

Inorganic and Organic Phosphorus in Sediments in the Walnut Creek Watershed of Central Iowa, USA

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Abstract The dynamics of phosphorus (P) reactions in stream water are important because of their potential to trigger eutrophication. This study aimed to explore the nature of P in sediments associated with Walnut Creek, Jasper County, Iowa. The Walnut Creek watershed supports row crop production, grazing, and riparian buffer zones. The alluvial cross section is composed of a sequence of sediments that contribute differentially to the amounts and forms of P entering the stream. Twenty-five sediment samples collected near Walnut Creek (classified as bank, in-stream, and floodplain deposits) were sequentially extracted for P. Across all 25 samples, the inorganic P (P_i) fractions followed the order Fe-bound P_i > Ca-bound P_i > reductant-soluble P_i > Al-bound P_i > soluble and loosely bound P_i . For the organic (P_o) fractions, the order was nonlabile P_o > fulvic acid-bound P_o > humic acid-bound P_o > labile P_o > moderately labile P_o . The ranges of total P (TP), Mehlich-3-extractable P ($P\text{-}M_3$), and ammonium oxalate-extractable P (P_{ox}) were 386 to 1134, 5 to 85, and 60 to 823 mg kg⁻¹, respectively. Among the sample

groups, the highest concentrations of TP, $P\text{-}M_3$, and P_{ox} were measured in in-stream deposits. Total P was significantly correlated with Fe oxides, clay, and soil organic matter, especially in the bank and floodplain deposits. Because of the potential release of P from these sediments, we can speculate that changes in land use within the riparian areas may, at least initially, have little direct effect on soluble or particulate P loads in Walnut Creek.

Keywords Stream sediments · Phosphorus loss · Eutrophication · Sequential extraction · Soil organic phosphorus

1 Introduction

Past studies have linked nutrients discharged through the Mississippi River in the Midwestern United States to extensive hypoxia in the Gulf of Mexico (Bianchi et al. 2010; Royer et al. 2006). Nitrogen is widely accepted as a major contributing nutrient to the hypoxia (Rabalais et al. 2002); however, Sylvan et al. (2006) suggested that phosphorus (P) is also important in promoting the hypoxic zone in the Gulf of Mexico. Phosphorus loads in the Mississippi River have been associated with intensive agricultural activities in tributary watersheds. Jacobson et al. (2011) found that the fraction of land in row crops and the use of fertilizer P were correlated with total and dissolved P loads, respectively, in the Mississippi River basin. A model developed by Alexander et al. (2008) estimated the contribution to P

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loads of pasture and rangeland where manure from grazing animals was present, row crop land where fertilizers had been applied, and other crop land was 37, 25, and 18%, respectively. The contribution of each of these agricultural sources was higher than that from urban sources (12%).

Besides direct runoff from agriculturally managed lands, another pathway for P to enter surface waters is through stream bed and bank erosion (Schilling et al. 2011; Wilson et al. 2008). In Iowa, streambank erosion is considered the main source of suspended sediments in stream water (Schilling and Wolter 2000). Certainly, transport of dissolved P occurs (Sinaj et al. 2002; Turner and Haygarth 2000), but the quantity (load) is commonly less than P transported with eroded sediments. The bioavailability of sediment-bound P varies with the physicochemical properties of the sediments, which reflect sediment origin and land-use history (McDowell et al. 2003). The processes that control sediment transport are influenced by stream velocity and the aggregate stability of the sediments. Quite often, these processes favor transport of finer particles that have higher P sorption capacity than coarser sediments (McDaniel et al. 2009).

Eroded sediments carry both inorganic P (Pi) and organic P (Po) forms. Inorganic P consists of water-soluble or loosely bound fractions, as well as fractions that are precipitated with or adsorbed to Al, Fe, and Ca components or occur as hydroxyapatite (Hedley et al. 1982; Tiessen and Moir 2008; Zhang and Kovar 2009). For Po fractions, the dominant compounds in soils are inositol phosphates. Phospholipids, nucleic acids, phosphoproteins, and sugar phosphates usually occur in smaller concentrations (Dalal 1977). McLaren et al. (2015) found that a substantial proportion of Po in soils is present in large molecular weight phosphomonoesters. Organic phosphorus in chemically and physically stable forms can represent more than 90% of the total Po (Hedley et al. 1982). These forms slowly degrade, contributing to the labile Po pool. The environmental behavior of sediment P depends on the form in which it appears in the sediment (Hund et al. 2013), and to predict the potential release of P from eroded sediments, reliance only on measurements of total P content is not likely to be accurate (Kisand 2005). Therefore, characterizing Pi and Po fractions can be of value in predicting the fate of P in eroded materials entering the stream.

The aim of the present study was to characterize Pi and Po fractions associated with eroded and erodible

sediments in the Walnut Creek watershed and to investigate the relationship of various P fractions with other sediment properties. We hypothesized that an analysis of stream sediments can provide insight into how P inputs and sediment P losses may impact water quality within the watershed. The characterization and differentiation of near-stream and in-stream sediments is essential for robust modeling efforts to predict the fate of P in this and other Midwestern streams.

2 Materials and Methods

2.1 Watershed Characteristics

Walnut Creek is in Jasper County, Iowa, and it drains an area of approximately 7951 ha (Fig. 1). The creek discharges into the Des Moines River, a tributary of the Mississippi River, at the upper end of the Red Rock Reservoir (Schilling et al. 2006). The watershed supports a variety of land uses, including row crop production, grazing, and riparian buffer zones within the Neal Smith National Wildlife Refuge, a large-scale prairie restoration area (3502 ha) in central Iowa. Alluvium in the watershed is composed of a characteristic sequence of sediments with potential to contribute differentially to the amounts and forms of P entering the stream.

