

Z. L. He  
M. Zhang  
P. J. Stoffella  
X. E. Yang

## Vertical distribution and water solubility of phosphorus and heavy metals in sediments of the St. Lucie Estuary, South Florida, USA

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Z. L. He · M. Zhang · X. E. Yang  
College of Resource and Environmental  
Sciences, Zhejiang University, Huajiachi  
Campus, 310029 Hangzhou,  
People's Republic of China

Z. L. He (✉) · P. J. Stoffella  
Institute of Food and Agricultural Sciences,  
Indian River Research and Education  
Center, University of Florida,  
2199 South Rock Road,  
Fort Pierce FL 34945-3138, USA  
E-mail: zhe@mail.ifas.ufl.edu  
Tel.: +1-772-4683922  
Fax: +1-772-4685668

**Abstract** Accumulation and distribution of heavy metals and phosphorus in sediments impact water quality. There has been an increasing concern regarding fish health in the St. Lucie Estuary, which is related to increased inputs of nutrients and metals in recent decades. To investigate vertical changes of contaminants (P, Cd, Cr, Co, Cu, Ni, Pb, Zn, and Mn) in sediments of the St. Lucie Estuary in South Florida, 117 layer samples from six of the 210 to 420 cm depth cores were analyzed for their total and water-soluble P and heavy metals, clay, total Fe, Al, K, Ca, Mg, Na, and pH. Principal component analysis (PCA) was used in two sets of analytical data (total and water-soluble contaminant concentrations) to document changes of contaminants in each core of sediments. The PCA of total contaminants and minerals resulted in two factors (principal components). The first and second factors accounted for 61.7 and 17.2 % of the total variation in all variables, and contrast indicators associated with contaminants of P, Cd, Co, Cr, Ni, Pb,

Zn, and Mn and accumulation of Fe and Al oxides, respectively. The first factor could be used for overall assessment of P and heavy metal contamination, and was higher in the upper 45–90 cm than the lower depths of each core. The concentrations of P and heavy metals in the surface layers of sediments significantly increased, as compared with those in the sediments deeper than 45–90 cm. The PCA of water-soluble contaminants developed two factors. The second factor (Cu–P) was higher in the upper than the lower depths of the sediment, whereas the highest score of the first factor (Cd–Co–Cr–Ni–Pb–Zn–Mn) occurred below 100 cm. The water-soluble Cu and P concentrations were mainly dependent on their total concentrations in the sediments, whereas the water-soluble Cd, Co, Cr, Ni, Pb, Zn, and Mn concentrations were mainly controlled by pH.

**Keywords** Heavy metals · Muck sediment · Phosphorus · Vertical distribution · Water solubility · South Florida

### Introduction

Estuaries are water systems receiving sediments because of decreased flow velocities and increased flocculation of fine particles due to raised salt concentration from the draining canals to the estuary (Gibbs 1987). The

deposited sediments can be resuspended and contaminant adsorption/desorption cycles can set in with changing physico-chemical conditions. As many estuaries are located in urban areas, or surrounded by agricultural land, sediment pollution by P and heavy metals is a common phenomenon in the estuaries

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(Menon et al. 1997; Chen et al. 2000). With intensification of human activity and urban development, aquatic sediments become an important reservoir for P and heavy metals. In the last decade, studies on aquatic sediments have increased due to growing awareness of environmental pollution and its impact on the ecosystem. Sediment-associated P and heavy metal contaminants and their behavior have received wide public attention. Anthropogenic and natural processes can contribute to P and heavy metal contamination in the sediments. The P and heavy metal variability in the sediments is related to environmental changes. Mining, smelting, and agricultural development may result in P and heavy metal variability. Previous studies have demonstrated that P and heavy metal concentrations in estuary sediments are dependent on site-specific metal inputs (Perez et al. 1991; Menon et al. 1997; Chen et al. 2000). The vertical changes of heavy metal concentrations in the sediments can be useful for the assessment of pollution history in the sediments and anthropogenic activities (Williams 1992; Presley 1994; Ravichandran et al. 1995; Summers et al. 1996; Frankowski et al. 2002; Singh et al. 2002).

Phosphorus and heavy metals in sediment have caused considerable concern over their potential contamination to surface waters. Phosphorus and heavy metals in sediments can be mobilized by biogeochemical processes, causing water pollution or eutrophication of surface waters. Sediment pollution is often complex, with multicontaminants. More comprehensive characterization of accumulation and behavior of P and heavy metals in sediments are needed. However, minimal information exists on comprehensive characterization of accumulation and behavior of P and toxic metals in sediments. The objectives of this research were to evaluate the vertical distribution and water solubility of P and heavy metals in the sediments of the St. Lucie Estuary. This information could be useful for assessing the accumulation trends of P and heavy metals in these sediments and for improving management of the estuary and its watershed.

