 0.2-µm capsule filters. Filtered pore water was analyzed for total P. The remaining solids were measured for water content, total P, total extractable iron (Fe), and organic matter concentrations.

Table 3. Ambient pH of water in the Lower Great Miami River at time of sediment sampling and ranges of pH in water of sediment flux chambers during incubations.

| | pH | | | | | |
| | August | | mid-Sept | | late-Sept | |
Site	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 and 4b	--	--	8.45	8.03–8.13	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

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

| | Dissolved oxygen (mg L^{-1}) | | | | | |
| | August | | mid-Sept | | late-Sept | |
Site	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 and 4b	--	--	9.30	6.76–7.12	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	10.9	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

The flux (F, mg m^{-2} d^{-1}) of P from river sediment in each flux chamber was estimated from the slope of a least-squares linear regression analysis (i.e., dC/dt) of measured concentration in overlying water versus incubation times, such that (Hammerschmidt and Fitzgerald, 2008):

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

where C is the aqueous P concentration at time t (i.e., the slope of regression), V is the volume of overlying water in the chamber (determined from height of water in chamber × surface area), and A is the surface area of the core (0.0032 m^2). The uncertainty of the flux from each core was estimated as the product of V/A multiplied by the standard error of the slope of the linear regression. The flux of P from sediment was deemed statistically significant if the p-value of the

slope was < 0.05. To best estimate the benthic P flux for each site and account for intra-site variability, we calculated a mean flux (± 1 SD) determined from the three replicate flux chamber cores (labeled A, B, C), including if either one or more chambers had a statistically significant negative flux (i.e., sediment uptake) or statistically insignificant flux based on uncertainty of the linear regression slope. Figure 5 is an example of the linear regression analysis of filtered total P concentration versus time for three cores from the West Carrollton pool (Site 4) in late-Sept and illustrates the variability among cores from the same site.
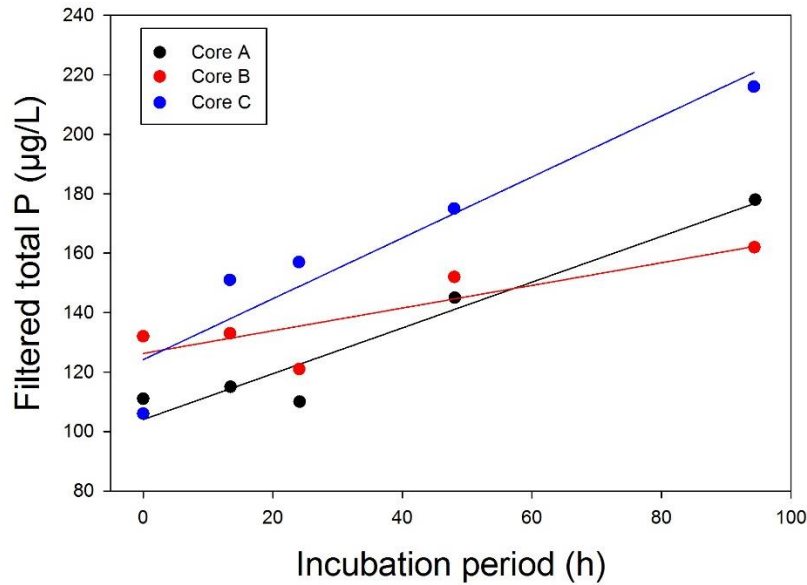

Figure 4. Linear regression analysis of filtered total P concentration versus incubation time for three sediment cores sampled from the West Carrollton pool in late-Sept, 2015.

Estimated diffusional fluxes. Benthic fluxes measured with the chambers were compared to estimated Fickian diffusion fluxes based on water concentration gradients of filtered P. Diffusion-only effluxes of P from sediment were estimated with the following equation:

$$F = \left(\frac{\varphi D_w}{\theta^2}\right) \times \frac{\partial C}{\partial x}$$

where C is the concentration of P at depth x, φ is sediment porosity, θ is tortuosity, and D_w is the diffusion coefficient of the solute in water (infinite dilution) in the absence of the sediment matrix (Hammerschmidt et al., 2004). Porosity was estimated from the measured water content and estimated densities of solid (1.9 g cm^{-3}) and pore water (1.0 g cm^{-3}) phases, and θ was estimated from φ (Boudreau, 1996). We assumed that P in filtered pore water existed primarily as uncharged sodium ion pairs, with a coreponding D_w of 7.9 × 10^{-6} cm^2 s^{-1} for a 1:1 mixture of NaH$_2$PO$_4$ and Na$_2$HPO$_4$ at 25 °C (Li and Gregory, 1974). Diffusional effluxes were estimated from the concentration gradient between pore water in surface sediments and river water at the same location (both 0.2 µm filtered). The mean concentration of P in filtered fluids between the 0–1 and 1–2 cm horizons (when both were available) was used for the pore water value,

applying the mean to 1.0 cm depth (i.e., *x*) for the flux calculation. The D_w of P at 25 °C was corrected to the ambient temperature of river water (Lerman, 1979) at each location and time to estimate benthic efflux.