2.2 Sediment Sampling and Characterization

Twenty-five sediment samples were collected from the channel and floodplain along an 8-km reach of Walnut Creek. The samples were grouped into three categories: bank sediments, in-stream deposits, and floodplain soils (Table 1). Samples from the streambanks came from the major stratigraphic units in Walnut Creek, namely the Camp Creek, Roberts Creek, and Gunder Members of the Holocene DeForest Formation, with dates of deposition from the last 380 years, 4000 to 400 years BP, and 11,000 to 4000 years BP, respectively. The fourth material sampled, Pre-Illinoian Till, is associated with glaciation that occurred between 2,000,000 and 500,000 years BP (Baker et al. 1996; Schilling et al. 2004). In-stream deposit samples consisted of materials found in a debris dam, a sand bar, in-stream slumps, a beaver dam, and stream bottom sediment (Table 1). Floodplain samples were collected from the surface horizon (0–20 cm depth) at sites in row-crop production (maize (*Zea mays* L.) and soybean (*Glycine max* L.

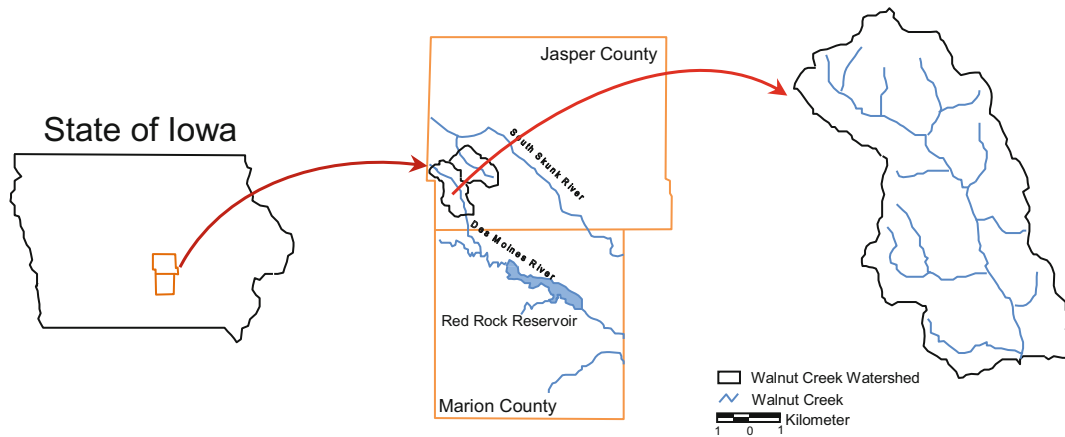


Fig. 1 Map indicating location of the Walnut Creek watershed in Jasper County Iowa adapted from Schilling et al. (2006)

Table 1 Selected chemical and physical properties of 25 sediment samples, where pH_w is pH in water, TP is total P, P_{M3} is Mehlich-3-extractable P. The sample codes indicate the order in which samples were collected, moving north to south along the reach of Walnut Creek

Group	Code	Description	OM %	C	N	Sand	Silt	Clay	pH_w	TP $mg\ kg^{-1}$	P_{M3}
Banks	B-2	Camp Creek (1)	4.52	1.54	0.16	6	73	21	5.7	499	39
	B-17	Camp Creek (2)	3.38	1.32	0.14	11	64	25	6.2	491	29
	B-21	Camp Creek (3)	4.38	1.66	0.13	19	59	22	6.0	573	35
	B-3	Roberts Creek (1)	7.53	3.12	0.25	2	62	36	6.0	847	55
	B-18	Roberts Creek (2)	4.51	1.84	0.14	13	60	27	6.3	588	41
	B-22	Roberts Creek (3)	4.23	1.54	0.14	6	69	25	5.7	522	29
	B-7	Till (1)	1.65	0.25	0.06	49	28	23	7.1	370	26
	B-20	Till (2)	1.71	1.06	0.03	49	30	21	8.1	473	5
	B-19	Gunder	1.51	0.31	0.06	6	72	22	7.4	484	28
In-stream deposits	I-4	Stream bottom sediment (1)	3.19	0.88	0.15	9	59	32	6.7	666	61
	I-11	Stream bottom sediment (2)	2.57	0.84	0.10	30	51	19	5.9	974	85
	I-24	Stream bottom sediment (3)	5.90	2.40	0.19	13	63	24	5.9	566	27
	I-5	Slump, debris dam	5.59	2.06	0.16	6	60	34	5.9	386	13
	I-6	Stream bed sediment, debris dam	3.64	1.00	0.10	22	53	25	7.2	966	58
	I-8	Sand bar	2.98	0.99	0.10	52	33	15	7.2	566	76
	I-12	Slump (1)	3.87	1.49	0.14	34	51	15	6.6	558	84
	I-23	Slump (2)	2.33	0.34	0.05	33	37	30	6.3	815	45
	I-13	Bar	4.25	1.47	0.12	6	63	31	6.5	1134	67
Floodplain	I-25	Stream bed sediment, beaver dam	4.52	1.71	0.16	27	56	17	7.1	673	71
	F-1	Pasture	5.19	2.23	0.24	1	81	18	5.6	567	34
	F-9	Forest (1)	5.09	1.95	0.20	18	63	19	5.7	556	56
	F-10	Forest (2)	6.41	2.52	0.24	4	70	26	6.1	730	55
	F-14	Corn field, with tillage	4.21	1.49	0.15	10	67	23	6.3	559	37
	F-15	Soybean field	4.38	1.59	0.16	17	61	22	6.5	505	30
F-16	Corn field, no tillage	4.69	1.91	0.18	22	57	21	6.2	617	72	

Merr.), pasture (the majority being beef cattle (*Bos taurus* L.) operations that rely on grassland for grazing, with little or no confinement of livestock), and riparian buffer zones (forest). After collection, samples were transported to the lab, air dried, and sieved to pass a 2-mm screen. Coarse mineral fragments and organic materials were removed.