#### Site description

The St. Lucie Estuary in Martin and St. Lucie Counties, Florida, is a biogeographic transition zone, rich in habitats, and with a high number of both flora and fauna species. There is growing evidence that the ecological and biological integrity of the estuary has declined during the last 50 years, probably due to the decline in water quality induced by pollution from point and non-point sources (Sigua et al. 2000). The St. Lucie Estuary has undergone significant changes over the last 200 years as increasing development occurred along its shores and within the surrounding watersheds. Histori-

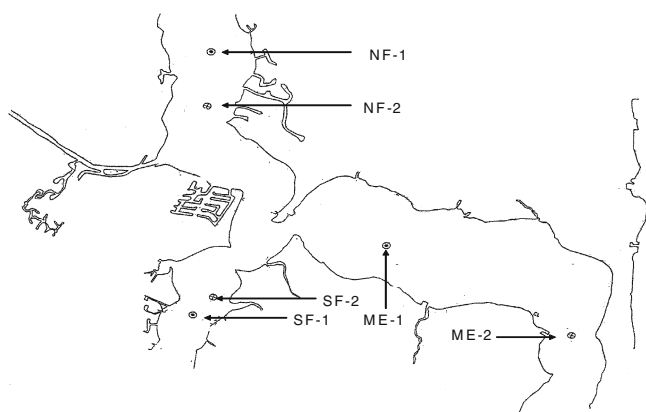
cally, the St. Lucie Estuary had a long and narrow drainage basin. In the late 1800s, the St. Lucie was a predominately freshwater system discharging into the southern end of the Indian River Lagoon. In 1892, the first artificial inlet was established and the St. Lucie Estuary began its transformation from a freshwater system to an estuarine system. The inlet was improved and enlarged, providing a more efficient connection to the sea and resulting in the present estuarine system. Since, the late 1800s, a series of drainage canals (C-44, C-23, and C-24) and other smaller drainage systems that discharge into the St. Lucie Estuary were constructed to provide storm water drainage for individual residential, commercial, and agricultural development projects. These drainage systems discharge large volumes of freshwater, as well as pollutants from urban and agricultural runoff to the estuary and are believed to have contributed to the accumulation of sediment in the estuary. Sediment layers range from non-existent to >4 m throughout the Indian River Lagoon and are most abundant in the intracoastal waterway, connecting channels and tributaries, as well as deeper pockets of water adjacent to developed areas (Trefy 1996a). The accumulation rate of sediment in some locations ranges from 2 to 10 mm per year with higher loadings in tributary creeks (Trefy 1996b). Potential impacts from the sediment include alteration of benthic ecosystems, increased biological O<sub>2</sub> demand, enhanced buildup of nutrients and contaminants, increased turbidity, and adverse effect on sea grasses (Trefy 1996a).

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#### Materials and methods

##### Sampling and processing

Six cores were collected from representative locations (NF1, NF2, SF1, SF2, ME1, and ME2; Fig. 1) of the St. Lucie Estuary using a liner percussion hammer advancing 7.5-cm dia × 400-cm long PVC core tubes. These sites were chosen based on the properties and profile characteristics of the muck sediments in the estuary obtained from previous study (He et al. 2001). The core tubes had a sharpened, but fully open leading edge. The top of each core tube was rigidly mounted and sealed into a headspace chamber at the base of the hammer. This chamber vented differential hydrostatic pressure as the core tube was advanced. At the end of the advance, the headspace chamber was sealed and a vacuum was applied to facilitate the capture of the core. The full height core tubes were then capped and sealed top and bottom and labeled and maintained in a vertical orientation. The sampling depths for locations NF1, NF2, SF1, SF2, ME1, and ME2 were 420, 210, 315, 390, 210, and 210 cm, respectively. These cores were segmented into approximately 100 cm increments for



**Fig. 1** Sampling locations of muck sediments in the St. Lucie Estuary

handling after having being frozen. Each increment was then capped, sealed, and labeled alphabetically A, B, C, etc. proceeding from the top horizon to the bottom of the core. The segmented cores were maintained in their original vertical orientation in a freezer. Prior to chemical analysis, the cores were cut into 15 cm length. Samples in each length of the tube were transferred to a plastic bag, thawed, mixed thoroughly in the bag, air-dried, and ground to  $< 2$  mm. The samples were directly used for measurement of pH, electrical conductivity, and water-soluble P and metal contents. Subsamples of the air-dried muck were further ground to  $< 0.15$  mm and analyzed for total minerals and heavy metal contents.