Sample analysis. All physiochemical analyses were performed with accompanying assessments of accuracy. Water samples for analysis of P were acidified to 2% (pH < 2) with high-purity HNO_3. Unfiltered and filtered total P were quantified with a quadrupole inductively coupled plasma mass spectrometer (ICP-MS; U.S. EPA 6020a) after calibration with aqueous standards prepared from a NIST-traceable solution. Soluble-reactive P (measured as ortho-P) was determined spectrophotometrically with an automated, colorimetric Lachat Quikchem 8500 flow injection analysis system (Standard Method 4500-P F, APHA et al., 1995; Lachat Applications Group, 2008). Organic content of sediment was measured gravimetrically as loss-on-ignition (Heiri et al., 2001) and calibrated with ASTM Class 1 reference weights. Total P and total extractable Fe in freeze-dried sediment were quantified by ICP-MS after hot-block digestion with either H_2SO_4 and ammonium persulfate (for P; U.S. EPA, 2004) or concentrated HNO_3 (for Fe; Standard Method 3030E, APHA et al., 1995); analyses of P and Fe in sediment digestates were calibrated with matrix standards prepared from NIST-traceable solutions. Dissolved oxygen was measured with a YSI ProODO optode and pH determined with a YSI electrode.

Quality control included analysis of procedural and analytical blanks, replicates, certified reference materials, and calibration standards. Precision of P determinations in water averaged (± SD) 4.5 ± 3.6% (*n* = 36 sets of triplicates) relative standard deviation (RSD) for total P and 1.0 ± 1.5% RSD for SRP (*n* = 357 triplicates). Procedural imprecision (i.e., variability among separately extracted and analyzed replicates) of measurements of sediment averaged 10.5 ± 6.7% RSD for total P (*n* = 13 triplicates), 12.1 ± 9.1% RSD for organic content (*n* = 27 triplicates), and 10.1 ± 6.8% RSD for total extractable Fe (*n* = 6 triplicates). The imprecision of these measurements reflects uncertainty introduced by sample preparation and analysis, as well as natural heterogeneity of sediment. Recovery of total P from certified reference material MESS-4 (marine estuarine sediment, National Research Council Canada) averaged 0.98 ± 0.14 mg g^{-1} (*n* = 15), similar to the certified value of 1.04 ± 0.16 mg g^{-1}, indicating quantitative recovery and little bias. We also measured total extractable Fe in HNO_3-extracts of certified reference materials MESS-3 and MESS-4. Recovery of Fe from MESS-4 averaged 82 ± 5% (*n* = 3) of the certified mean, and recovery from MESS-3 averaged 73 ± 2% (*n* = 9) of the certified mean value. We did not expect to achieve full recovery of Fe from the reference materials because we did not use hydrofluoric acid to digest. However, quality of analysis of the environmentally active fraction of Fe in sediments is assured by the consistency of Fe recovery among multiple replicates and digestion batches.

Statistical analysis. All statistical analyses were conducted with SigmaPlot 12 software. Nonparametric tests of comparison were conducted when conditions or either normality or equal variance were not met.

Results

River water. Aqueous concentrations of P in the Lower Great Miami River varied among sampling locations (Table 5). The downstream distribution of P concentrations in river water varied substantially among sites and consistently increased markedly between Site 3 and either Sites 4 or 5 for all three fractions of P in water (Figure 6). Among all sites, concentrations of unfiltered, filtered, and SRP were significantly greater at Sites 4–8 than Sites 1–3 (Mann-Whitney, $p < 0.05$). These distributions indicate a significant source(s) of P to river water between the Tait Station low-head dam (upstream of Site 3) and the West Carrollton pool (Site 4). Likely sources include either benthic remobilization or point-source discharges to the river. Concentrations of unfiltered total P, filtered total P, and SRP decreased downstream of Site 5 in August and mid-September, but concentrations remained elevated downstream of Site 5 in late-September. Among all sites, the fraction of total P that was dissolved (i.e., < 0.2 µm) averaged 65 ± 20% of total P in unfiltered water. Similarly, about half of the filtered P concentration was in a soluble reactive form (60 ± 22%).

Table 5. Aqueous concentrations of total phosphorus (P) and soluble reactive phosphorus (SRP) in water of the Lower Great Miami River in 2015. Water for analysis of filtered total P and SRP was filtered through 0.2-µm membranes.