Following initial processing, selected physical and chemical properties were determined. Total carbon and total nitrogen were analyzed using high-temperature dry combustion (Nelson and Sommers 1996), particle size distribution was determined gravimetrically (Kettler et al. 2001), and pH was determined at a soil to water ratio of 1:1. Organic matter content was determined with the loss-on-ignition (LOI) method (Konen et al. 2002). A perchloric acid digestion method (Kuo 1996) was used to extract the total phosphorus (TP), and the P concentration in the digest was determined colorimetrically with the molybdate blue-ascorbic acid method (Watanabe and Olsen 1965). The molybdate blue-ascorbic method was also used to determine P in Mehlich-3 (Mehlich 1984) extracts (P_{M3}), while Ca in extracts (Ca_{M3}) was determined with inductively coupled plasma-atomic emission spectrometry (ICP-AES). Citrate-bicarbonate-dithionite extractable Fe (Fe_{CBD}) was determined by atomic absorption spectroscopy (Shang and Zelazny 2008). Ammonium oxalate extractable Fe, Al, and Mn (Fe_{ox} , Al_{ox} , and Mn_{ox}) were determined using ICP-AES, while P in oxalate extracts (P_{ox}) was determined colorimetrically with a malachite green method (D'Angelo et al. 2001).

2.3 Phosphorus Fractionation

Inorganic P and Po were sequentially extracted following the methods outlined by Zhang and Kovar (2009) (Figs. 1 and 2, respectively, of Online Resource 1). For Pi fractionation, 0.5 g of air-dried sediment (< 2 mm) was sequentially extracted with 1 M NH_4Cl , 0.5 M NH_4F , 0.1 M NaOH, citrate-bicarbonate-dithionite (CBD), and 0.25 M H_2SO_4 . A different scheme was used for Po fractionation: 0.5 g of air-dried sediment (< 2 mm) was sequentially extracted with 0.5 M $NaHCO_3$, 1.0 M HCl, and 0.5 M NaOH, after which the samples were ignited at 550 °C and then extracted with 1.0 M H_2SO_4 . To determine Pt, a modification from the original method was applied, in which ammonium persulfate was used for the digestion in an autoclave instead of potassium persulfate on a hot plate.

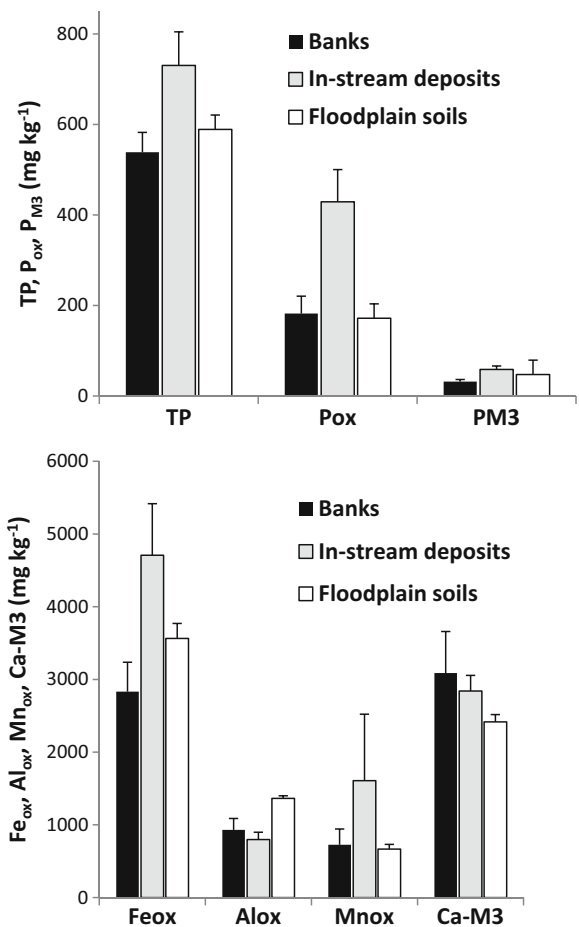


Fig. 2 Mean total P (TP), oxalate-extractable P (P_{ox}), Mehlich 3-extractable P (P_{M3}), Mehlich 3-extractable Ca (Ca_{M3}), oxalate-extractable Fe (Fe_{ox}), oxalate-extractable Al (Al_{ox}), and oxalate-extractable Mn (Mn_{ox}) concentrations in the sample groups of bank ($n = 9$) in-stream deposit ($n = 10$) and floodplain ($n = 6$) sediments. Error bars represent standard error

Phosphorus concentration in the extracts was determined colorimetrically with the molybdate blue-ascorbic acid method (Watanabe and Olsen 1965). Absorbance was read at a wavelength of 880 nm, using a spectrophotometer. Inorganic P and Pt were determined directly from the extracts, whereas Po fractions were determined by subtracting Pi from Pt.

