Phosphorus availability in sediments from a tidal river receiving runoff water from agricultural fields

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ABSTRACT

Eutrophication of surface water is a worldwide concern. Sediments may play an important role in buffering phosphorus (P) concentration in the overlying water column. However, information on the spatial variation of sediment P availability as affected by agricultural water discharge and hydrological conditions is limited. In this study river sediments were sampled in spring, summer, fall and winter, respectively from seven locations along a main tributary (Ten Mile Creek, TMC), which receives surface runoff water from agricultural lands and discharges into the Indian River Lagoon, south Florida, USA, and analyzed for P availability. Simultaneously, hydrological variables were measured on the spot and river water samples were collected for analyses of water quality. The results demonstrated that available P in the sediments of TMC as measured by several commonly used extraction procedures had a large spatial variation. The downstream locations had a greater amount of available P in the sediments than the upstream locations, which is attributable to the settlement of finer particles due to slower water flow and increased influence from salt water in the downstream locations where the fresh river water gradually mixed with salt water from the Indian River Lagoon. Phosphorus availability in the sediments appeared to be related to P sorption by iron and aluminum oxides and the competition for adsorbing sites between SO_4^{2-} and PO_4^{3-}. This spatial variation of P availability agrees with the elevation of chlorophyll a (Chla) in overlying water body in the downstream locations of TMC, indicating that the internal P source plays an important role in triggering an algal boom in surface water systems.

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1. Introduction

Eutrophication of surface waters has become a major environmental issue worldwide (Khan and Ansari, 2005; Smolders et al., 2006). In freshwater ecosystems, phosphorus (P) and/or nitrogen (N) availability is commonly considered as a major limiting factor for phytoplankton growth (Phlips et al., 1997; Howarth et al., 2002; Piehler et al., 2004). Discharge of waste water and nutrient laden water from agriculture often contributes to N and P enrichment in aquatic ecosystems (Biggs, 2000; Camargo et al., 2005). Suspended solid particles (SSP) enriched with P and N in agricultural surface runoff are eventually settled down onto sediment of receiving water or further transported to downstream in a river system, depending on water dynamic conditions.

Under the conditions of strong water dynamic or change of redox potential, the settled SSP can be re-suspended or dissolved, thus resulting in release of N and P into the overlying water column.

Therefore, even without external inputs of N and P, re-suspension of solid particles from sediments could serve as an internal source of N and P. This process is controlled by several factors such as redox potential, pH, salinity, and ionic environment of river water (Perry et al., 2002). At the depth of 0–15 cm of sediments, oxygen, FeO(OH), NO_3^-, and SO_4^{2-} can each serve as oxidant to elevate the availability of PO_4^{3-} in reductive sediments (Perry et al., 2002). NO_3^- was reported to actually prevent eutrophication of Dutch alder carr fens (Lucassen et al., 2004) because the reduction of NO_3^- caused oxidation of Fe^{2+}, thus increasing PO_4^{3-} fixation in sediments (Ripl, 1976; Uhlmann and Paul, 1994). Smolders et al. (2003) reported SO_4^{2-}-induced eutrophication due to an increase in PO_4^{3-} and NH_4^+ levels resulting from high SO_4^{2-} loads. Dissolution of P-containing minerals is strongly influenced by pH. A decrease in pH, favored by high SO_4^{2-} or NO_3^-, enhances the dissolution of phosphate minerals such as $Ca_5(PO_4)_3(OH, F, Cl)$ (Stumm and Morgan, 1981).

Carbonate sediments (such as $CaCO_3$, $Ca(HCO_3)_2$, and $(Ca, Mg)CO_3$) have a high holding capacity for phosphate, though the involved processes are strongly influence by pH, salinity, and redox potential, etc. (Kitano et al., 1978). Lamers et al. (2002) observed that bicarbonate alkalinity is correlated with

Table 1
A summary of P release mechanisms from sediments and their possible affecting processes.

Release mechanism	Factors	Relevant forms of P in sediments
Desorption (Boström et al., 1982)	1. pH decrease induced P release (Boström et al., 1988)	Ca, Mg–P
	2. Temperature elevation induced pH decrease (Lehtoranta, 2004)	Fe, Mn, Al–P
	3. Increase in SO_4 and Cl^- can increase competition for PO_4 of sorption on Fe-oxides (Stumm and Morgan, 1981)	
Dissolution (Boström et al., 1982)	1. Microbial activity:	Ca, Mg–P
	Inorganic or organic acid production (Ehrlich and Newman, 2008)	Fe, Mn, Al–P
	Chelators, such as gluconate and 2-ketogluconate (Banik and Dey, 1983)	
	H_2S induced reduction (Sperber, 1958)	
	Fe reduction (Jansson, 1987)	
	Solubility by a drop in the pH due to the uptake of ammonium by fungi (Cochrane, 1958)	
	2. Redox (reduction):	
	NO_3 enhanced increase of redox potential (Gatcher et al., 1988)	
	SO_4 reduction to form FeS or FeS_2 (Caraco et al., 1993)	
	CH_4 reduction (Boström et al., 1988)	
	Temperature induced decrease in pH (Lehtoranta, 2004)	
	3. Salinity and pH	
	Reducing P sorption on Fe-oxides by increased salinity and reduced pH (Stumm and Morgan, 1981; Kitano et al., 1978)	
Ligand exchange (Boström et al., 1982)	1. High pH produce ligand exchange (OH^- for PO_4^-) on iron-hydroxy complexes (Cooke et al., 1993)	Fe–PO_4
Enzymatic hydrolysis (Boström et al., 1982)	1. Microbial activity:	Organic-P
	Mineralization (Marsden, 1989)	Fe, Mn–P
	Temperature enhanced bacterial activity (Lehtoranta, 2004)	
	2. Decomposition:	
	Decomposition produces reduction environment, therefore, enhances release of Fe-bound P in the sediment (Nielsen and Andersen, 2003)	

the concentrations of PO_4^{3-} and NH_4^+ in porewater of the sediments.