| Site	Period	Concentration in river water ($\mu g\ L^{-1}$)			Filtered/ unfiltered P(%)	SRP/filtered P (%)
		Unfiltered total P	Filtered total P	SRP		
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
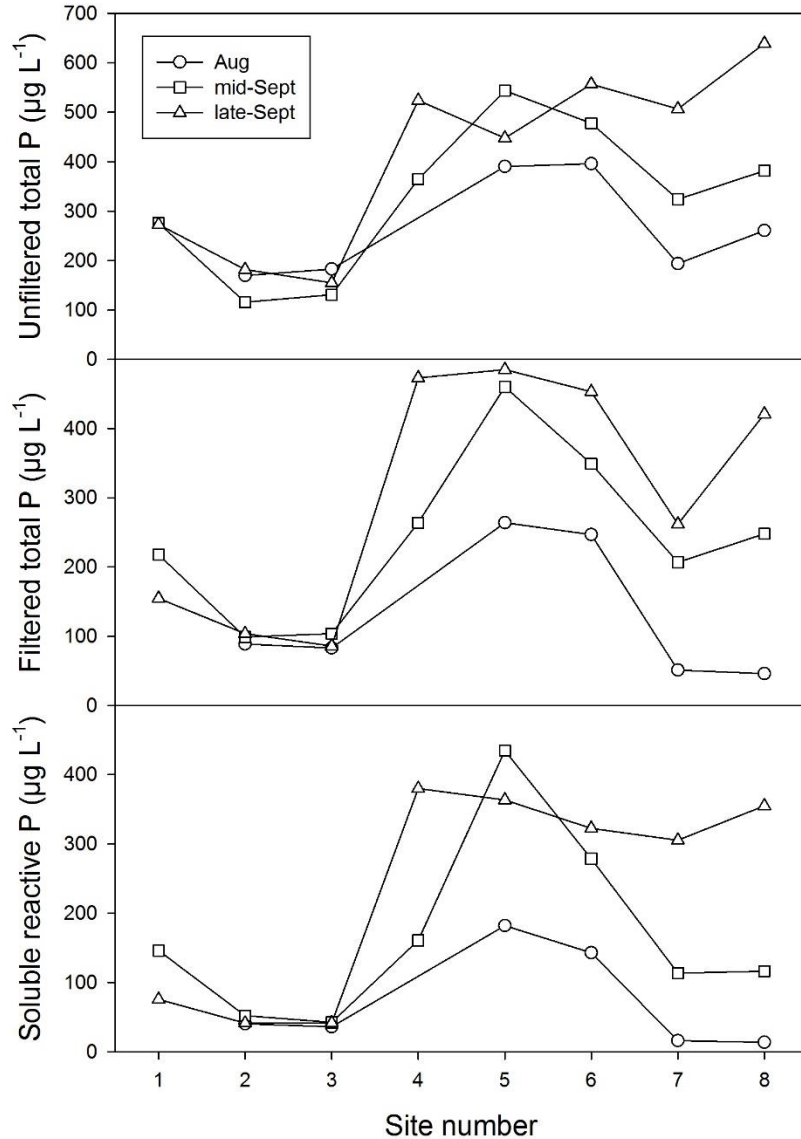
Figure 6. Downstream distribution of unfiltered total P, filtered P (<0.2 μm), and soluble reactive P in water of the Lower Great Miami River during the three sampling periods in 2015. Site 1 is the farthest upstream (Island Park; Dayton, OH) and Site 8 is downstream (Hamilton, OH).

Sediment. Total P concentrations in surface sediment (0−2 cm) ranged from 0.65 to 7.87 mg g^{-1} dry weight among individual samples ($n = 131$), with a mean (± SD) measured concentration of 1.98 ± 1.18 mg g^{-1}. Phosphorus, iron, organic, and water contents of surface sediment are summarized for each core in Table 6. Concentrations of total P in sediment were unrelated to either total extractable Fe ($p = 0.16$) or organic matter ($p = 0.95$) in the same samples. However, concentrations of total extractable Fe and organic matter were related ($p < 0.001$, $r = 0.78$; Figure 7). Concentrations total extractable Fe ranged from 3.5 to 21.7 mg g^{-1} dry weight (mean = 8.1 ± 2.9 mg g^{-1}) and organic matter ranged from 0.64 to 7.70% of dried sediment mass (mean = 2.02 ± 1.65%) among individual samples.

Table 6. Dry-weight concentrations of total phosphorus (P), total extractable iron (Fe), organic matter (OM), and water contents (percent mass basis) in surface sediment from 11 sites in the Lower Great Miami River. Values are the average of measurements of the 0–1 and 1–2 cm depth horizons. Water content values marked with an asterisk are biased low due to noticeable water draining from the core during sectioning.

Site	Core	August Total P (mg g⁻¹)	Fe (mg g⁻¹)	OM (%)	Water (%)	mid-Sept Total P (mg g⁻¹)	Fe (mg g⁻¹)	OM (%)	Water (%)	late-Sept Total P (mg g⁻¹)	Fe (mg g⁻¹)	OM (%)	Water (%)
1	A	--	--	--	--	1.56	6.9	1.53	6.7*	--	--	--	--
	B	--	--	--	--	2.08	6.4	0.82	7.1*	--	--	--	--
	C	--	--	--	--	1.56	6.7	0.67	6.1*	--	--	--	--
1b	A	--	--	--	--	--	--	--	--	1.35	14.6	3.67	38.7
	B	--	--	--	--	--	--	--	--	1.82	10.2	4.77	31.7
	C	--	--	--	--	--	--	--	--	1.17	18.8	7.12	43.5
2	A	1.23	7.0	1.20	17.5	1.35	8.4	0.94	13.6	1.51	10.3	1.02	7.6
	B	1.41	7.3	1.17	10.6	2.00	7.5	0.97	5.4*	1.43	9.0	1.10	8.5
	C	1.21	6.0	1.08	10.4	1.69	6.5	1.55	8.4	1.85	7.6	1.44	11.9
3	A	1.59	6.1	0.95	7.1*	1.62	8.9	1.04	10.3	1.59	7.4	0.96	10.2
	B	1.86	6.6	1.63	8.8*	1.64	6.5	0.93	9.0	1.54	7.2	0.95	9.5
	C	1.85	6.5	0.88	8.5*	1.87	7.4	1.69	25.6	1.52	7.8	0.75	7.5
4	A	--	--	--	--	2.45	6.9	1.22	13.2	1.00	9.2	3.36	33.0
	B	--	--	--	--	0.88	6.5	0.86	9.2	0.97	6.1	4.21	37.3
	C	--	--	--	--	--	--	--	--	1.29	9.0	4.61	42.3
4b	A	--	--	--	--	1.20	15.9	5.40	41.1	--	--	--	--
	B	--	--	--	--	0.93	15.2	4.57	41.9	--	--	--	--
5	A	3.41	7.9	1.96	17.8	4.32	10.2	3.32	33.2	4.17	8.0	2.56	32.1
	B	3.39	7.8	2.82	20.6	4.35	8.7	2.52	31.0	5.92	8.0	4.45	33.5
	C	1.99	6.2	1.18	20.6	4.19	9.2	2.64	32.5	4.92	7.8	2.51	34.4
6	A	1.41	6.4	0.84	14.5	1.86	3.5	0.85	8.2	1.50	6.2	0.99	8.4
	B	1.34	6.2	0.92	8.5	1.99	4.3	0.76	13.3	1.55	5.2	0.73	9.0
	C	1.66	7.3	0.79	6.3*	1.27	6.0	0.68	7.5	1.90	7.3	1.10	7.2*
7	A	1.49	7.4	1.67	10.1*	--	--	--	--	--	--	--	--
	B	1.84	7.3	1.03	11.3*	--	--	--	--	--	--	--	--
	C	1.67	6.2	1.09	12.1*	--	--	--	--	--	--	--	--
7b	A	--	--	--	--	0.95	11.0	4.05	35.1	1.15	15.5	6.49	39.4
	B	--	--	--	--	1.32	10.8	3.94	34.0	0.97	9.9	4.44	32.8
	C	--	--	--	--	1.29	12.2	4.44	34.7	0.87	7.8	3.14	29.1
8	A	3.37	5.6	0.80	16.5	2.33	9.0	1.33	17.5	0.91	6.6	1.09	19.3