#### Analysis methods

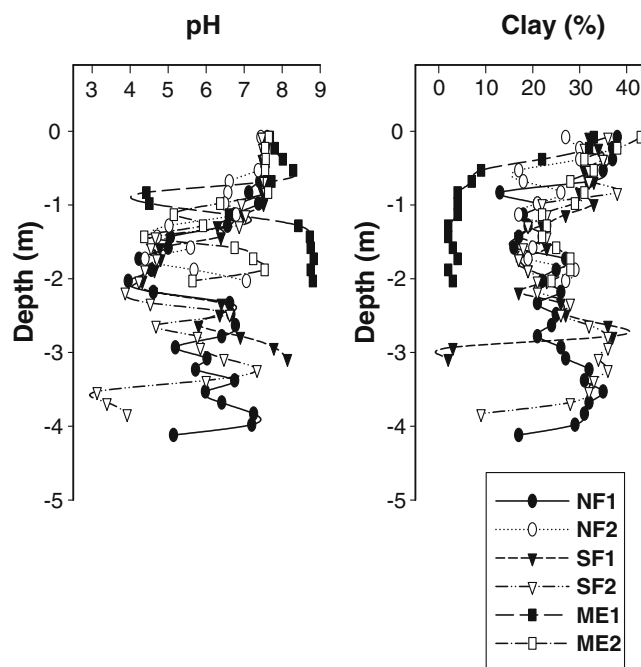
Sediment pH was measured in water at solid: water ratios of 1:1 using a pH/ion/conductivity meter (Accumet Model 50, Fisher Scientific, Atlanta, GA, USA). Clay content of sediment sample was determined following the micropipette method by Miller and Miller (1987). For determination of total concentration of mineral elements and heavy metals in the sediments, the  $< 0.15$  mm ground samples (each 0.5g) were weighed into a 100 ml Teflon beaker, and 3 ml concentrated  $\text{HNO}_3$ , 5 ml 50% (v/v) HF and 1 ml concentrated  $\text{HClO}_4$  were then added. Samples and reagents were well mixed, and digested using a hot plate (Hossner 1996). To completely remove fluoride ( $\text{F}^-$ ) ions, 5 ml conc. HCl were added twice to the dried residue and evaporated to incipient dryness. The final residue was diluted to 50 ml with 3 ml concentrated  $\text{HNO}_3$  and deionized water following filtration (Whatman no. 42). The concentrations of Ca, Al, Fe, P, Mn, Zn, Pb, Cu, Co, Cr, Cd, and Ni in the acid digests were determined using an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Ultima, JY Horiba Inc. Edison, NJ, USA).

The detection limits of the ICP-AES are 0.22, 0.52, 0.42, 2.5, 0.61, 2.0, 0.60, 0.11, 2.5, 1.2, 0.63, 1.6, 11, and  $3.9 \mu\text{g l}^{-1}$ , respectively for Cd, Co, Cr, Cu, Ni, Pb, Zn, Mn, P, Al, Fe, Ca, Na, and K. Standard stock solutions of  $1000 \text{ mg l}^{-1}$  Ca, Al, Fe, Mn, Zn, Cu, Co, Cr, Cd, Ni, P, Na, and K were obtained from Spex Industries (Metuchen, NJ, USA). Nitric acid, HCl, and HF of trace-metals grade were obtained from Fisher Scientific (Atlanta, GA, USA). Instrument calibration standards were also obtained from Spex Industries. Quality assurance samples (a blank, a spike) were analyzed every 15 samples. All the target elements had matrix spike recoveries within  $\pm 5\%$ .

Water-soluble P and heavy metals in the muck sediment were determined by extracting the soil with deionized water and measuring the P and metal concentrations in the extracts using the ICP-AES. Briefly, 10g air-dried sediment samples were placed into 50 ml polystyrene centrifuge tubes, and 40 ml deionized water was added. The suspension was shaken for 2 h and filtered through Whatman 42 filter paper. Concentrations of extractable P and metals in the filtrate were analyzed using the ICP-AES.