High sediment uptake of NH_4^+ was observed at low salinity, but high NO_3^- release is often coupled with high salinity (Bianchi et al., 1999). The fluctuation of NH_4^+/NO_3^- ratio can be a reflection of the redox conditions of sediments, and thus a potential indicator of P concentration in the water column. Therefore, the salinity condition can indirectly affect nutrient levels in the overlying water of river sediments. Suggested mechanisms for P release from sediments are summarized and illustrated in Table 1.

In Florida, nutrient enrichment of the Indian River Lagoon (IRL), which relates to observed ecological degradation of the lagoon, has become a major surface water quality issue. Ten mile Creek, a main tributary discharging into the North Fork of the Indian River, delivers approximately 8.6×10^5 kg of N, 9.1×10^5 kg of P, and 3.6×10^8 kg of suspended solids (SS) to the IRL each year together with two other artificial canals (Graves and Strom, 1992). A visible effect of this N and P input is the rapid increases in certain phytoplankton species (so-called algal blooms) (Phlips et al., 2002). The Indian River watershed is a major citrus and vegetable production area in Florida. During heavy irrigation and frequent rainfalls, surface runoff water carries large quantities of soil particles enriched in N and P into creeks and canals. These particles will eventually settle down to become a part of river sediments or be transported to the IRL. However, few studies have examined the sediments of the TMC as a possible supplier of P and subsequent effects on eutrophication of the estuary. The objectives of this study were: (1) to investigate the spatial variation of P availability in river sediment of TMC, and (2) to understand the mechanisms of potential release of sediment P into the overlying water column.

2. Materials and methods

2.1. Site descriptions

Ten Mile Creek is the largest tributary draining water to the St. Lucie River Estuary, which ultimately discharges into the IRL. Upstream, it receives surface runoff from agricultural fields. Seven

sampling sites were selected for water quality monitoring along the TMC, of which Site SL4 is located where a smaller river, Five Mile Creek (FMC), discharges into the TMC. Sites SL1 and SL2 are in the upper reach, receiving head water of surface runoff from agricultural fields; Sites SL5B and SL6 are located downstream, which are affected by seasonal tidal fluctuation; whereas, Sites SL3 and SL5 are situated in the midstream of TMC (Fig. 1). The TMC watershed is dominated by a carbonate geological background with a hydrological water body of the K–Na–Ca type (Yang et al., 2008).

2.2. Field sampling procedures

River sediment samples were collected on April 11th, 2006, June 27th, 2006, October 25th, 2006, and January 9th, 2007, respectively, representing spring, summer, fall and winter in Florida. Surface sediments in the TMC were collected using a grabbing sampler, and each sample was composed of 5 random grabs. Sediment samples were then sealed in a plastic bag, stored in an ice chest, and transported to the laboratory. After air-drying in a dark room to lessen decomposition of organic substances, the sediment samples were ground to pass through a 2-mm sieve prior to chemical analyses.

2.3. Chemical analyses

For the determination of sediment pH and electrical conductivity (EC), portions of the sediment sample (each 10 g) were weighed into plastic centrifuge tubes, and the suspensions were shaken for 30 min after 10 ml (for pH) or 20 ml (for EC) of deionized (DI) water was added to each tube; the pH and EC readings were then taken using a pH/ion/conductivity meter (Model 220, Denver Instrument, Denver, CO, USA). The concentrations of total organic carbon (TOC) and total N (TN) in the sediment samples were determined by the combustion method (Schumacher, 2002) using a C/N analyzer (Vario Max CN, Elemental Analysensystem GmbH, Hanau, Germany). Available N in the sediments was extracted using 2 mol l^{-1} KCl solution at the solid:solution ratio of 1:10 (w/w) and the concentrations of NH_4-N and NO_3-N in the extracts were determined using a N/P discrete autoanalyzer (Easychem Plus, Systea Scien-
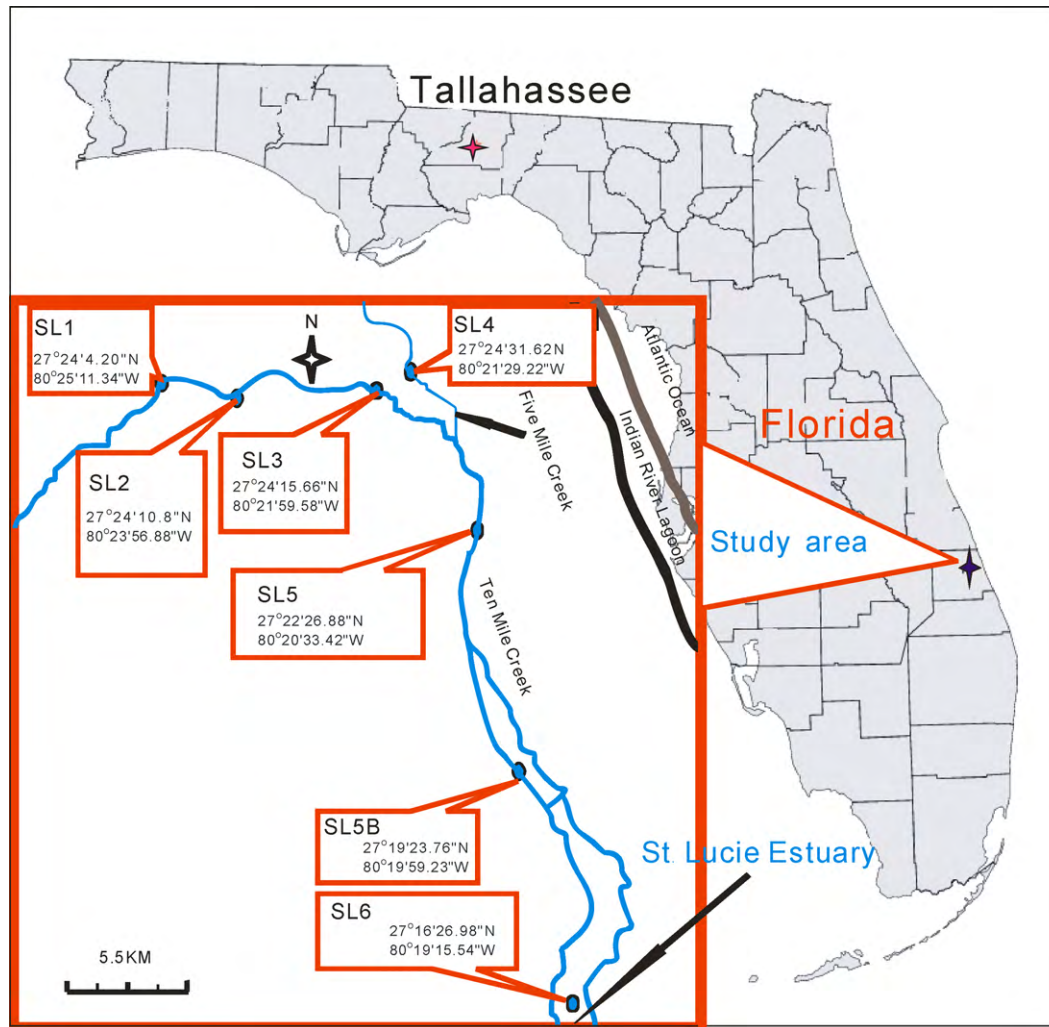
Fig. 1. A sketch map of water and sediment sampling locations in the Ten Mile Creek, South Florida, USA.