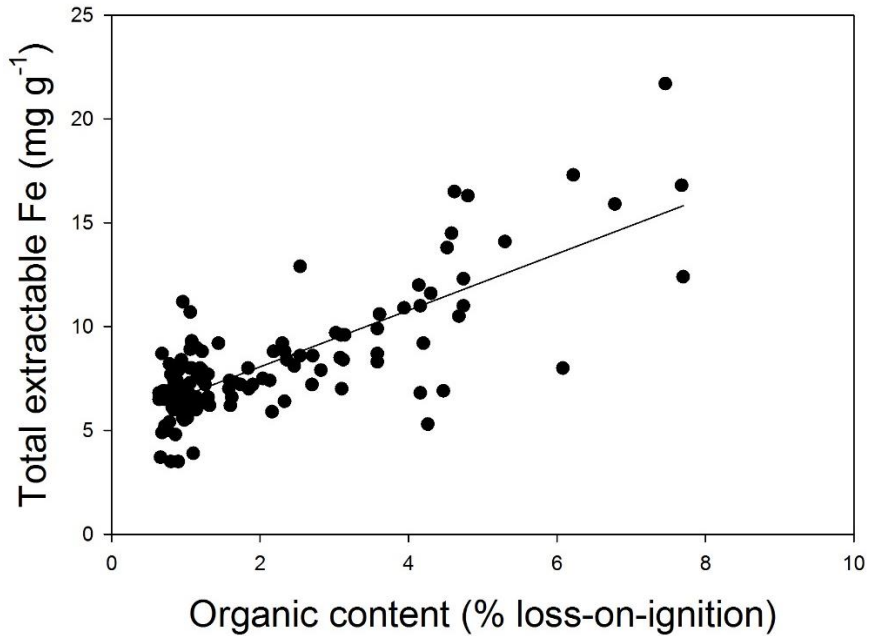|											
B	2.80	6.8	1.29	17.9	3.92	7.1	1.00	20.1	1.06	7.2	1.50	26.7
C	2.39	6.5	0.93	18.4	3.80	7.3	1.05	18.6	1.15	6.8	1.60	21.2

Figure 7. Relationship between the concentration of total extractable iron and organic content of surface sediment (0−2 cm) in the Lower Great Miami River.

Based on our measurements, we estimate that reservoir of P in surface sediment (upper 2 cm) of the Lower Great Miami River is about 903,000 ± 580,000 kg. This estimate is based on a mean measured total P concentration of 1.98 ± 1.18 mg g^{-1}, river area of 1.2 (±0.4) × 10^7 m^2 (i.e., 81 river miles × 95 ± 32 m wide), estimated sediment density of 1.9 g cm^{-3}, and the assumption that sediment covers the entire bottom of the river (i.e., no sediment free surfaces). However, the reservoir of P in sediment deeper than 2 cm may also be a potential source of P to river water.