#### Statistical analyzes

Statistical analysis was conducted with the General Linear Model of Statistical Analysis System (SAS GLM) and the principal component (PC) procedures

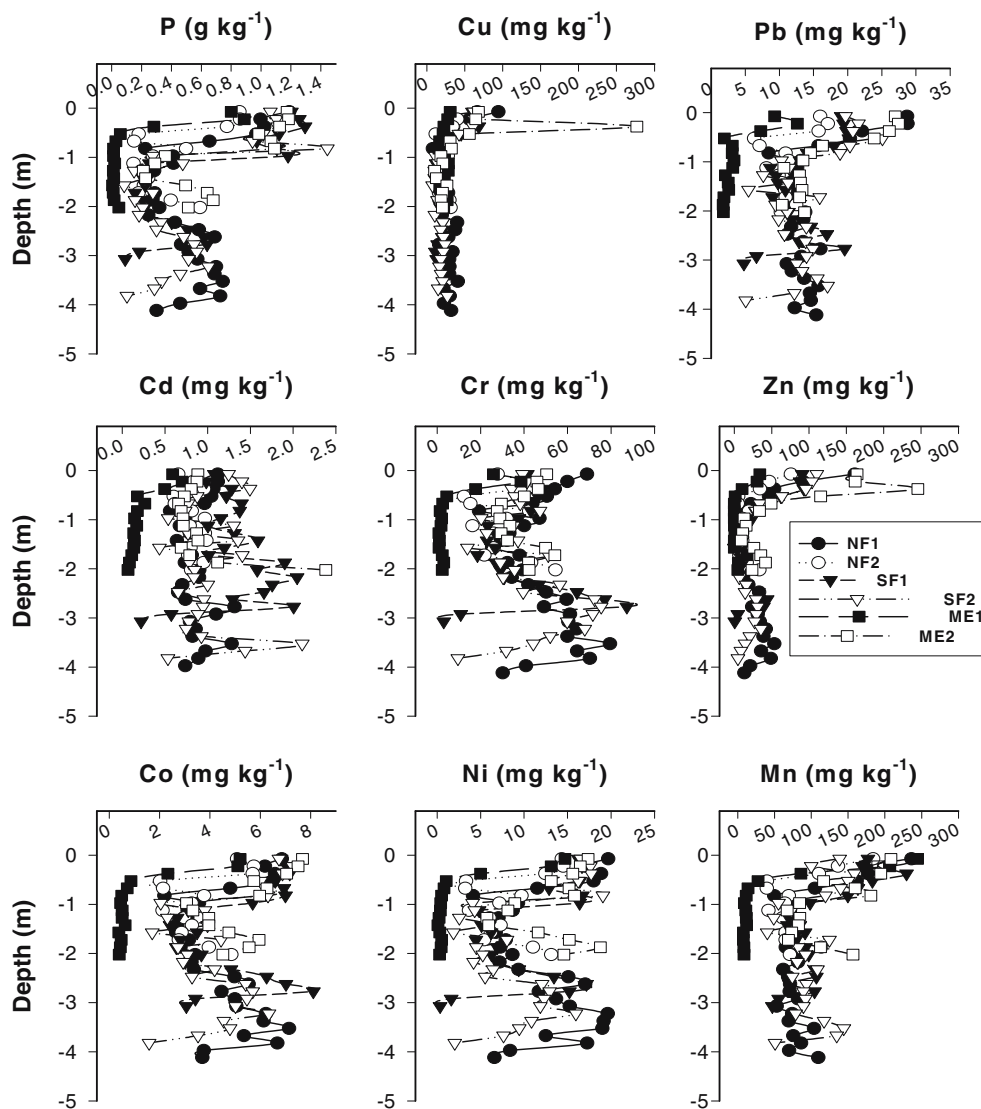


**Fig. 2** Vertical changes of pH and clay content in the sediments

(SAS Institute 2001). Principal component analysis (PCA) is a multivariate ordination technique used to extract information on patterns and clusters of data, thereby reducing data sets containing many variables to a smaller number of composite variables (components or axes), and obtaining the strongest covariation among variables within the first few axes. This analysis uses linear transformations of original variables to create a new set of uncorrelated variables, called the principal components (PCs). Each PC is responsible for the correlation among the group of soil attributes that comprise it. The total and water-soluble concentrations of P and eight heavy metals (Cd, Co, Cr, Cu, Ni, Mn, Pb, and Zn) were employed to evaluate whether sampling layer had tendencies or clustering patterns for each location.

A stepwise multiple linear regression analysis was performed on the total concentrations of P and heavy metals, pH and water-soluble P, and heavy metal concentrations using the SAS REG procedure (SAS Institute 2001). The model is set by:  $Y$  (water-soluble) =  $aX$  (total) +  $b$  pH +  $c$ , where  $a$ ,  $b$ , and  $c$  are parameters. An optimum subset model is one that, for a given number of variables, produces the minimum error sum of squares (SSE), or, equivalently, the maximum coefficient of multiple determination ( $R^2$ ). Final models in this study were selected using the maximum  $R^2$  and all individual variables that enter into the model should meet the requirement of significance at  $P < 0.05$ . Simple correlation coefficients ( $r$ ) were calculated among concentrations of individual element and properties of the muck sediments.