tific, LLC, Illinois, USA). Available P (Olsen-P) in the sediments was measured by extracting the samples with $0.5 \, mol \, l^{-1}$ NaHCO$_3$ solution at the solid:solution ratio of 1:20 (w/w) (Olsen and Sommers, 1982), and the concentrations of P in the extracts were determined by the molybdenum-blue method (Kuo, 1996). Labile P, Fe, Ca, and Al in the sediments were determined by extracting the samples with deionized water (Kuo, 1996), Mehlich 1 (M1) solution (Mehlich, 1953), and Mehlich 3 (M3) solution (Mehlich, 1984) at

the solid (w):solution (w) ratios of 1:10, 1:4, and 1:10, respectively. After shaking for 60, 5, and 5 min, respectively, their concentrations in the extracts were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Ultima, JY Horiba, Edison, NJ, USA) according to EPA method 200.7 (USEPA, 1998). Labile NO_3^--N, SO_4^{2-}-S, and PO_4^{3-}-P in the sediments were extracted with deionized water at the solid:water ratio of 1:10 (w/w). After shaking for 60 min, the concentrations of NO_3^-, SO_4^{2-}, and PO_4^{3-}

Table 2
Features of extractants adopted in this study.

Extractants	Composition	Salinity	pH	Shaking time	Source
Mehlich 1	$0.0125 \, mol \, l^{-1}$ H$_2$SO$_4$, $0.05 \, mol \, l^{-1}$ HCl	14.4	1.91	5 min	Mehlich (1953)
Mehlich 3	$0.2 \, mol \, l^{-1}$ CH$_3$COOH, $0.001 \, mol \, l^{-1}$ EDTA, $0.25 \, mol \, l^{-1}$ NH$_4$NO$_3$, $0.015 \, mol \, l^{-1}$ NH$_4$-F, $0.013 \, mol \, l^{-1}$ HNO$_3$	17.1	3.01	5 min	Mehlich (1984)
$0.5 \, mol \, l^{-1}$ NaHCO$_3$ (Olsen)	$0.5 \, mol \, l^{-1}$ NaHCO$_3$	17.2	8.50	30 min	Kuo (1996)
Deionized water (DIW)	H$_2$O	0.00	5.45	1 h	Kuo (1996)
Reconstructed riverwater (RW)	NaHCO$_3$ (96 mg l^{-1}), CaSO$_4$·2H$_2$O (60 mg l^{-1}), MgSO$_4$ (60 mg l^{-1}), and KCl (4 mg l^{-1})	0.10	7.38	1 h	Eaton et al. (1995)
Reconstructed seawater (SW)	NaF (3 mg l^{-1}), SrCl·6H$_2$O (20 mg l^{-1}), H$_3$BO$_3$ (30 mg l^{-1}), KBr (100 mg l^{-1}), KCl (700 mg l^{-1}), CaCl$_2$·2H$_2$O (1470 mg l^{-1}), Na$_2$SO$_4$ (4000 mg l^{-1}), MgCl$_2$·6H$_2$O (10,780 mg l^{-1}), NaCl (23,500 mg l^{-1}), Na$_2$SiO$_3$·9H$_2$O (20 mg l^{-1}), and NaHCO$_3$ (200 mg l^{-1})	30.9	8.50	1 h	Eaton et al. (1995)
Reconstructed brackish water (BW)	Mixture of seawater and riverwater in 1:1 (v/v)	15.0	8.01	1 h	Chang et al. (2007)

Table 3

Spatial and temporal variations of pH, electrical conductivity (EC, $\mu S\,cm^{-1}$), total organic C (TOC, $gC\,kg^{-1}$), total N (TN, $gN\,kg^{-1}$) and labile P measured by different extraction procedures ($mg\,kg^{-1}$) in the sediments of the Ten Mile Creek.