Benthic flux. Benthic fluxes of filtered total P determined from the flux chambers differed substantially among sampling sites and periods, and, as expected, there was a considerable degree of intra-site variability (Figure 8, Table 7). Mean measured benthic fluxes of P ranged from -1.6 mg m^{-2} d^{-1} (i.e., uptake by sediment) at Site 5 to as much as 12 mg m^{-2} d^{-1} at Site 1b in the Island Park pool in late-Sept. Among all sites and sampling periods, the benthic P flux determined from core incubations averaged 2.9 ± 3.3 mg m^{-2} d^{-1}.
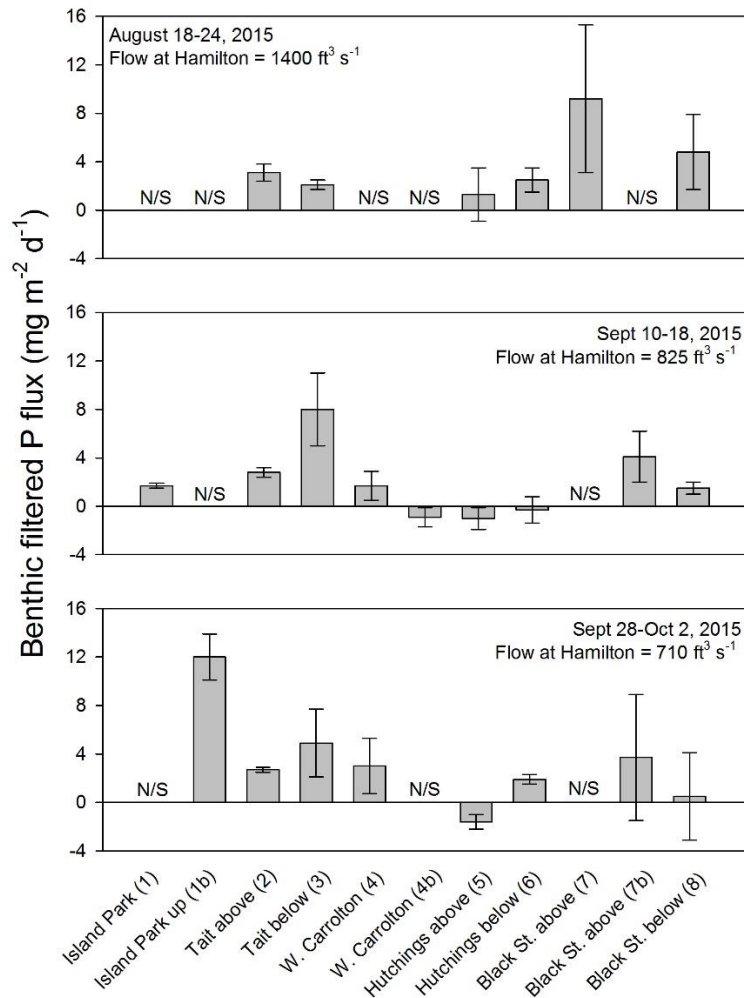

Figure 8. Comparison of sediment-water fluxes of filtered P, determined from chamber incubations, among 11 sampling sites in the Lower Great Miami River. Bars are the mean (±SD) flux among three replicate cores. N/S denotes that the site was not sampled during a particular sampling period. Site numbers are in parentheses.

Table 7. Fluxes of filtered total P from sediment, determined from core incubations, at locations in the Lower Great Miami River during three different sampling periods. Core-specific fluxes labeled with an asterisk are not statistically significant from zero (i.e., p-value of regression slope for flux calculation > 0.05). Only two cores each were sampled for Sites 4 and 4b in mid-Sept.

Site	Core	August flux (mg m^{-2} d^{-1}) Core specific (± SE)	Site mean (± SD)	mid-Sept flux (mg m^{-2} d^{-1}) Core specific (± SE)	Site mean (± SD)	late-Sept flux (mg m^{-2} d^{-1}) Core specific (± 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 ± 1.1*		−1.4 ± 1.4*		2.2 ± 0.7*	
7	A	15.3 ± 1.2	9.2 ± 6.1	--	--	--	--
	B	9.1 ± 0.9		--		--	
	C	3.1 ± 0.6		--		--	
7b	A	--	--	3.6 ± 1.4*	4.1 ± 2.1	9.5 ± 4.9*	3.7 ± 5.2
	B	--		2.2 ± 0.3		−0.4 ± 0.8	
	C	--		6.4 ± 0.7		2.0 ± 0.7	
8	A	3.2 ± 0.3	4.8 ± 3.1	1.5 ± 0.2	1.5 ± 0.5	−3.6 ± 0.6	0.5 ± 3.6

B	8.4 ± 1.4	2.0 ± 1.4*	2.5 ± 0.2
C	2.9 ± 0.1	0.9 ± 1.0*	2.5 ± 0.4

Benthic fluxes of P were related inversely with the concentration of filtered total P in overlying river water (Figure 9). This relationship suggests that elevated concentrations in river water inhibit mobilization of P from sediment, likely by minimizing a concentration gradient between pore fluid and overlying water. Accordingly, upstream sources that increase concentrations of P in river water could increase the potential for P to be stored in, as opposed to remobilized from, downstream sediment. Indeed, the flux of P from sediment was related inversely to the concentration of total P in sediment (Figure 10). This relationship is counterintuitive because one might expect the flux to increase with a greater reservoir in sediment. However, the relationships in Figures 9 and 10, when considered together, suggest that concentrations in the water column are the main driver of P exchange across the sediment-water interface. That is, and when concentrations of P in the water column are elevated, efflux from the sediments is inhibited and P concentrations in sediment may increase as a result of net uptake.
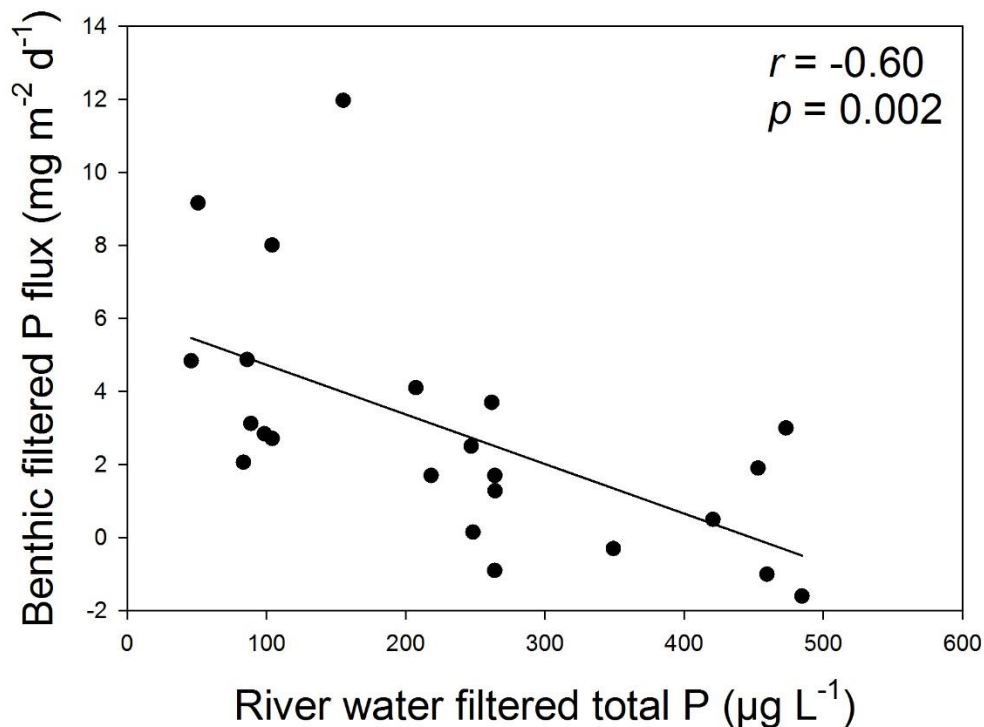

