River Sediment——as a Sink/Source of Phosphorus and Nitrogen for Overlying Water Body?

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INTRODUCTION

- **Eutrophication of surface waters is a major environmental issue worldwide (Khan and Ansar, 2005; Smolder et al., 2006). In freshwater ecosystems, phosphorus (P) and nitrogen (N) are commonly considered as main limiting nutrients for phytoplankton growth (Howarth et al., 2002; Phlips et al., 1997; Piehlera et al., 2004).**
- **Suspended solid particles (SSP) from surface runoff waters carrying nutrients can settle down onto sediment or being transported downstream, depending on water dynamic conditions. The settlement of SSP is commonly observed in upstream. However, under conditions of strong water dynamic or change of redox potential, settled SSP can be re-suspended, and result in release of nutrients (N and P) into overlying water body. Therefore, N and P in sediment could serve as an internal source . This process is controlled by many factors such as redox potential, pH, salinity, and physical stability of river water (Perry et al., 2002).**
- **In Florida, nutrient enrichment of the Indian River Lagoon (IRL) is a major surface water quality issue. Ten Miles Creek (TMC), a major tributary discharging nutrient-enriched drainage into North Fork of Indian River, delivers some $8.6x10^5$ kg of N, $9.1x10^5$ kg of P, and $3.6x10^8$ kg of suspended solids (SS) to the IRL estuary each year together with other two artificial canals (Graves and Strom, 1992).**
- **The Indian River watershed is a dominant citrus and vegetable production area in Florida. During heavy irrigation and frequent rainfalls, surface runoff water carries large quantities of soil particles containing N and P into creeks and canals, and the particles precipitate as part of river sediments or being carried into the Indian River Lagoon. To date, few studies have examined the sediments of the TMC as a possible source of N and P and the effects on eutrophication of the estuary.**

OBJECTIVES

The objectives of this study were: 1) To determine temporal and spatial variation and availability of N and P in the sediments of TMC, and 2) To examine the possibility of sediment N, P as an internal source of N, P for overlying water body.

MATERIALS AND METHODS

Sediments were seasonally collected from Ten Mile Creek. Sediment pH and EC were measured using a pH/ion/conductivity meter. TOC and TON were measured using a Vario MAX C/N analyzer. Available N was extracted by 2M KCl. Available P was determined by the 0.5 M $NaHCO_3$ (Kuo, 1996). Labile P, Fe, Ca, and Al were determined by extracting the samples with deionized water, Mehlich 1 (Mehlich, 1953), and Mehlich 3 solution (Mehlich, 1984), respectively. Water extractable NO_3, SO_4, and PO_4 were determined using an IC after the samples were filtered through a 0.45 µm membrane. Mimic river waters were also used to extract sediment samples from Sites SL1-SL4, and mimic sea water for sediment samples from Sites SL5-SL6 where tidal sea water can reach. The concentrations of P, Fe, and Al in the extracts were determined using ICP-AES. Reactive P in water samples was determined by the molybdenum-blue method; total P was determined with unfiltered samples after being digested with acidified ammonium persulfate.

Table 1. Spatial and seasonal variations of extractable P and N (mg kg^{-1}) in river sediments of Ten Miles Creek.