2.4 Data Analyses and Comparisons

Statistical analyses were performed with SAS version 9.4 (SAS Institute 2012). These analyses included simple regression, paired t tests, and ANOVA, and they were used to evaluate differences in physicochemical properties among sediment types. The PROC REG

procedure in SAS was used to determine correlation of sediment properties with selected P fractions.

3 Results and Discussion

3.1 Sediment Characteristics

Sediment characteristics varied greatly across all 25 samples. Organic matter content ranged from 1.51 to 7.53% (Table 1). Over all, the physical composition of the in-stream deposits tended to be coarser than that of the bank sediments, which may reflect downstream transport of finer material with stream flow (McDowell and Sharpley 2001). The pH values ranged

from 5.5 to 8.1, indicating a wide range of sediment acidity.

Total P in the sediments ranged from 370 to 1134 mg kg⁻¹ (Table 1), which is comparable to the TP concentrations in stream bed sediments (389–964 mg P kg⁻¹) collected by Zaimet et al. (2008) in several watersheds in southeast Iowa. Mehlich-3-extractable P ranged from 5 to 85 mg kg⁻¹ (Table 1), and ammonium oxalate-extractable P concentrations ranged from 60 to 823 mg kg⁻¹ (Table 2). Among the three sample groups, the in-stream deposits had the highest average TP, P_{M3}, and P_{ox} values (Fig. 2), indicating their potential to contribute to P loss from the watershed when bed sediments are re-suspended during high-flow events. Although use of P_{M3} as an environmental threshold to predict the likelihood of P loss from

Table 2 Selected chemical properties of 25 sediment samples, where Fe_{ox}/Al_{ox}/Mn_{ox}/P_{ox} is ammonium oxalate-extractable Fe/Al/Mn/P, Fe_{CBD} is citrate bicarbonate dithionite-extractable Fe,

Ca_{M3} is Mehlich-3-extractable Ca. The sample codes indicate the order in which samples were collected, moving north to south along the reach of Walnut Creek

Group	Sample code	Description	Fe _{ox} mg kg ⁻¹	Al _{ox}	Mn _{ox}	P _{ox}	Fe _{CBD}	Ca _{M3}
Banks	B-2	Camp Creek (1)	2816	1321	595	127	8620	2646
	B-17	Camp Creek (2)	3348	1002	702	158	6825	1975
	B-21	Camp Creek (3)	3925	1116	801	188	8745	2243
	B-3	Roberts Creek (1)	4424	1742	2182	479	7274	5170
	B-18	Roberts Creek (2)	3947	1076	1263	193	5862	2983
	B-22	Roberts Creek (3)	2654	947	403	129	7272	1965
	B-7	Till (1)	1665	496	267	124	11,858	1927
	B-20	Till (2)	743	235	166	106	10,124	6750
	B-19	Gunder (1)	1967	445	154	137	3813	2135
In-stream deposits	I-4	Stream bottom sediment (1)	3068	837	9794	499	5095	3729
	I-11	Stream bottom sediment (2)	4009	455	532	648	7404	1976
	I-24	Stream bottom sediment (3)	6169	957	423	275	7562	2144
	I-5	Slump, debris dam	1951	1542	689	60	4294	4038
	I-6	Stream bed sediment, debris dam	9903	1058	1290	655	15,571	2905
	I-8	Sand bar	3948	602	919	351	6888	2278
	I-12	Slump (1)	3947	678	740	329	7338	2380
	I-23	Slump (2)	4340	649	872	297	15,948	2764
	I-13	Bar	6310	585	147	823	8426	3129
	I-25	Stream bed sediment, beaver dam	3431	609	672	353	7401	3065
Floodplain	F-1	Pasture	3914	1367	511	160	7341	2387
	F-9	Forest (1)	3348	1379	809	170	8171	2242
	F-10	Forest (2)	4228	1319	618	292	8615	2897
	F-14	Corn field, with tillage	3496	1451	740	129	8557	2417
	F-15	Soybean field	3644	1453	852	119	8876	2282
	F-16	Corn field, no tillage	2751	1216	471	161	9195	2271

soils or sediments has not yet been defined in Iowa, the environmental threshold for P_{M3} has been set at 150 mg kg^{-1} in Arkansas (Sharpley et al. 2003). According to this standard, floodplain soils and sediments in the Walnut Creek watershed have a low risk of P loss.

Simple correlations between total P and oxalate-extractable P and sediment properties are summarized in Table 3, and several details may be inferred. First, across all sediment types, TP was not significantly correlated with clay or organic matter (OM). This observation does not agree with other reports that total P concentrations are correlated with soil clay because clay contributes to Pi retention, or that total P in soils may be strongly influenced by Po in OM (e.g., Dalal 1977; Deng and Dixon 2002; Holford 1997; Kirkby et al. 2011; Quintero et al. 1999). However, when the analysis included only data from the bank and the floodplain deposits ($n = 15$), i.e., excluding the in-stream deposits (which had more heterogeneous soil characteristics), TP was significantly correlated with clay and OM (Table 3). Second, TP was not significantly correlated with total Fe

oxides (Fe_{CBD}), but it was positively correlated with poorly crystalline Fe oxides (Fe_{ox}), which have a high capacity for P binding (Kleinman and Sharpley 2002; van Rotterdam et al. 2012).