Figure 9. Relationship between benthic flux of filtered total P and concentration of filtered total P in overlying river water of the Lower Great Miami River in 2015.

This hypothesis is supported observationally by low, including negative (i.e., sediment uptake), benthic fluxes of P at Sites 4 and 5, despite relatively high sediment total P concentrations, and greater effluxes to the water column where P concentrations in river water and sediment are considerably less (e.g., Sites 2 and 3). Accordingly, the undetermined source(s) of P to the river between Sites 3 and 4 likely impacts the efflux of P from sediment at, for example, Sites 4 and 5 downstream, where there is a greater benthic reservoir and potential for mobilization. These relationships and observations suggest that a reduction of external loadings of P to the river, by

reducing water-column concentrations, may have the unintended consequence of exacerbating P efflux from sediment in the river.
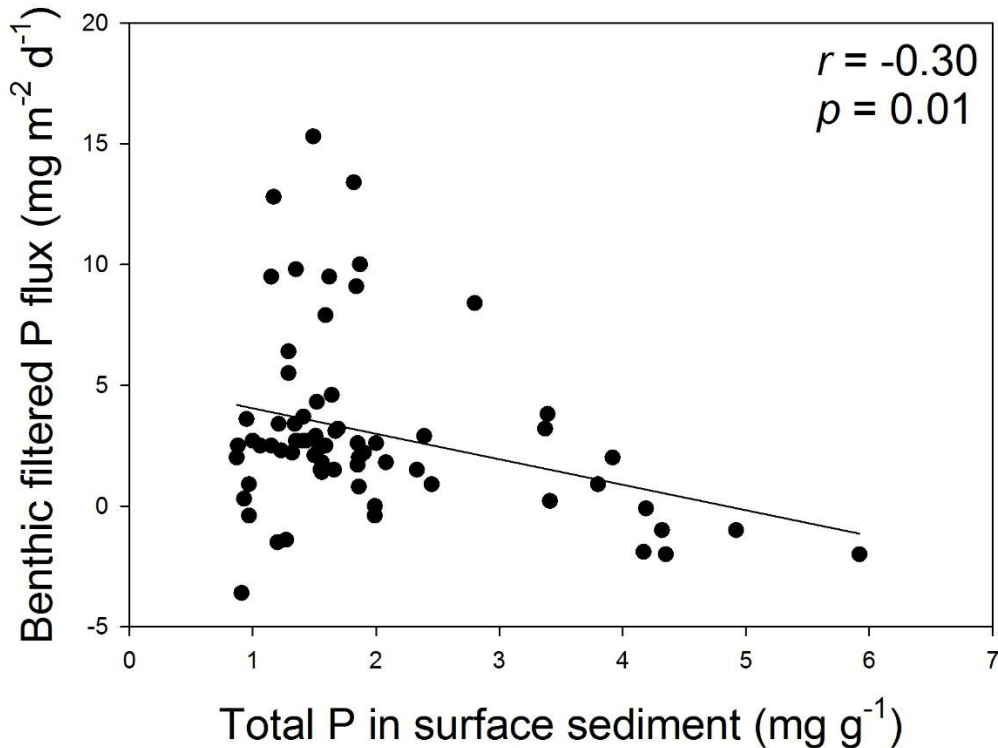

Figure 10. Flux of filtered total P from Lower Great Miami sediment is inversely related to the average concentration of total P in the 0–1 and 1–2 cm horizons of surface sediment.

Estimated diffusional fluxes of P. Estimated diffusional fluxes of filtered P were often much less than those measured with the flux chambers (Table 8). Diffusional fluxes ranged from – 0.03 to 0.56 mg m^{-2} d^{-1} (mean = 0.14 ± 0.16 mg m^{-2} d^{-1}). The measured efflux was greater than the estimated diffusional flux at most sites and times, suggesting that sediment deeper than 2 cm (not sampled in this study) contributes considerably to the P flux to river water at many sites. A greater measured than estimated P efflux may also be attributed to bioturbation, which is not accounted for in the diffusional flux model. It is also possible that the diffusion model does not adequately describe diffusion of soluble P at the sediment-water interface.

Scaling of the benthic flux. The average P flux determined from chamber incubations was 2.9 ± 3.3 mg m^{-2} d^{-1} among all sites during low-flow conditions in late summer and early fall of 2015. Scaled to a river area of about 1.2 (±0.4) × 10^7 m^2, the benthic flux equates to an estimated loading of about 35 ± 38 kg P d^{-1} to the Lower Great Miami River during low flow in 2015. This estimate is biased high because some areas of the river are not covered by fine sediment. Nonetheless, input of soluble P from sediment is a minor source to the river compared to other sources, including point sources that are estimated to contribute about 700 kg P d^{-1}.