**Fig. 3** Vertical changes of total P, Cu, Pb, Cd, Cr, Zn, Co, Ni, and Mn concentrations in the sediments



## Results and discussion

### pH and clay content

Both pH and clay content of the sediments varied as a function of depth (Fig. 2). Surface sediments within a depth of 80 cm for all locations had pH higher than 7.0. However, each location contained layers with very low pH that occurred at various depths, 135–225 cm for NF1 (pH=3.95–5.06), 220–195 cm for NF2 (pH=4.39–5.68), 165–225 cm for SF1 (pH=4.32–4.78), 135–305 cm for SF2 (pH=3.87–5.85), 75–105 cm for ME1 (pH=4.43–4.51), and 105–150 cm for ME2 (pH=4.37–5.92). Lower pH was probably associated with S accumulation in the sediments from the growth of mangroves in the previous times. Sulfur was then oxidized to sulfuric acid after exposed to the air. Clay content fluctuated with depth. Generally, surface sediments had higher clay content as compared with deeper layers. However, distribution patterns of clay content in

the depth varied with locations. The clay layers with clay content > 30% occurred 0–75 and 315–405 cm for NF1, 0–45 and 180–210 cm for NF2, 0–105 and 255–285 cm for SF1, 0–95 and 255–360 cm for SF2, 0–30 cm for ME1, and 0–90 cm for ME2. The fluctuation of clay content with depth indicates that the sources of sediments varied in different depths.

### Vertical distribution of phosphorus and heavy metals

As expected, total P, Cu, Pb, Cd, Cr, Zn, Co, Ni, and Mn concentrations in the sediments varied widely, and ranged from 0.01 to 1.44 g kg<sup>-1</sup>, 0.84 to 87.26, 7.51 to 244, 0.37 to 8.11, 7.58 to 277, 1.75 to 28.8, 0.07 to 2.38, and 0.10 to 19.67 mg kg<sup>-1</sup>, respectively (Fig. 3). These wide ranges attributed to differences in sedimentation environments. The differences with depths at the same location were greater than those from the same depth but different locations. For all six locations, P, Cu, Pb,

**Table 1** Correlations (*r*) of total Cd, Co, Cr, Cu, Ni, Pb, Zn, Mn, and P with Ca, Fe, Al or clay in the sediment samples

Element	NF1 (n = 28)	NF2 (n = 14)	SF1 (n = 21)	SF2 (n = 26)	ME1 (n = 14)	ME2 (n = 14)	All samples (n = 117)
Cd/Ca	0.34	0.03	0.04	0.08	0.95***	-0.24	0.13
Cd/Fe	0.06	0.37	0.85***	0.58**	0.89***	0.46	0.59***
Cd/Al	0.61***	0.77***	0.50*	0.21	0.95***	0.26	0.50***
Cd/clay	0.57***	0.41	0.39	0.21	0.98***	-0.19	0.51***
Co/Ca	0.47*	0.81***	0.76***	0.68***	0.95***	0.82***	0.67***
Co/Fe	0.03	0.25	-0.01	-0.27	0.79***	-0.35	0.23*
Co/Al	0.16	0.51	0.39	0.33	0.91***	0.21	0.54***
Co/clay	0.86***	0.94***	0.80***	0.86***	0.98***	0.81***	0.89***
Cr/Ca	0.39*	0.75***	0.42	0.04	0.96***	0.52	0.38***
Cr/Fe	0.06	0.76***	0.43	0.20	0.82***	0.19	0.50***
Cr/Al	0.19	0.79***	0.64***	0.88***	0.98***	0.51	0.79***
Cr/clay	0.76***	0.83***	0.80***	0.70***	0.96***	0.41	0.81***
Cu/Ca	0.61***	0.69***	0.64***	0.70***	0.46	0.49	0.53***
Cu/Fe	-0.06	-0.08	-0.23	-0.48*	0.27	-0.36	-0.17
Cu/Al	0.35	0.13	0.21	-0.25	0.36	0.16	0.07
Cu/clay	0.61***	0.64*	0.51*	0.44*	0.39	0.34	0.31***
Ni/Ca	0.47*	0.85***	0.76***	0.70***	0.92***	0.68**	0.68***
Ni/Fe	0.01	0.32	0.04	-0.42*	0.77**	-0.09	0.17
Ni/Al	0.06	0.54*	0.40	0.24	0.88***	-0.13	0.50***
Ni/clay	0.81***	0.94***	0.89***	0.86***	0.97***	0.65*	0.87***
Pb/Ca	0.64***	0.86***	0.79***	0.74***	0.95***	0.78***	0.71***
Pb/Fe	-0.16	-0.01	0.21	-0.25	0.82***	-0.56*	0.20*
Pb/Al	0.51***	0.46	0.54*	0.18	0.96***	0.48	0.58***
Pb/clay	0.68***	0.83***	0.82***	0.71***	0.95***	0.83***	0.82***
Zn/Ca	0.64***	0.74***	0.67***	0.71***	0.83***	0.74**	0.71***
Zn/Fe	-0.17	-0.02	-0.17	-0.50**	0.65*	-0.43	-0.13
Zn/Al	0.26	0.11	0.41	-0.18	0.79***	0.37	0.21*
Zn/clay	0.73***	0.70***	0.67***	0.58**	0.87***	0.73**	0.59***
Mn/Ca	0.56***	0.58*	0.80***	0.51**	0.92***	0.66*	0.67***
Mn/Fe	-0.21	-0.10	-0.06	0.08	0.77**	-0.50	0.12
Mn/Al	0.50***	0.29	0.24	0.24	0.87***	0.14	0.41***
Mn/clay	0.65***	0.76***	0.65***	0.59***	0.97***	0.72**	0.74***
P/Ca	0.66***	0.86***	0.87***	0.84***	0.94***	0.85***	0.80***
P/Fe	-0.15	0.08	-0.25	-0.58**	0.75**	-0.57*	-0.07
P/Al	0.21	0.28	0.18	0.01	0.92***	-0.04	0.31***
P/clay	0.86***	0.87***	0.75***	0.74***	0.96***	0.82***	0.80***