Location	W-P	STD	MW-P	STD	Olsen P	STD	M3-P	STD	M1-P	STD	TON	STD	NH_4-N	STD	NO_3-N	STD
SL1	1.60	0.15	1.47	0.16	8.84	0.64	12.54	1.69	37.02	5.75	222	150	5.55	1.80	1.34	0.79
SL2	1.25	0.10	1.18	0.13	3.89	0.67	5.42	0.59	32.82	4.97	146	52.74	3.51	1.00	1.43	0.73
SL3	2.58	0.15	2.67	0.16	5.31	0.57	10.38	0.51	17.89	3.15	143	60.74	4.13	1.72	1.51	1.06
SL4	1.55	0.18	0.69	0.10	5.96	3.21	10.08	0.38	11.13	0.70	227	149	7.17	5.44	1.27	0.67
SL5	2.09	0.28	2.53	0.20	10.53	2.41	32.48	2.60	37.32	3.35	314	71.58	7.09	4.14	1.92	1.13
SL5B	1.62	0.13	1.46	0.11	11.34	4.04	16.91	0.62	62.33	6.10	440	96.73	6.67	2.39	2.37	2.05
SL6	4.19	0.16	3.81	0.48	15.73	3.75	40.36	4.39	180	25.53	1263	482	10.53	5.08	2.36	1.72
Spring	2.32	1.55	2.73	1.86	7.25	4.40	19.35	19.31	49.33	42.91	284	269	3.94	2.05	1.32	0.38
Summer	2.18	1.31	2.10	1.53	7.80	6.13	15.43	11.72	69.01	98.87	314	256	5.05	1.24	2.11	0.83
Fall	2.16	0.87	1.64	0.81	8.34	4.90	16.88	13.17	53.63	62.63	550	620	10.67	5.16	0.359	0.11
Winter	1.85	0.88	1.42	0.73	11.81	5.73	21.59	14.43	44.37	35.53	426	404	5.86	2.52	3.18	1.26

W-P: deionized water extractable P; MW-P: mimic river water or mimic sea water extractable P; M3-P: Mehlich 3 extractable P; M1-P: Mehlich 1 extractable P; STD: standard deviation; TON: total organic nitrogen.