Sampling Site/season		pH	EC	TOC	TN	DIW-P	RW-P	BW-P	SW-P	Olsen-P	M3-P	M1-P
Upstream (SL1, SL2)	Mean	7.45a	785b	2.88b	0.183b	1.43b	1.32b	1.50b	1.80b	6.20bc	8.98b	34.9b
	Std. deviation	0.283	373	2.31	0.123	0.457	0.543	0.961	1.06	5.58	5.89	11.7
Midstream (SL3, SL5)	Mean	7.19a	727b	2.41b	0.226b	2.33a	2.60a	3.16a	2.92a	8.67b	21.4a	27.6b
	Std. deviation	0.298	316	1.47	0.114	0.924	1.34	0.722	1.27	4.71	15.9	13.0
Downstream (SL5B, SL6)	Mean	7.30a	4015a	13.8a	0.853a	2.91a	2.63a	3.15a	2.63a	13.3a	28.6a	121a
	Std. deviation	0.238	2632	8.57	0.566	1.42	1.55	1.28	1.51	6.47	13.8	81.8
Tributary (SL4)	Mean	6.05b	855b	2.40b	0.225b	1.55b	0.690b	0.913b	1.14b	3.84c	10.1b	11.1b
	Std. deviation	0.902	487	2.17	0.168	0.574	0.593	0.514	0.521	1.82	4.06	4.26
Spring	Mean	7.07y	1089x	7.93x	0.284x	2.32x	2.94x	2.20x	2.67x	7.25y	19.3x	49.3x
	Std. deviation	0.27	1147	10.2	0.269	1.48	1.97	1.70	1.75	6.35	18.4	42.2
Summer	Mean	6.93y	1824x	4.50x	0.314x	2.18x	2.30xy	2.26x	2.30xy	7.21y	15.4x	69.0x
	Std. deviation	0.75	1751	4.96	0.256	1.25	1.45	1.60	1.62	6.68	11.2	94.5
Fall	Mean	7.59x	2260x	4.68x	0.550x	2.16x	1.88y	2.29x	1.69y	8.25xy	16.9x	53.6x
	Std. deviation	0.29	3008	5.13	0.620	0.848	0.985	0.836	0.680	4.81	12.6	60.2
Winter	Mean	6.94y	1631x	6.08x	0.426x	1.85x	1.65y	2.76x	2.39xy	11.7x	21.6x	44.4x
	Std. deviation	0.68	1661	7.31	0.404	0.846	0.894	0.973	0.976	6.01	13.9	34.0

DIW, RW, BW, SW, M3, and M1 represent deionized water, river water, brackish water, seawater, Mehlich 3 solution, and Mehlich 1 solution, respectively. Different letters within a column (a, b, c or x, y) indicate significant differences at $P < 0.05$ by post hoc comparison of one-way ANOVA.

in the extracts were determined using Ion Chromatography (IC, DX 500; Dionex Corporation Sunnyvale, CA) according to EPA method 300.0 after filtering through a 0.45 μm membrane (Kuo, 1996).

To simulate P release as affected by salinity and pH, labile P, Fe, and Al in the sediments were extracted with brackish water and sea water (their salinity and pH values are presented in Table 2) at the solid:water ratio of 1:10 (w/w). After shaking for 60 min, the suspensions were filtered through a Whatman No. 42 filter paper (2.5 μm), and the concentrations of P, Fe, and Al in the extracts were determined using the ICP-OES according to EPA method 200.7 (USEPA, 1998).

Reconstructed river water (RW) consisted of $NaHCO_3$ (96 $mg\,l^{-1}$), $CaSO_4 \cdot 2H_2O$ (60 $mg\,l^{-1}$), $MgSO_4$ (60 $mg\,l^{-1}$), and KCl (4 $mg\,l^{-1}$), whereas reconstructed sea water (SW) contained NaF (3 $mg\,l^{-1}$), $SrCl \cdot 6H_2O$ (20 $mg\,l^{-1}$), H_3BO_3 (30 $mg\,l^{-1}$), KBr (100 $mg\,l^{-1}$), KCl (700 $mg\,l^{-1}$), $CaCl_2 \cdot 2H_2O$ (1470 $mg\,l^{-1}$), Na_2SO_4 (4000 $mg\,l^{-1}$), $MgCl_2 \cdot 6H_2O$ (10,780 $mg\,l^{-1}$), NaCl (23,500 $mg\,l^{-1}$), $Na_2SiO_3 \cdot 9H_2O$ (20 $mg\,l^{-1}$), and $NaHCO_3$ (200 $mg\,l^{-1}$) (Eaton et al., 1995). Reconstructed brackish water (BW) was prepared by mixing reconstructed river water and sea water at the ratio of 1:1 (v/v) (Chang et al., 2007).

Water samples were collected using grabbing devices. A large clean funnel (pre-rinsed with site water) was used to thoroughly mix water in the bucket and dispense water into the appropriate sampling bottles. Chlorophyll a samples were collected by filtering 300 ml of the water sample through a GF/F filter paper and wrapping the filter paper containing chlorophyll a in a piece of aluminum foil. All the samples were placed inside an ice chest immediately after collection and transported to the laboratory for physical, chemical, and biological analyses (Phlips et al., 2000). Reactive P in the water samples was determined by the molybdenum-blue method after filtering through a 0.45 μm membrane filter (Kuo, 1996); total P was determined with the same method after the unfiltered water samples were digested with acidified ammonium persulfate (EPA method 365.1). Total dissolved P was determined using the ICP-OES according to EPA method 200.7 after filtering through a 0.45 μm membrane. The concentrations of NO_3^--N, $PO_4^{3-}-P$, and $SO_4^{2-}-S$ in the water samples were determined using Ion Chromatography (IC) according to EPA method 300.0 after the samples were filtered through a 0.45 μm membrane.

2.4. Data processing

Laboratory analyses were conducted following the standard operation procedures of the National Environmental Laboratory Accreditation Conference (NELAC, 2003), with a recovery of 90–110%, and method detection limits of 0.010, 0.010, 0.029, 0.015, 0.003, 0.148, and 0.031 $mg\,l^{-1}$ for NO_3^--N, NH_4^+-N, $PO_4^{3-}-P$, $SO_4^{2-}-S$, Fe, Al, and P, respectively.

Analysis of variance together with a post hoc multiple comparison procedure (MCP) was conducted to compare the results among different locations and seasons; stepwise regression analyses were performed using SPSS 10.0 software (SPSS Inc., Richmond, CA). All figures were drawn using Sigma Plot 10.0 software (SPSS Inc., Richmond, CA, USA).