Significant at \**P* < 0.05, \*\**P* < 0.01, and \*\*\**P* < 0.001, respectively

**Table 2** Variable loading on the first two factors from a principal component analysis (PCA) of total compositions of the sediments

Variable	Factor 1	Factor 2
Clay	0.899	0.245
Ca	0.784	-0.367
Na	0.837	-0.383
Fe	0.173	0.853
K	0.819	0.227
Mg	0.882	-0.343
Al	0.546	0.658
Cd	0.483	0.572
Co	0.949	0.119
Cr	0.744	0.533
Cu	0.553	-0.477
Ni	0.934	0.078
P	0.931	-0.232
Pb	0.931	0.022
Zn	0.793	-0.391
Mn	0.859	-0.108
Variance explained (%)	61.7	17.2
Combination of variables	Contaminants, bases, clay	Fe, Al, Cd

Zn, and Mn were significantly enriched in the surface sediment (Fig. 3), but the degree of P, Cu, Pb, Zn, and Mn enrichment in the surface varied with locations. Concentrations of Cd, Cr, Co, and Ni in the sediments, except for location ME1, fluctuated with depth, which was comparable with the distribution of clay (Fig. 2). The results indicate that the accumulations of P, Cu,

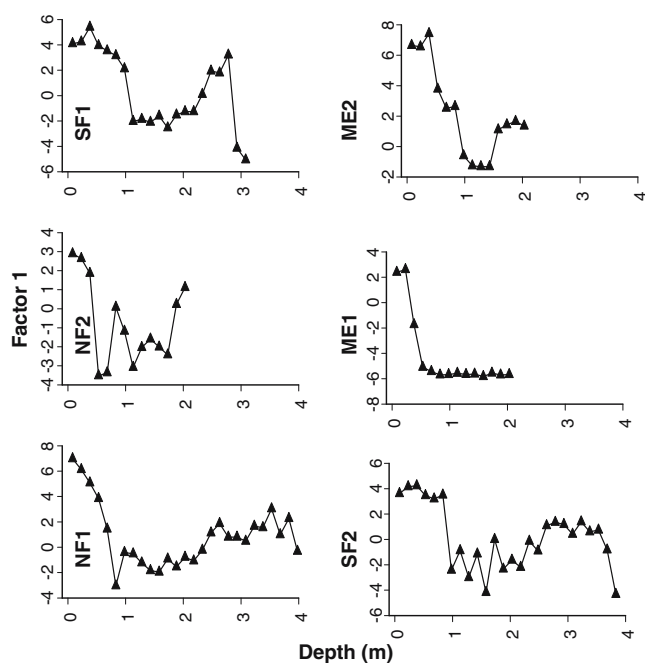
**Table 3** Depth delimiting of contaminant loadings in the sediments based on the first factor from a principal component analysis (PCA) of total compositions