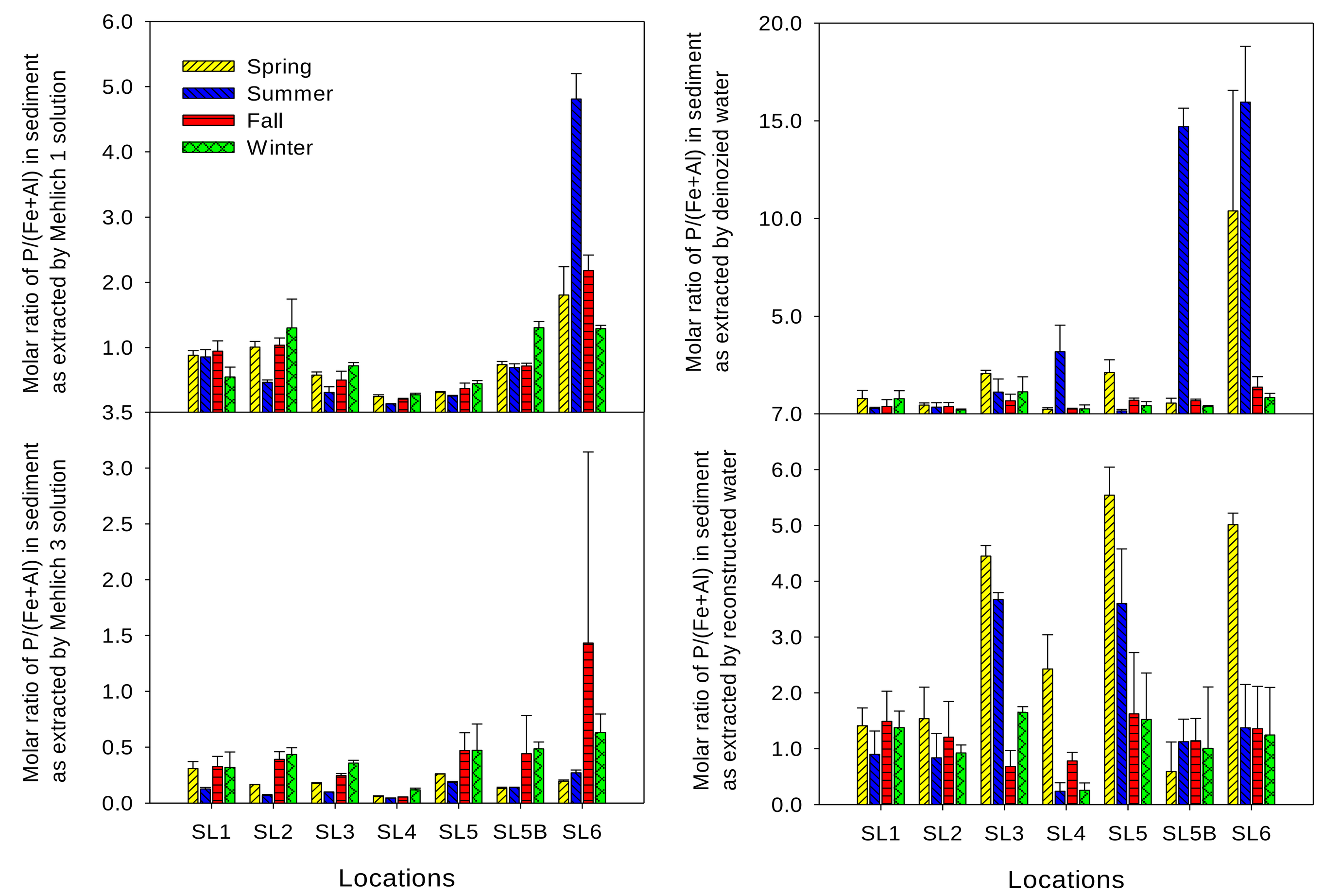

Fig. 1. Ratios of P/(Fe+Al) as measured by different extractants in river sediments of Ten Miles Creek