3. Results and discussion

3.1. Spatial variation of phosphorus availability

Available P in the sediments of TMC as measured by different extraction methods varied substantially, with Mehlich 1 extracting the most (M1-P), followed by Mehlich 3 (M3-P) and Olsen-P, and water of varying salinity providing the least estimate (Tables 2 and 3). All the water extracted similar amount of P regard-

less of salinity (Table 3), indicating that salinity has a minimal effect on P extraction from sediments.

However, spatial variations in P availability of TMC sediments were significant as indicated by all the estimations (Table 3). The sediments in the upstream locations, receiving head water of surface runoff from agricultural fields, generally had a low concentration of deionized water extractable P (DIW-P) (1.43 ± 0.457 mg kg^{-1}), Olsen-P (6.20 ± 5.58 mg kg^{-1}), M3-P (8.98 ± 5.89 mg kg^{-1}), and M1-P (34.9 ± 11.7 mg kg^{-1}) as compared with other locations (Table 3). The sediments in the downstream locations had higher concentrations of TOC (13.8 ± 8.57 g kg^{-1}) and TN (0.853 ± 0.566 g kg^{-1}) and were more influenced by tidal fluctuation (as indicated by high EC values) and subsequently contained a greater amount of DIW-P, Olsen-P, M3-P, and M1-P (2.91 ± 1.42, 13.3 ± 6.47, 28.6 ± 13.8, and 121 ± 81.8 mg kg^{-1}, respectively), as compared with those in the upstream, midstream, and tributary locations (Table 3). The spatial variation in P availability is likely related to the sources and properties of the sediments such as organic matter content and texture. When soil particles are flushed by surface runoff water from agricultural fields, large size particles normally precipitated in the upstream locations, whereas fine particles move to the downstream locations. The fine particles from agricultural fields generally contain more available P than the coarse particle fractions, thus resulting in higher extractable P in the sediments of downstream locations (Table 3).

In comparison, seasonal variations of extractable P in sediments were not so apparent. The observed discrimination merely occurred in Olsen-P, which was greater in winter (11.7 ± 6.01 mg kg^{-1}) (Table 3). This result suggests that seasonal variation of P availability in the TMC sediments is minimal, possibly because of the all year round warm weather in south Florida.

3.2. Association of phosphorus availability with Fe, Mn, Al, and Ca

Phosphorus in sediments can be bound to Ca (e.g., apatite), adsorbed by Fe, Al and Mn oxides, or tied in organic substances (Balzer, 1986); therefore, higher total P concentrations in the sediments may not represent greater availability. The ratio of Fe/P of 2 has been regarded as a threshold of P saturation in soil or sediments (Blomqvist et al., 2004). In the TMC sediments, Fe/P ratios measured by M1 and DIW extractions were generally below 2, with the lowest values occurring in the downstream locations (Fig. 2), indicating high P saturation in the sediments. However, the Fe/P ratios measured by the M3 extraction were higher than those by the M1 or water extraction. In addition, the difference in the Fe/P ratio was not significant among the different locations (Fig. 2). This result indicates that Fe/P ratio alone may not be reliable to indicate P availability in sediments.

Both Fe and Al can influence the availability of P in sediments (Smolders et al., 2001). The molar ratio of P/(Fe + Al), a useful P available index for sandy soils (Nair et al., 2004), may be a better indicator of the potential availability of P in river sediments. With the same extraction procedure, higher P/(Fe + Al) molar ratio means greater P release potential. The P/(Fe + Al) molar ratios in the TMC sediments varied with the extraction procedures, but were significantly higher in the downstream locations regardless of the estimation methods (Fig. 3). Of the three estimations, the P/(Fe + Al) ratios determined by water extraction appear to be better correlated with the available P in the sediments and therefore, may serve as a better indicator of P availability in the sediments. Based on this indicator, P availability in the TMC sediments significantly increased from the upstream to downstream locations (Fig. 3).

In the sediments, P can also be bound to Ca, such as $Ca_5(PO_4)_3(OH, F, Cl)$, which is highly insoluble and redox-insensitive, and can only be attacked by strong acids (Smolders et
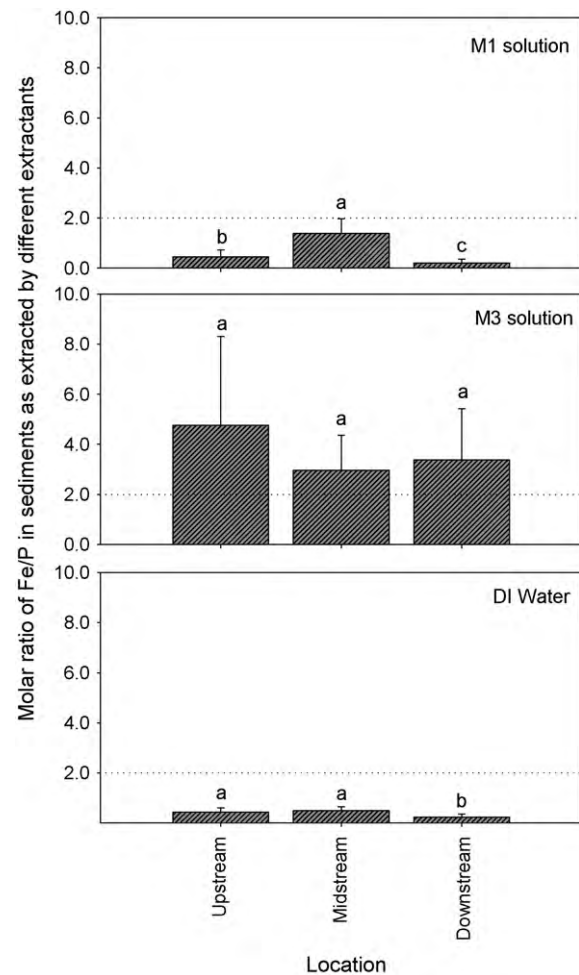

Fig. 2. Extractable Fe/P ratios in the sediments from varying locations in the Ten Mile Creek. DI Water, M3 solution, and M1 solution represent deionized water, Mehlich 3 solution, and Mehlich 1 solution, respectively.

al., 2006). Such P form hardly contributes to the available P pool in the sediments, particularly when Ca concentration is high as in the downstream locations which are affected by sea water. This may explain the highest Ca/P ratios (>100) in the water extract of TMC sediments at the downstream locations (Fig. 4).