Iron oxides are not the only potential source of P binding capacity. For example, phosphorus adsorption by manganese oxides (MnO_2) is possible when MnO_2 occurs in sufficient concentrations (Yao and Millero 1996). While TP was statistically associated with the sum of oxalate-extractable Fe, Al, and Mn across all sediments, the much stronger correlation of TP with poorly crystalline oxides in only the bank and floodplain deposits (0.76 , $p = 0.0029$) reflects the importance of those minerals in retaining P in stream materials that are only occasionally subject to flooding or submergence. These relationships were largely mirrored in the correlations between oxalate-extractable P (P_{ox}) and oxalate-extractable metals (Table 3).

The higher correlation coefficients obtained by excluding data from the in-stream deposits indicated that processes of P adsorption and desorption, precipitation and dissolution of P-containing minerals, and mineralization and immobilization of organic P would be less predictable for the in-stream deposits compared to the other groups. Regular contact with flowing stream water may have had an impact on the P-retention characteristics of the in-stream deposits compared with the bank sediments and floodplain soil samples (McDaniel et al. 2009).

Table 3 Simple correlations between total P and oxalate-extractable P (P_{ox}) and sediment properties

Property		Pearson's r	p value	Significance	
Total P	Clay ^a	0.29	0.1669	NS	
	Clay ^b	0.66	0.0074	**	
	OM ^a	0.12	0.5530	NS	
	OM ^b	0.88	<0.0001	**	
	Fe_{CBD} ^a	0.33	0.1069	NS	
	Fe_{CBD} ^b	-0.23	0.4138	NS	
	Fe_{ox} ^a	0.70	0.0001	**	
	Fe_{ox} ^b	0.70	0.0036	**	
	$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$ ^a	0.64	0.0006	**	
	$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$ ^b	0.71	0.0029	**	
	$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}} + \text{Mn}_{\text{ox}}$ ^a	0.52	0.0083	**	
	$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}} + \text{Mn}_{\text{ox}}$ ^b	0.76	0.0029	**	
	P_{ox}	Fe_{ox} ^a	0.26	0.2114	NS
		Fe_{ox} ^b	0.52	0.0472	*
$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$ ^a		0.59	0.0019	**	
$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$ ^b		0.60	0.0214	*	
$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}} + \text{Mn}_{\text{ox}}$ ^a		0.60	0.0014	**	
$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}} + \text{Mn}_{\text{ox}}$ ^b		0.69	0.0048	**	

^a Includes all sediment sample data ($n = 25$)

^b Includes only data for sediments within the bank and floodplain sample groups ($n = 15$)

3.2 Phosphorus Fractionation

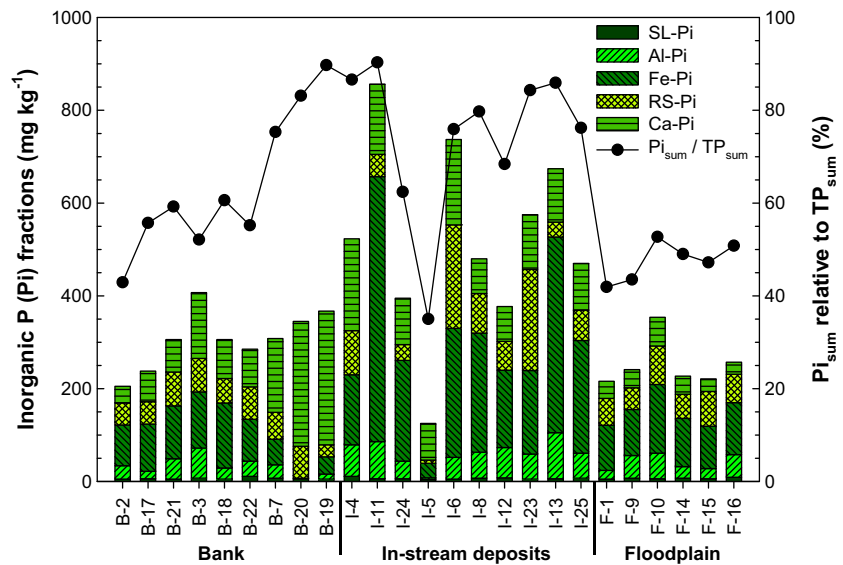
3.2.1 Comparison of Total P and Sum of all Fractions

Total P (TP) extracted with perchloric and nitric acid was highly correlated with the sum of all individual P fractions (TP_{sum}) (i.e., $\text{TP}_{\text{sum}} = 0.78 \text{ TP} + 86.4$, $R^2 = 0.83$; Fig. 3 of Online Resource 1). Thus, we conclude that the fractionation methodology used in this study reasonably recovered total P in the individual Pi and Po fractions.

3.2.2 Inorganic P Fractions

Following the method described by Zhang and Kovar (2009), inorganic P fractions were classified as soluble and loosely bound Pi (SL-Pi), Al-bound Pi (Al-Pi), Fe-bound Pi (Fe-Pi), reductant-soluble Pi (RS-Pi), and Ca-bound Pi (Ca-Pi). Results for each of the 25 samples are shown in Fig. 3. The total of all individual Pi fractions

Fig. 3 Distribution of inorganic P (Pi) fractions in 25 sediment samples collected from the Walnut Creek watershed. Bars represent Pi concentrations in five fractions, including soluble and loosely bound Pi (SL-Pi), Al-bound Pi (Al-Pi), Fe-bound Pi (Fe-Pi), reductant-soluble Pi (RS-Pi), and Ca-bound Pi (Ca-Pi). Line chart represents percentage of Pi_{sum} relative to TP_{sum}



(Pi_{sum}) ranged from 125 to 856 $mg\ kg^{-1}$ or 35 to 90% of TP_{sum} . As expected for these soils and sediments, SL-Pi ranged from 4 to 11 $mg\ kg^{-1}$ or only 0.7 to 3.5% of Pi_{sum} .