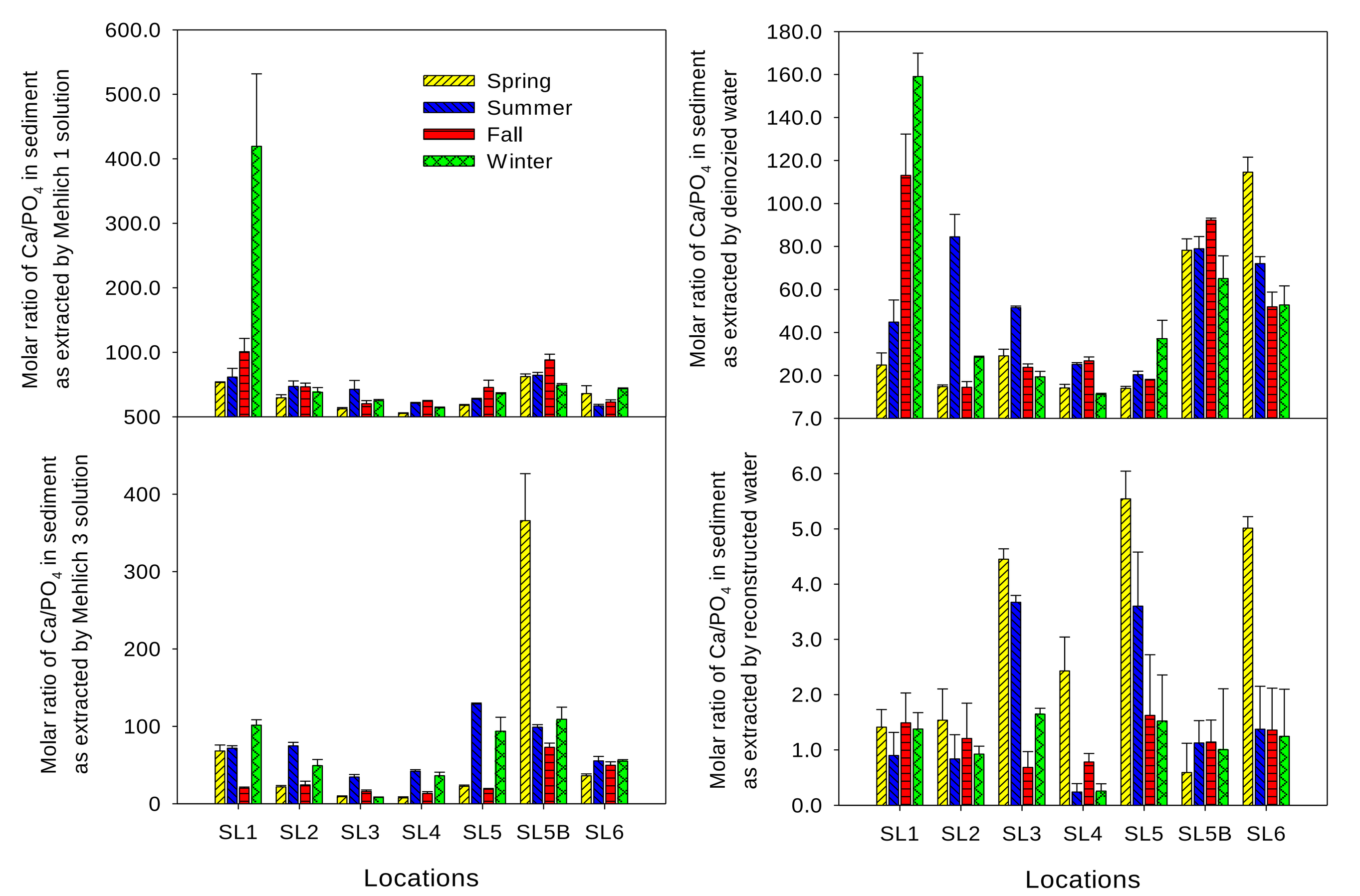

Fig. 2 Ratios of Ca/SO_4 as measured by different extractants in river sediments of Ten Miles Creek

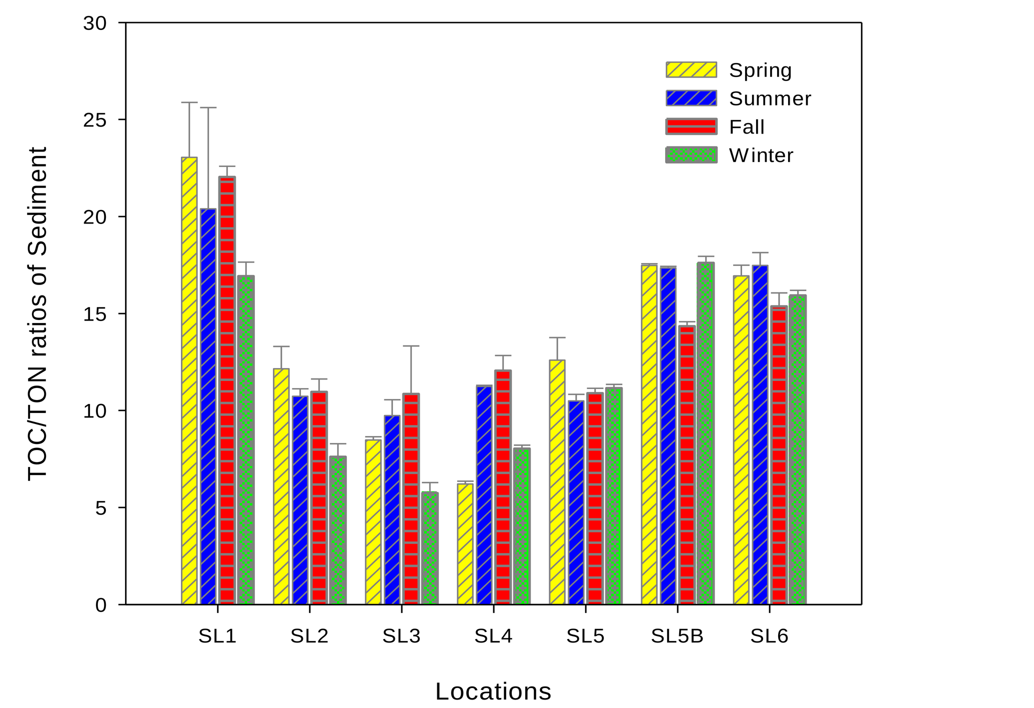

Fig. 3. Ratios of TOC/TON of different seasons in river sediments of Ten Miles Creek .