Phosphorus in sediments is frequently associated with Al, Fe and Mn oxides and hydroxides (Pardo et al., 2003). In sediments, Al generally occurred as crystalline Al-silicate species (95%) (Jonsson, 1997), and only strong acidic extractant (M1 solution) can attack such Al minerals and result in release of Al-bound P (as evidenced by a close relationship between P and Al in M1 extracts, Table 5). Even though Al phosphate is NH$_4$-F extractable (Weir and Soper, 1962); sediment P was weakly correlated to Al in M3 extracts (Table 5) that contains 0.015 M NH$_4$-F (Table 2), indicating that Al phosphate was less available in the sediments of TMC. Phosphorus can be associated with Fe crystalline oxides and silicates in the sediments (Buffle et al., 1989), especially in spring season due to discharge of surface runoff (Jonsson, 1997). However, amorphous Fe can strongly bind P, and is closely related to C and N (Jonsson, 1997), as indicated by their significant correlations (Table 4). It is possible that dissolved humic substance–Fe-PO$_4$ complex enhanced the release of PO$_4^{3-}$-P (de Hann et al., 1990) from the sediments in the downstream locations. Also, in the sediments, Ca-bound P (Ca-PO$_4$, such as apatite) could be available under strong acidic condition (Lamers et al., 2002), which may explain the close correlations between Ca and P in the M3 and M1 extracts (Table 5).
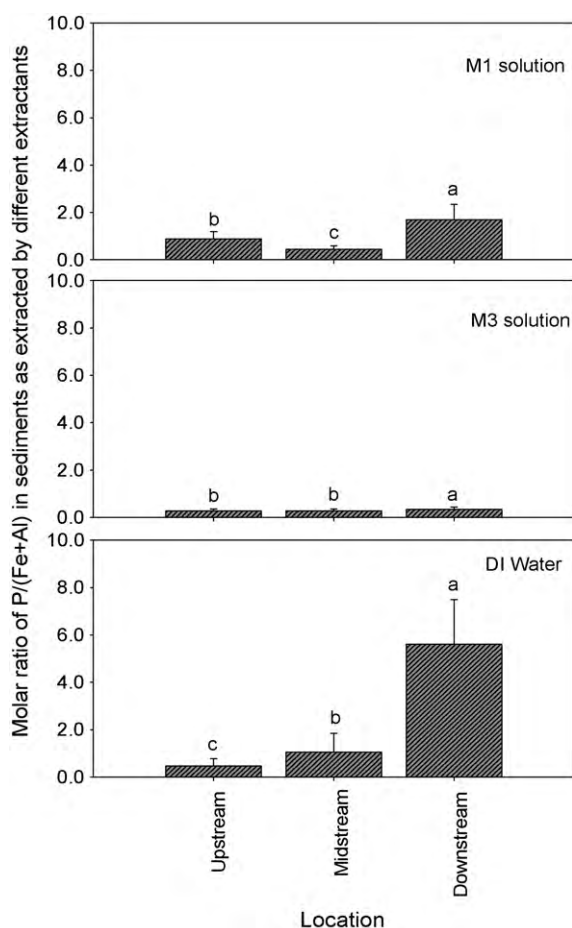
Fig. 3. Extractable P/(Fe + Al) ratios in the sediments from varying locations in the Ten Mile Creek. DI Water, M3 solution, and M1 solution represent deionized water, Mehlich 3 solution, and Mehlich 1 solution, respectively.

Furthermore, Mn was observed to be more closely related to P than Al, Ca, or Fe in the TMC sediments (Table 5). Similar to Fe, Al, or Ca, Mn tends to bind P through surface adsorption, but Mn also showed strongest affinity to organic matter in the soil (Zhang et al., 1997). In TMC, the downstream sediments had the highest content of organic substances (Table 3), and the higher extractable P in the sediments of downstream is likely associated with organic substances through the bridge of Mn (Table 4), which could explain the strong positive correlations between Mn and DI Water, M3, or M1 extractable P in the sediments (Table 5).

Table 4
Correlation coefficients (r) between sediment variables (pH; electrical conductivity, EC; total organic C, TOC; total N, TN; NO_3/SO_4 extracted by DIW, or NO_3/NH_4 extracted by 2 mol l^{-1} KCl solution) and labile P measured by several commonly used extraction methods in the sediments of the Ten Mile Creek ($N = 28$).

	DIW-P	Olsen-P	M3-P	M1-P
pH	0.112	0.134	0.069	0.256
EC	0.027	0.628[**]	0.645[**]	0.825[**]
TOC	0.628[**]	0.679[**]	0.705[**]	0.773[**]
TN	0.611[**]	0.599[**]	0.705[**]	0.717[**]
NO_3/SO_4	0.388[*]	−0.128	−0.206	−0.208
NO_3/NH_4	0.191	0.054	−0.037	−0.068

DIW, M3, and M1 represent deionized water, Mehlich 3 solution, and Mehlich 1 solution, respectively.