Table 8. Estimated diffusional versus chamber measured fluxes of filtered P from sediment at locations in the Lower Great Miami River during three different sampling periods. Filtered P concentrations and associated fluxes were determined only for cores with sufficient pore water for analysis. Measured fluxes labeled with an asterisk are not statistically significant from zero (i.e., p-value of regression slope for flux calculation > 0.05).

Period	Site	Core	Flux (mg m^{-2} d^{-1}) Estimated diffusion	Flux (mg m^{-2} d^{-1}) Chamber measured
August	2	A	0.004	2.3 ± 0.5
	5	A	0.005	0.2 ± 0.2*
	5	B	0.001	3.8 ± 0.9
	5	C	0.002	0.0 ± 0.7*
	8	A	0.012	3.2 ± 0.3
	8	B	0.021	8.4 ± 1.4
	8	C	0.021	2.9 ± 0.1
mid-Sept	2	A	0.005	2.7 ± 0.3
	3	C	0.023	10.0 ± 0.8
	4b	A	0.255	−1.5 ± 0.2
	4b	B	0.240	−0.3 ± 0.6*
	5	A	0.275	−1.0 ± 1.5*
	5	B	0.161	−2.0 ± 0.6*
	5	C	0.105	−0.1 ± 0.4*
	7b	A	0.194	3.6 ± 1.4*
	7b	B	0.058	2.2 ± 0.3
	7b	C	0.145	6.4 ± 0.7
	8	A	0.036	1.5 ±0.2
	8	B	0.019	2.0 ± 1.4*
	8	C	−0.003	0.9 ± 1.0*
late-Aug	1b	A	0.414	9.8 ± 0.7
	1b	B	0.244	13.4 ± 2.0
	1b	C	0.533	12.8 ± 0.9
	4	A	0.041	2.7 ± 1.3*
	4	B	0.230	0.9 ± 0.5*
	4	C	0.449	5.5 ± 1.4
	5	A	0.109	−1.9 ± 1.1*
	5	B	0.147	−2.0 ± 1.2*
	5	C	0.140	−1.0 ± 0.5*
	7b	A	0.557	9.5 ± 4.9*
	7b	B	0.148	−0.4 ± 0.8
	7b	C	0.082	2.0 ± 0.7
	8	A	−0.026	−3.6 ± 0.6
	8	B	0.048	2.5 ± 0.2
	8	C	0.041	2.5 ± 0.4

References

APHA et al. (American Public Health Association, American Water Works Association, Water Environmental Federation), (1995). Standard Methods for the Examination of Water and Wastewater, 19th edition. Method 3030E. American Public Health Association, Washington, D.C.

Boström, B., Andersen, J.M., Fleischer, S., Jansson, M., (1988). Exchange of phosphorus across the sediment-water interface. Hydrobiologia 170, 229–244.

Boudreau, B.P., (1996). The diffusive tortuosity of fine-grained unlithified sediments. Geochemica et Cosmochimica Acta 60, 3139–3142.

Chowdhury, M., Al Bakri, A., (2006). Diffusive nutrient flux at the sediment-water interface in Suma Park Reservoir, Australia. Hydrological Sciences Journal 51, 144–156.

Goolsby, D.A., Battaglin, W.A., Lawrence, G.B., Artz, R.S., Aulenbach, B.T., Hooper, R.P., Keeney, D.R., and Stensland, G.J., (1999). Flux and sources of nutrients in the Mississippi-Atchafalaya River Watershed, Topic 3 report for the Integrated Assessment on Hypoxia in the Gulf of Mexico: Silver Spring Md., National Oceanic and Atmospheric Administration, Coastal Ocean Program Decision Analysis Series, no. 17, 130 p.

Hammerschmidt, C.R., Fitzgerald, W.F., (2008). Sediment-water exchange of methylmercury determined from shipboard benthic flux chambers. Marine Chemistry 109, 86–97.

Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H., Balcom, P.H., Visscher, P.T., (2004). Biogeochemistry of sediments in Long Island Sound. Marine Chemistry 90, 31–52.

Hammerschmidt, C.R., Bowman, K.L., Tabatchnick, M.D., Lamborg, C.H., (2011). Storage bottle material and cleaning for determination of total mercury in seawater. Limnology & Oceanography Methods 9, 426–431.

Hecky, R.E., Kilham, P., (1988) Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment. Limnology & Oceanography 33, 796–822.

Heiri, O., Lotter, A.F., Lemcke, G., (2001). Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of Paleolimnology 25, 101–110.

Jarvie, H.P., Jurgens, M.D., Williams., R.J., Neal, C., Davies, J.L., Barrett, C., and White, J., (2004). Role of riverbed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: the Hampshire Avon and Herefordshire Wye: Journal of Hydrology, v. 304, issues 1-4, 10 March 2005, pages 51-74.

Jones, W., Schiefer, M., and Sainey, E.B., (1996). Identification of the hydrologic system and nonpoint source impacts in the Mad River Watershed: Ohio Department of Natural

Resources, Division of Water, Water Resources Section, Non-point Source Pollution Report 2, 306 p.

Krom, M.D., Berner, R.A., (1980). The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments. Limnology and Oceanography 25, 327–337.