For each group of sediments, SL-Pi averaged 6 $mg\ kg^{-1}$ in the bank sediments and 7 $mg\ kg^{-1}$ in the floodplain soils and the in-stream deposits (Table 4). The small concentrations of SL-Pi in this study agreed with those reported by Wang et al. (2010) for the surface sediments of a river system in China. The amounts, however, were much less than the SL-Pi values reported by Kisand (2005) for sediment in Lake Verevi, a eutrophic temperate lake in South Estonia. Although the loosely bound P fraction was almost negligible compared with Pi_{sum} , SL-Pi is probably the solid-phase P which may be released to solution first when sediments are re-suspended during the high-flow events. Hence, its

impact on causing impairment of water quality may be more direct than that of other P fractions.

Among the other fractions, Al-Pi and Fe-Pi values ranged from 0 to 99 $mg\ kg^{-1}$ and from 1 to 571 $mg\ kg^{-1}$, respectively (Fig. 3). The Fe-Pi fraction has potential to elevate soluble P levels in the water column under anaerobic conditions when Fe^{3+} can be reduced to Fe^{2+} , and P-adsorbing Fe oxides are dissolved (Pettersson 1998). The lowest values of Al-Pi and Fe-Pi were found in the stream bank sample of Pre-Illinoian Till (sample B-20, Fig. 3). This sample had some characteristics that could promote P retention (e.g., large values for Fe_{CBD} and Mehlich 3-extractable Ca), yet there were also other characteristics that would be unlikely to lead to P accumulation (e.g., high sand content, low oxalate-extractable Fe, Al, and Mn) (Table 2). It is likely that the low concentrations of Fe-Pi in the till are

Table 4 Mean of inorganic P (Pi) fractions in the bank ($n = 9$), in-stream deposit ($n = 10$), and floodplain ($n = 6$) sample groups. Percent of total Pi for each fraction is shown. Numbers in parentheses are standard deviation

Pi fractions	Bank		In-stream deposit		Floodplain	
	$mg\ kg^{-1}$	%	$mg\ kg^{-1}$	%	$mg\ kg^{-1}$	%
SL-Pi	6 (1.9)	2	7 (2.0)	1	7 (1.4)	3
Al-Pi	28 (19.0)	9	57 (25.3)	11	37 (16.1)	14
Fe-Pi	83 (44.3)	27	252 (150.6)	48	109 (20.6)	43
RS-Pi	57 (15.6)	19	87 (75.0)	17	63 (13.8)	25
Ca-Pi	133 (91.0)	43	120 (44.3)	23	38 (13.0)	15
Pi_{sum}	307 (61.9)	100	523 (206.3)	100	254 (51.8)	100

because it was relatively unweathered and had not been exposed to biological activity that would promote P cycling (Hongthanat et al. 2011).

Reductant-soluble Pi ranged from 7 to 223 mg kg⁻¹ (Fig. 3). Both the lowest and the highest RS-Pi values were found in the in-stream deposit samples. Of the three sample groups, the in-stream deposits had the highest average Al-Pi, Fe-Pi, and RS-Pi. Calcium-bound Pi ranged from 26 to 288 mg kg⁻¹ (Fig. 3). Unlike other Pi fractions, the highest average Ca-Pi concentration was found in the bank sediments. Further, Ca-Pi concentrations in the bank sediments followed the order Camp Creek < Roberts Creek < till < Gunder, indicating that Ca-Pi concentrations were lowest in the youngest sediments.

Averaged over all 25 sediments in this study, the Pi fractions followed the order Fe-Pi > Ca-Pi > RS-Pi > Al-Pi > SL-Pi. This order was similar to the distribution of P fractions reported by Huanxin et al. (1997) for Washington tidal river sediments, which followed the order Fe-P > Ca-P > Al-P. The order for the in-stream deposits was similar to the composite average order (Table 4). However, the orders of Pi fractions in the floodplain soils and the bank deposits were different. The Pi fractions followed the order Fe-Pi > RS-Pi > Ca-Pi > Al-Pi > SL-Pi in the floodplain soils and Ca-Pi > Fe-Pi > RS-Pi > Al-Pi > SL-Pi in the bank samples, reflecting the diversity of P forms in watershed sediments that might contribute to P in the stream.

3.2.3 Organic P Fractions

Following the sequential extraction procedures outlined by Zhang and Kovar (2009), Po fractions in this study were classified as labile (Lab-Po), moderately labile (MLab-Po), associated with humic acid (HA-Po), associated with fulvic acid (FA-Po), and nonlabile (NLab-Po). Results are shown in Fig. 4. Labile Po ranged from 2 to 47 mg kg⁻¹ or 0.5 to 8.5% of the total of all individual Po fractions (Po_{sum}). Averaged over each sample group, Lab-Po concentrations were 20, 14, and 32 mg kg⁻¹ in the bank deposits, in-stream deposits, and floodplain soils, respectively (Table 5). Especially in the bank sediments, Lab-Po concentrations in Camp Creek and Roberts Creek samples were higher than those in the Gunder (sample B-14; Fig. 4) and till (samples B-7 and B-20; Fig. 4). As reported by Xu et al. (2013), the decrease of Lab-Po with increasing depth likely

indicates a transformation of the labile Po fraction into nonlabile Po pools over time.