[*] Significant differences at $P < 0.05$.
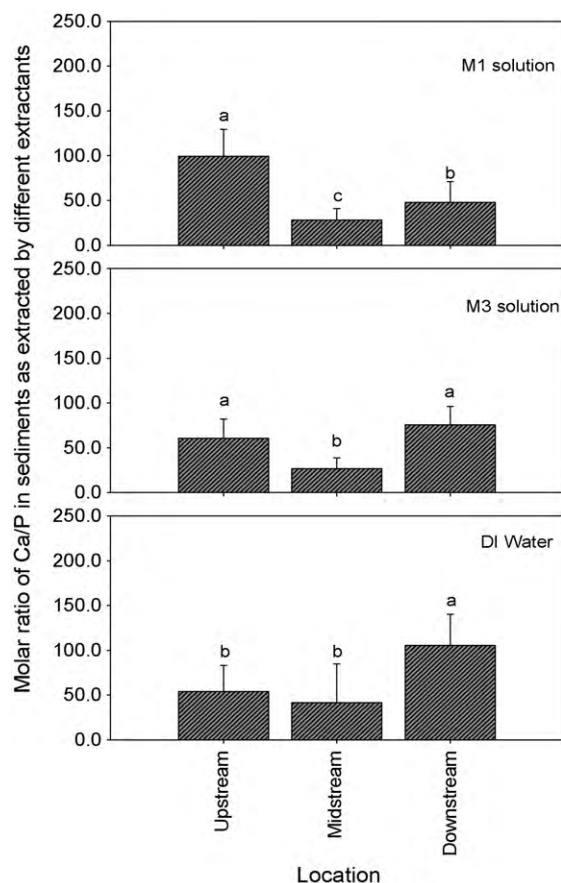[**] Significant differences at $P < 0.01$.

Fig. 4. Extractable Ca/P ratios in the sediments from varying locations in theTen Mile Creek. DI Water, M3 solution, and M1 solution represent deionized water, Mehlich 3 solution, and Mehlich 1 solution, respectively.

3.3. Effects of SO_4^{2-} and NO_3^- on P availability

The TMC water had higher concentrations of SO_4^{2-}-S (>100 mg L^{-1}) in the downstream than in the upstream locations (<50 mg L^{-1}), which coincided with the greater Olsen-P, M3-P, and M1-P concentrations in the sediments (Fig. 5). Furthermore, the concentrations of SO_4^{2-}-S in the river water had positive correlations ($P < 0.01$, $N = 28$) with Olsen-P, M3-P, and M1-P, of which the most significant correlation was observed between SO_4^{2-}-S and M1-P ($r^2 = 0.908$, $P < 0.01$, Fig. 5). Higher DIW extractable SO_4^{2-}-S concentrations in the sediments were also observed in the downstream locations (>500 mg kg^{-1}) than in the upstream locations (<350 mg kg^{-1}), which was accompanied by higher extractable P (DIW-P, Olsen-P, M3-P, and M1-P) in the downstream sediments (Fig. 5). Caraco et al. (1989) explained this phenomenon as an anion competition between SO_4^{2-} and PO_4^{3-} for adsorbing sites in the sediments that enhances the availability of P in the downstream

Table 5
Correlation coefficients (r) between labile P and Al, Ca, Fe, or Mn measured by different extraction procedures in the sediments of the Ten Mile Creek ($N = 28$).

	DIW-P	M3-P	M1-P
Al	−0.267	−0.140	0.609[**]
Ca	0.321	0.614[**]	0.597[**]
Fe	−0.039	0.656[**]	−0.201
Mn	0.648[**]	0.711[**]	0.769[**]

DIW, M3, and M1 represent deionized water, Mehlich 3 solution, and Mehlich 1 solution, respectively.
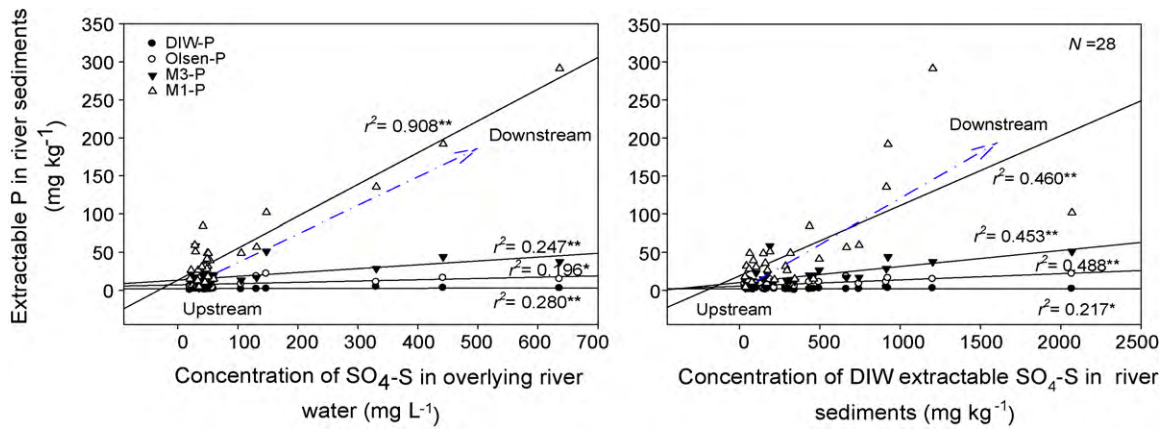
[**] Significant differences at $P < 0.01$.