Location	Boundary Depth (cm)	Upper		Bottom	
		Depth (cm)	Factor 1	Depth (cm)	Factor 1
NF1	60	0-60	3.84-6.98	60-420	-3.04 to 3.03
NF2	45	0-45	1.86-2.89	45-210	-3.52 to 1.12
SF1	90	0-90	3.15-5.40	90-315	-5.06 to 3.20
SF2	90	0-90	3.194.23	90-390	-4.33 to 1.39
ME1	45	0-45	-1.74 to 2.60	45-210	-5.83 to -5.10
ME2	90	0-90	2.52-6.64	90-210	-1.32 to 1.64

Pb, Zn, and Mn in the sediments have increased recently.

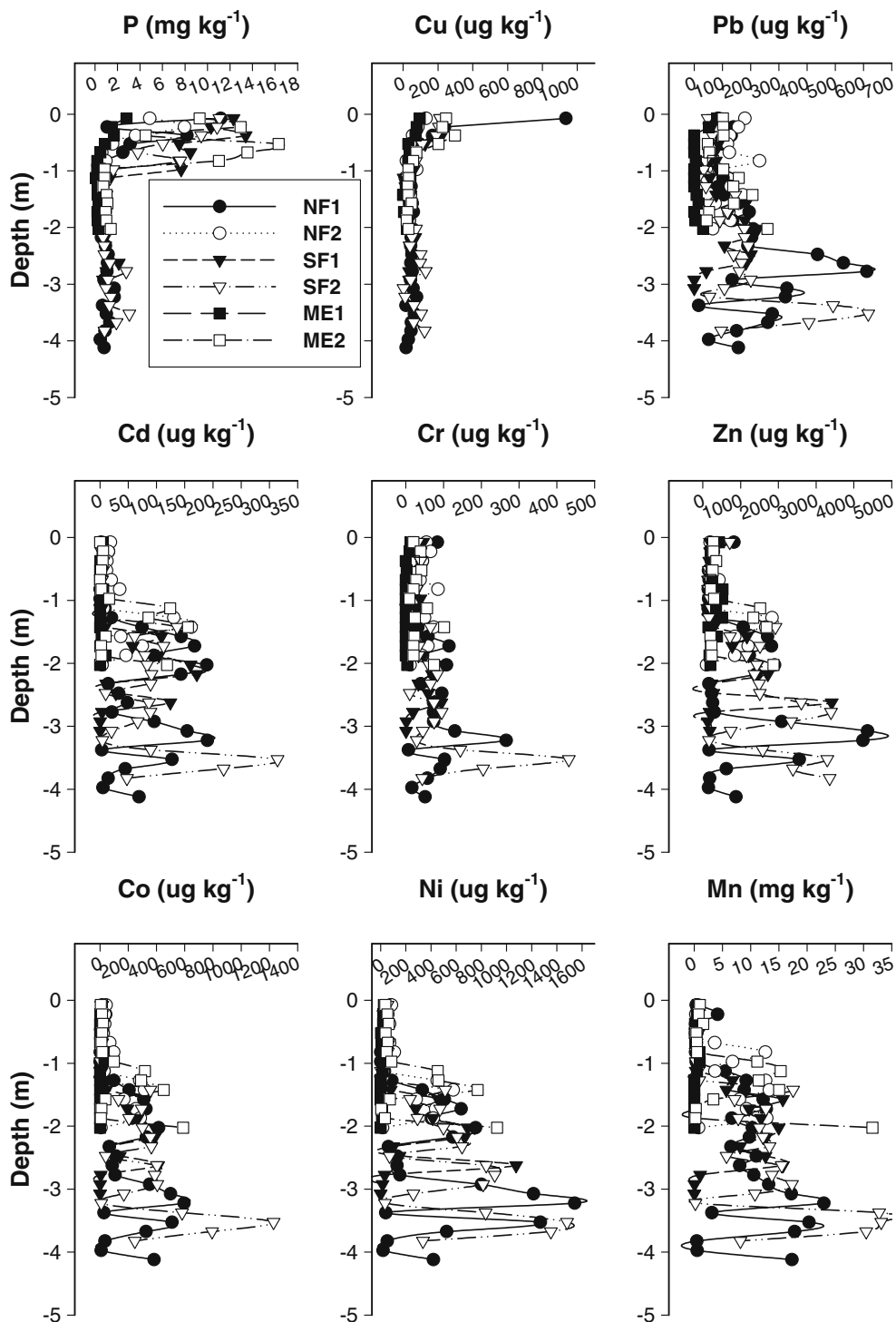
Significant correlations occurred among the concentrations of Co/Cr, Co/Cu, Co/Ni, Co/Pb, Co/Zn, Co/Mn, Co/P, Cr/Ni, Cu/Zn, Cu/Mn, Cu/P, Ni/Pb, Ni/Zn, Ni/Mn, Ni/P, Pb/Zn, Pb/Mn, Pb/P, Zn/P, and Mn/P for each of all six locations (data not shown). This result suggests that P and heavy metals in the sediments had similar sources and sinks. Correlation analysis between P, heavy metals and sediment properties indicates that Ca and clay content were major factors controlling the concentrations of P and heavy metals except for Cd (Table 1).