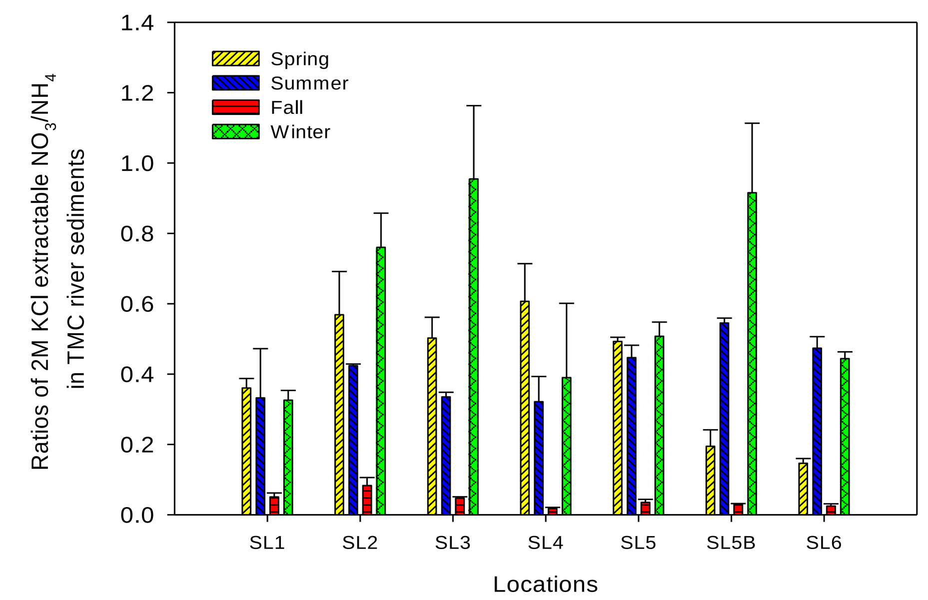

Fig. 4. Ratios of 2M KCl extractable NO_3/NH_4 of different seasons in river sediments of Ten Miles Creek .

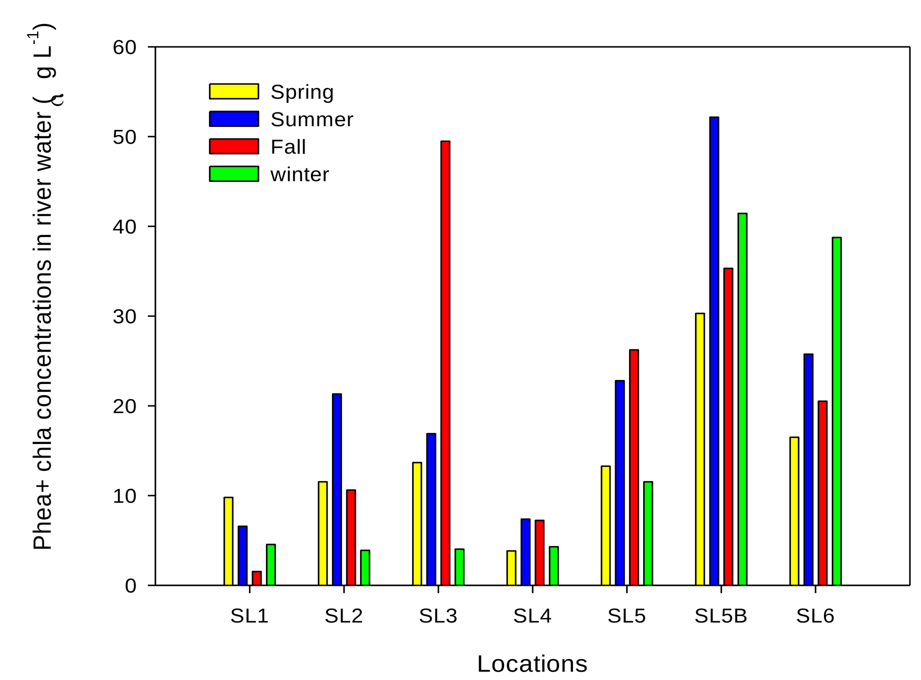

Fig. 5. Concentrations of phea (pheophytin)+chla (chlorophyll a) in river waters of overlying water bodies in the TMC.