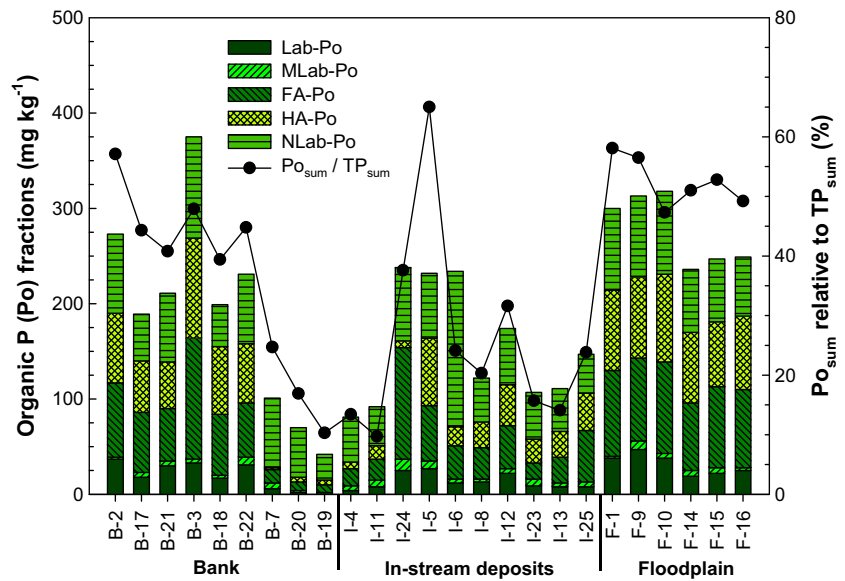
In general, Lab-Po was greater than MLab-Po, likely because of differences in the pH of the extracting solution for each fraction. As demonstrated by You et al. (2006), soil organic matter (SOM) fractions are more readily extractable from soil/sediment samples with a higher pH extracting solution. Labile Po was fractionated by extraction with 0.5 M NaHCO₃ at pH 8.5, while MLab-Po was extracted with 1 M HCl at pH 0. Fulvic acid-Po and HA-Po are two fractions that are extracted with alkaline extracting solution (0.5 M NaOH) and are thought to be associated with humic substances. Across all 25 sediments, the ranges of FA-Po and HA-Po were 8 to 127 and 2 to 105 mg kg⁻¹, respectively. On average, FA-Po was 29% of total Po (Po_{sum}), and HA-Po 24% of Po_{sum}. Paing et al. (1999) reported FA-Po and HA-Po values of 58 to 60 and 19 to 28%, respectively, for sediments in two French Mediterranean coastal lagoons, a very different ecological setting. Hong and Yamane (1980) reported that about 60% of FA-Po was inositol hexakisphosphate, and 40% was other forms of Po. Further fractionation of FA-Po or HA-Po, however, was beyond the scope of the present study.

The final Po fraction estimated with sequential extraction in this study was NLab-Po. These Po forms are thought to be associated with nonhumic substances. Nonlabile Po for the samples ranged from 27 to 163 mg kg⁻¹ (Fig. 4). Nonlabile Po comprised the greatest proportion of Po_{sum}, especially for the bank and the in-stream deposit samples (Fig. 4; Table 5).

Across all samples, the Po fractions followed the order NLab-Po > FA-Po > HA-Po > Lab-Po > MLab-Po. The overall order was similar in the bank and the in-stream deposits, but in the floodplain soils, Po fractions followed a different order: FA-Po > HA-Po > NLab-Po > Lab-Po > MLab-Po. Interestingly, whether in the bank sediments, the in-stream deposits, or the floodplain soils, the ratio of (NLab-Po + FA-Po + HA-Po) to (Lab-Po + MLab-Po) was ~9:1. This indicates that the ratio of labile organic P to Po_{sum} remained stable across the sample groups, although the reason is unclear.

The sum of all individual Po fractions (Po_{sum}) in this study ranged from ~10 to 65% of TP_{sum}. The Po_{sum} was strongly correlated with organic matter content determined by the LOI method (Fig. 4 of Online Resource 1). For samples in the floodplain, it was reasonable that about half of TP_{sum} would be organic P, since all samples in this group were collected from soil surface

Fig. 4 Distribution of organic P (P_o) fractions in 25 sediment samples collected from the Walnut Creek watershed. Bars represent P_o concentrations in five fractions, including labile (Lab-Po), moderately labile (MLab-Po), associated with humic acid (HA-Po), associated with fulvic acid (FA-Po), and nonlabile (NLab-Po). Line chart represents percentage of $P_{o_{sum}}$ relative to TP_{sum}



horizons where organic matter generally accumulates. Differences in the values of $P_{o_{sum}}$ among the major stratigraphic units in the stream banks of Walnut Creek were consistent with sediment age. The OM content and the fraction of $P_{o_{sum}}$ in the younger materials in the upper part of the stratigraphic column, i.e., Camp Creek (samples B-2, B-17, and B-21) and Roberts Creek (samples B-3, B-18, and B-22) sediments, were greater than those in older Gunder sediments (sample B-19) and Pre-IllinoianTill (samples B-7 and B-20) deposits (Fig. 4).