Fig. 5. Correlations (r) among SO_4^{2-} concentrations in river water (left), DIW extractable SO_4^{2-} in the river sediments (right) and labile phosphorus in the sediments of the Ten Mile Creek measured by several commonly used extraction procedures. DIW-P, Olsen-P, M3-P, and M1-P represent deionized water, Olsen, Mehlich 3 solution, and Mehlich 1 solution extractable P, respectively; (*) and (**) indicate significant levels of $P < 0.05$ and 0.01, respectively.

locations. In river sediments, both NO_3^- and SO_4^{2-} can serve as electron acceptors (oxidant) at the gradient depths of 0.5–5 cm and 5–100 cm, and the competition between NO_3^- and SO_4^{2-} for electrons can elevate the availability of PO_4^{3-} and NH_4^+ in reduced sediments (Perry et al., 2002). The formation of FeS_2 in reduced environment can also induce the release of P from $FePO_4$ or $Fe(OH)_3$. However, NO_3^- (+200 mV of redox potential) is a stronger rival of accepting electrons than SO_4^{2-} (0 mV of redox potential). Increasing leaching of nitrate from agricultural lands can also result in increased SO_4^{2-} concentrations in surface water (Smolders et al., 2006), therefore, the potential of PO_4^{3-} releasing into surface water could increase. Although, the relationship between 2 mol l^{-1} KCl extractable NO_3^-/NH_4^+ ratio or DIW extractable NO_3^-/SO_4^{2-} ratio and extractable P (Olsen-P, DIW-P, M3-P, and M1-P) in the river sediments were generally poor, the significant correlation between DIW extractable NO_3^-/SO_4^{2-} ratio and DIW-P (Table 4) in the downstream sediment may suggest that such phenomenon could be more apparent in the downstream locations.

The downstream sediments had apparently higher salinity (as evidenced by higher EC values, 4015 μS cm^{-1}), which was accompanied by higher extractable P (DIW-P, Olsen-P, M3-P, and M1-P) (Table 3). This agreed with the observation of Blomqvist et al. (2004), and was probably related to the competitive adsorption between phosphate and sulfate (Geelhoed et al., 1997). River water at the downstream locations had much higher SO_4^{2-}, Na^+, and Cl^- concentrations than the other sampling sites. Sodium tends to disperse soil particles, thus elevating the contacting surface area for SO_4^{2-} to compete with PO_4^{3-} for adsorbing sites, and facilitate the mobilization of phosphate. Even though Cl^- concentrations were also high in the river water of the downstream locations, sulfate had a much higher competitive adsorption capacity than chloride (Katou et al., 1996; Rasiah et al., 2004). Therefore, sufficient supply of sulfate may lead to the mobilization of phosphate in the sediments (Van der Welle et al., 2007). Higher DI Water extractable

SO_4^{2-} could be one possible explanation for the higher extractable P in these sediments (Table 3, Fig. 5).

3.4. Sediment P affecting overlying water Chla

Release of P from sediments under altered conditions affects overlying water quality (Perry et al., 2002), and often causes an algal boom without notice. The concentration of reactive P (RP) in the overlying water column was found to correlate with P availability parameters in the sediments: negatively with M1 extractable Fe/P ratio ($P < 0.01$), and positively with M1 extractable P/(Fe + Al) ratio ($P < 0.05$) (Table 6). The concentration of dissolved total P (DTP) in the TMC river water was positively correlated with M1 extractable P/(Fe + Al) ratio ($P < 0.01$) and DIW extractable P/(Fe + Al) ratio ($P < 0.05$) in the sediments (Table 6). These results indicate that sediment P can serve as an internal source for the overlying water, and the higher concentrations of reactive P (RP) and total dissolved P (DTP) in the downstream river water of TMC are related to higher P availability in the sediments (Table 3, Fig. 5).

The concentration of Chla is commonly used to indicate water eutrophication (Biggs, 2000; Phlips et al., 2002). In the TMC river water, Chla was observed to correlate positively with DIW extractable P/(Fe + Al) ratios ($P < 0.05$) in the sediments but negatively with DIW extractable NO_3/SO_4 ratio ($P < 0.01$) (Table 6). A positive linear correlation between Chla concentrations in river water and DIW extractable SO_4^{2-} concentrations in sediments was also observed ($r = 0.545$, $N = 28$, $P < 0.01$). In the TMC, enriched concentrations of Chla in river water were observed at the downstream locations, with a median value of 12.1 μg l^{-1} during August, 2005–December, 2007 (Yang et al., 2008), much higher than 8.0 μg l^{-1}, a threshold value for meso-eutrophication for streams (Rast et al., 1989). Such enrichments coincided with the elevated available P and SO_4^{2-} in the downstream sediments (Fig. 5). This result suggested a possible SO_4^{2-}-mediated eutrophication at the

Table 6
Regression fitting models between Chla or P concentrations in the overlying water column and P availability variables in the sediments.

Dependent variable (Y)	Independent variable (X)	Regression equation	Correlation coefficients
Chla	DIW-P/(Fe + Al)	$Y = 0.0069X^2 - 0.1112X + 1.592$	$r = 0.416$, $P < 0.05$, $N = 28$
	DIW-NO_3/SO_4	$Y = -0.005 \ln X + 0.0195$	$r = -0.645$, $P < 0.01$, $N = 28$
RP	M1-Fe/P	$Y = -0.862 \ln X - 1.063$	$r = -0.487$, $P < 0.01$, $N = 28$
	M1-P/(Fe + Al)	$Y = 3.734X^{0.7671}$	$r = 0.527$, $P < 0.01$, $N = 28$
DTP	M1-P/(Fe + Al)	$Y = 33.54X^2 - 4.439X + 0.6433$	$r = 0.534$, $P < 0.01$, $N = 28$
	DIW-P/(Fe + Al)	$Y = 264.6X^2 - 51.24X + 3.186$	$r = 0.445$, $P < 0.05$, $N = 28$

Ratios refer to molar ratios. DIW and M1 represent deionized water and Mehlich 1 solution, respectively. RP and DTP denote reactive P and dissolved total P, respectively.

downstream water of TMC that was closely associated with sediment P availability.

4. Conclusions

The availability of sediment P in the TMC had a significant spatial variation, with a trend of increasing from upstream to downstream, which is likely related to more fine particles from agricultural runoff water being settled and increased influence of salt water in the downstream locations. This spatial difference in sediment P availability result in a corresponding response in total and reactive P in the overlying water column and subsequently affects the dynamic change of phytoplankton as indicated by the measurement of chlorophyll a concentration in the TMC water. The availability of P in the sediments can be measured by the molar ratio of $P/(Fe + Al)$ in the sediments.

Acknowledgments

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