Table 2. Correlations between ratios of M1 and M 3 extractable P/(Fe+Al) and water extractable PO_4-P, dissolved total P (DTP), the ratios of NO_3/SO_4, 2M KCl extractable ratio of NO_3/NH_4 in TMC sediments

Ratios	DI water extractable DTP	Mimic water extractable DTP	DI water extractable PO_4-P	DI water extractable NO_3/SO_4	KCl extractable NO_3/NH_4
$P/(Fe+Al)_{M1}$	0.686**	0.614**	0.232*	-0.261	-0.105
$P/(Fe+Al)_{M3}$	0.519**	0.547**	0.448**	-0.174	-0.020
$(Ca/PO_4)_{M1}$	-0.080	-0.085	-0.164	-0.153	-0.108
$(Ca/PO_4)_{M3}$	0.267*	0.236 *	-0.109	-0.334 *	-0.197

Statistic sample number=84; ratios refer to molar ratios.

- **Total dissolved P was determined using ICP-AES after filtered through a 0.45 µm membrane. The concentrations of NO_3-N, PO_4-P, and SO_4-S in water were determined using IC.**
- **Chlorophyll in water collected by filtering was extracted using 95% ethanol in a 78°C water bath for 5 min. Chlorophyll a and pheophytin concentrations in supernatant solution were colorimetrically determined using a dual beam spectrophotometer**

RESULTS AND DISCUSSION

- **Extractable P in river sediment varied greatly in the range of 0.69-180 mg kg^{-1}, and changed among the different extractions in the order of W-P) ≈ W-P < Olsen P< M3-P< M1-P (Table 1). The most downstream location (SL6) had the highest extractable P. Winter had the lowest W-P, RW-P, and M1-P, but the highest Olsen-P and M3-P, while spring had the highest W-P, MW-P, but lowest Olsen-P (Table 1). Total organic N (TON) varied from 143- 1263 mg kg^{-1} with peak occurred at SL6 (Table 1). KCl extractable NH_4-N and NO_3-N were in the range of 3.51-10.5 and 1.27-2.37 mg kg^{-1} with highest values occurred at the most downstream location (Table 1).**
- **M1, M3 and DI water extractable P/(Fe+Al) ratios were high at Sites SL5, SL5B, and SL6. Summer had high ratios in downstream locations, suggesting high P availability in downstream sediments (Fig. 2). The ratios of Ca/PO4 were less than 100, but larger than 5/3 [atomic ratios of $Ca_5(PO_4)_3(OH, F, Cl)$] , suggesting an over-saturation of Ca to PO_4 in the river sediment (Fig. 3). TOC/TON ratios were in the range of 5.74-23 varying with location and seasons (Fig. 3).**
- **Ratios of KCl extractable NO_3/NH_4 were less than 1, and the lowest ratios were found in fall, highest in winter, indicating a relatively reducing environment in the sediments (Fig. 3).**
- **Molar ratios of P/(Fe+Al) in M1 and M3 extraction were positively correlated with DI water extractable PO_4-P, DTP, and mimic water extractable DTP at significant levels of P<0.01(Table 2). However, molar ratios of Ca/PO_4 in M3 extraction showed positive correlations (P<0.05) with DI water and mimic water extractable DTP, but had a negative correlation with DI water extractable NO_3/SO_4 (Table 2). These correlations showed that the availability of P and N in TMC sediment was more influenced by chemical adsorption-desorption process than redox condition .Water hydrological background might have some constraints on P and N availability.**
- **Phytoplankton was found blooming at downstream locations, which is related to high concentrations of N and P in underlying river sediments (Fig. 5).**

CONCLUSIONS

1. **The concentrations of extractable N and P in TMC river sediment are high, especially at downstream location, and mainly controlled by chemical adsorption-desorption process.**
2. **River sediments in the TMC, especially at its downstream could serve as a potential secondary P or N source for overlying river water, and probably be a driver to the blooming of phytoplankton.**

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