The values of $P_{o_{sum}}$ and total C in the 25 samples were highly correlated (Fig. 5a), and this agrees with previous research by Kirkby et al. (2011) for Australian and other soils. However, a stronger correlation was obtained when the data from the in-stream deposits were excluded from the analysis (Fig. 5b). The average

C: $P_{o_{sum}}$ ratio in the bank sediments and floodplain soils was similar (~68:1), while the ratio in the in-stream deposits was ~88:1. As noted earlier, characteristics of the in-stream deposits that are relevant to the fate and transport of P may have been affected by continuous contact with the flowing stream. We speculate that the relative physical stability of the bank sediments and floodplain deposits led to a more constant C:P ratio than in the in-stream deposits. This is based on assumption that organic matter in stream banks and floodplains could be related to consistent vegetation cycling, while organic matter in the in-stream deposits was affected by a continuous process of transport, sorting, and deposition by stream flow. While the extraction scheme did not differentiate P in microbial biomass, some variation in organic P could also be related to variations in microbial

Table 5 Mean of organic P (P_o) fractions in the bank ($n = 9$), in-stream deposit ($n = 10$), and floodplain ($n = 6$) sample groups. Percent of total Po for each fraction is shown. Numbers in parentheses are standard deviation

Po fractions	Bank		In-stream deposit		Floodplain	
	mg kg ⁻¹	%	mg kg ⁻¹	%	mg kg ⁻¹	%
Lab-Po	20 (13.9)	11	14 (8.1)	9	32 (11.1)	11
MLab-Po	4 (2.4)	2	6 (2.6)	4	5 (2.5)	2
FA-Po	53 (38.4)	28	43 (29.8)	28	85 (8.4)	31
HA-Po	47 (36.1)	25	28 (19.3)	18	80 (8.7)	29
NLab-Po	64 (23.7)	34	64 (36.9)	41	75 (11.8)	27
$P_{o_{sum}}$	188 (104.6)	100	155 (61.7)	100	277 (37.1)	100

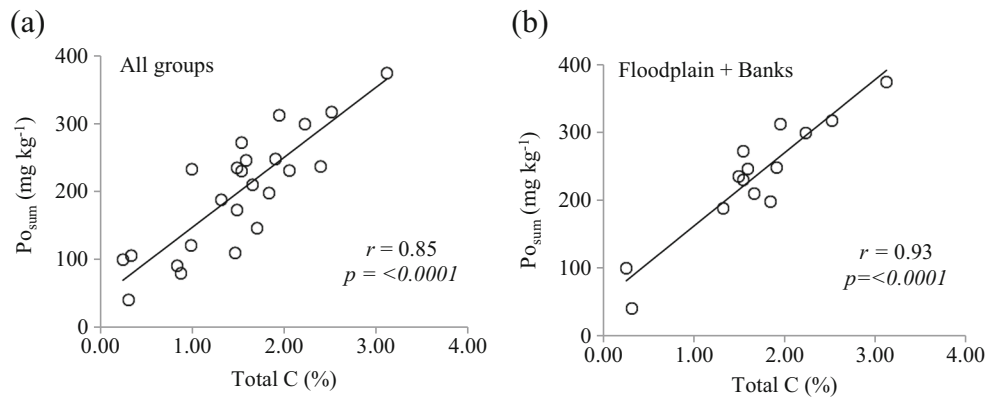


Fig. 5 Correlation between total C and $P_{o\text{sum}}$ when data from all three sample groups were pooled (a) and when data from the in-stream deposit group were excluded (b)

communities in the stream banks and floodplains versus the in-stream deposits. The C:P ratio of soil microbial biomass can vary greatly in freshwater ecosystems. According to Cross et al. (2005), the C:P ratio for fungi in a freshwater benthic system ranged from 5 to 370; for bacteria, it ranged from 300 to 1190. Further research is needed to explore the reasons that these ratios differ among the Walnut Creek watershed soils and sediments.

4 Summary and Conclusions

Sediment characteristics, as well as P forms associated with eroded sediments in the Walnut Creek watershed, varied greatly across all 25 sediments we studied. Among the sediment types, the highest concentrations of TP, P_{M3} , and P_{ox} were measured in the in-stream deposits, indicating that they are potentially major contributors to P leaving the watershed from bed sediment re-suspension during high-flow events. We found strong correlations between extractable P forms and other sediment properties when data from bank sediments and floodplain soils were pooled. Across all 25 sediments, the relative amounts of extractable inorganic P followed the order Fe-bound P_i > Ca-bound P_i > reductant-soluble P_i > Al-bound P_i > soluble and loosely bound P_i . For the organic P fractions, the relative order was nonlabile P_o > fulvic acid-bound P_o > humic acid-bound P_o > labile P_o > moderately labile P_o . Further research is needed to relate these P fractions directly to P loads in Walnut Creek.

Phosphorus mobility in streams is regulated by a number of interacting biotic and abiotic processes that make both prediction and control challenging (Hongthanat et al.

2016). In some cases, sediments alone are thought to exert significant control on water-column P, while in others, sediments in combination with microbes and macrophytes act to buffer stream P loads (Haggard et al. 2007; McDaniel et al. 2009). Sediment P content, readiness to release P to the stream (that is, to act as a source of P), and ability to retain soluble P (that is, act as a sink for P) may vary significantly. As pointed out by Jarvie et al. (2013) and Sharpley et al. (2013), the release of “legacy” P from stream sediments can buffer against rapid water quality improvement after nutrient management measures are introduced. Still, if P inputs from eroded bank sediments are reduced, whether by riparian management, stream bank stabilization, or some other practice, it is likely that P loads in Walnut Creek can be gradually reduced as well.

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