Lachat Applications Group, (2008). Determination of orthophosphate by flow injection analysis. QuikChem method 31-115-01-1-I. Lachat Instruments, Loveland, CO.

Lerman, A., (1979). Geochemical Processes: Water and Sediment Environments. Wiley, New York. 481 pp.

Li, Y.-H., Gregory, S., (1974). Diffusion of ions in sea water and deep-sea sediments. Geochimica et Cosmochimica Acta 38, 703–714.

Loftus, T., (2004). The Ohio Tributary Monitoring Program: 2004 Annual Report: Prepared for the Ohio Department of Natural Resources, Division of Soil and Water Conservation accessed March 29, 2012 at URL http://www.heidelberg.edu/sites/default/files/jfuller/images/OTMPreportJuly04.pdf

Nüurnberg, G.K, (1994). Phosphorus release from anoxic sediments: What we know and how we can deal with it. Limnetica 10, 1–4.

OEPA, (1997). Biological and water quality study of the Middle and Lower Great Miami River and selected tributaries, 1995—Volume I: Technical Report MAS/1996-12-8, 293 p.

OEPA, (1999). Association between nutrients, habitat, and the aquatic biota in Ohio rivers and streams: Technical Bulletin MAS/1999-1-1, 78 p.

OEPA, (2001). Biological and water quality study of the Stillwater River Watershed, Darke, Miami, and Montgomery counties: Technical Report MAS/2000-12-8, 334 p.

OEPA, (2011). Biological and water quality study of the Upper Great Miami River and selected tributaries 2008: Technical Report EAS/2011-1-1, 192 p.

OEPA, (2012). Biological and water quality study of the Lower Great Miami River Watershed Butler, Hamilton, Montgomery, Preble, and Warren Counties: Technical Report EAS/2012-5-7, 171 p.

Phillips, G., Jackson, R., Bennett, C., Chilvers, A., (1994). The importance of sediment phosphorus release in the restoration of very shallow lakes (The Norfolk Broads, England) and implications for biomanipulation. Hydrobiologia 275/276, 445–456.

Puckett, L.D., (1995). Identifying the major sources of nutrient water pollution: Environmental Science and Technology, v. 29, no. 9, 408A p.

Rabalais, N.N., Turner, R.E., and Wiseman, W.J. Jr., (2002). Gulf of Mexico hypoxia, A.K.A. "The Dead Zone": Annual Review of Ecology Systematics, v. 33, 235 p.

Reddy, K.R., Flaig, E., Scinto, L.J., Diaz, O., and DeBusk, T.A., (1996). Phosphorus assimilation in a stream system of the Lake Okeechobee Basin: Journal of the American Water Resources Association, v. 32, no. 5, October 1996, pages 901-915.

Reutter, D.C., (2003). Nitrogen and phosphorus in streams of the Great Miami River Watershed, Ohio, 1998-2000: U.S. Geological Survey Water Resources Investigations Report 02-4297, 67 p.

Richards, R.P., (1998). Estimation of pollutant loads in rivers and streams: A guidance document for NPS programs. Project report prepared under Grant X998397-01-0, U.S. Environmental Protection Agency, Region VIII, Denver. 108 p.

Rowe, G.L., Jr., Reutter, D.C., Runkle, D.L., Hambrook, J.A., Janosy, S.D., and Hwang, L.H., (2004). Water quality in the Great and Little Miami River Watersheds, Ohio and Indiana, 1999-2001: U.S. Geological Survey Circular 1229, 40 p.

Scavia, D., Dubravko, J., and Bierman, V.J., (2004). Reducing hypoxia in the Gulf of Mexico: advice from three models: Estuaries and Coasts, v. 27, n. 3, 419 p.

Schindler, D.W., (1977). Evolution of phosphorus limitation in lakes. Science 195, 260–262.

Smith, J.H., (2011). Miami River algae draws local attention: Dayton Daily News, Local Story, July 18, 2011.

Søndergaard, M., Jeppesen, E., Kristensen, P., Sortkjaer, O., (1990). Interactions between sediment and water in a shallow and hypertrophic lake: a study on phytoplankton collapses in Lake Søbygård, Denmark. Hydrobiologia 191, 139–148.

Søndergaard, M., Kristensen, P., Jeppesen, E., (1992). Phosphorus release from resuspended sediment in the shallow and wind-exposed Lake Arresø, Denmark. Hydrobiologia 228, 91–99.

Steinman, A.D., Nemeth, L., Nemeth, E., Rediske, R., (2006). Factors influencing internal P loading in a western Michigan drowned river-mouth lake. Journal of the North American Benthological Society 25, 304–312.

Taylor, A, (2012). Phosphorus mass balance for hypertrophic Grand Lake St. Marys, Ohio. M.S. Thesis, Wright State University, Dayton, OH.

The Miami Conservancy District, (2013). 2012 water resources report for the Great Miami River Watershed: Miami Conservancy District Report No. 2012-16, 73 p.

U.S. EPA, (2004). Standard operating procedure for total phosphorus in sediments by persulfate oxidation digestion (Lachat method), Method LG600. *In* Sampling and Analytical Procedures for GLNPO's Open Lake Water Quality Survey of the Great Lakes. U.S. EPA, Great Lakes National Program Office, Chicago, IL. http://www.epa.gov/glnpo/monitoring/sop/chapter_6/LG600.pdf

Yeh, H.S., Wills, G.B., (1970). Diffusion coefficient of sodium nitrate in aqueous solution at 25° C. as a function of concentration from 0.1 to 1.0M. Journal of Chemical and Engineering Data 15, 187–189.