The PCA extracted two factors with eigenvalues > 1.0 from the data set of total P, heavy metals, minerals (K, Na, Ca, Mg, Fe, Al), and clay contents. These two factors explained 78.9% of the total variance in the data (Table 2). Each factor represented a set of variables that were highly correlated. The first factor extracted as much as 61.7% of the total variance, which was significantly correlated with total P, Co, Cr, Cu, Ni, Pb, Zn, and Mn (variable loading ranged from 0.553 to 0.949,  $P < 0.001$ ). Therefore, the score for each layer sediment samples on factor 1 could reflect degree of P and heavy metal contamination. The higher the score, the greater the contamination. The second factor was associated mainly with the differences in Fe, Al, and Cd, but it only accounted for 17.2% of the variance. Based on the scores of the first factor, the overall contaminations of P and heavy metals varied with sampling locations and depths (Fig. 4). The highest overall contamination occurred at NF1, whereas the lowest contamination occurred at ME1. The differences in the overall contamination of P and heavy metals (scores on factor 1) within each location were also noted. There was a significant depth gradient. The contaminants were significantly higher in the upper than the lower depths of the sediment. A significant boundary of the score occurred on factor 1 between the upper and lower



**Fig. 4** Vertical distributions of scores on the first factor 1 from a principal component analysis (PCA) of total compositions

**Fig. 5** Vertical changes of water-soluble P, Cu, Pb, Cd, Cr, Zn, Co, Ni, and Mn concentrations in the sediments



depths (Fig. 4). The depths of boundary ranged from 45 to 90 cm, dependent on the sampling locations (Table 3). This result indicates that the overall contamination of P and heavy metals in recent sediments significantly increased, as compared with old sediments deposited over 1,000 years ago.

#### Water-solubility of phosphorus and heavy metals

Water-soluble P and heavy metals in the sediments are labile contaminants. They had direct influences on water quality. The water soluble P and Cu in the sediments exhibit similar distribution patterns (Fig. 5).



**Table 4** Regression models of water-soluble P and heavy metal concentrations (*Y*) in relation to their total concentrations (*X*) and pH of the sediments (*n* = 117)

Element	Model	Partial R <sup>2</sup>		Total (R <sup>2</sup> )
		X	pH	
P	$Y_P (\text{mg kg}^{-1}) = -2.15 + 7.76 X_P (\text{g kg}^{-1})$	0.650**		0.650**
Cd	$Y_{Cd} (\mu\text{g kg}^{-1}) = 243 + 19.7 X_{Cd} (\text{mg kg}^{-1}) - 33.6 \text{ pH}$	0.017*	0.629**	0.646**
Co	$Y_{Co} (\mu\text{g kg}^{-1}) = 832 + 15.3 X_{Co} (\text{mg kg}^{-1}) - 116.2 \text{ pH}$	0.022*	0.568**	0.590**
Cr	$Y_{Cr} (\mu\text{g kg}^{-1}) = 136 + 0.91 X_{Cr} (\text{mg kg}^{-1}) - 19.1 \text{ pH}$	0.106**	0.261**	0.367**
Cu	$Y_{Cu} (\mu\text{g kg}^{-1}) = -13.4 + 1.14 X_{Cu} (\text{mg kg}^{-1})$	0.487**		0.487**
Ni	$Y_{Ni} (\mu\text{g kg}^{-1}) = 1371 + 14.7 X_{Ni} (\text{mg kg}^{-1}) - 195 \text{ pH}$	0.055**	0.480**	0.536**
Pb	$Y_{Pb} (\mu\text{g kg}^{-1}) = 336 + 4.83 X_{Pb} (\text{mg kg}^{-1}) - 42.4 \text{ pH}$	0.057**	0.219**	0.276**
Zn	$Y_{Zn} (\mu\text{g kg}^{-1}) = 3816 + 2.32 X_{Zn} (\text{mg kg}^{-1}) - 477 \text{ pH}$	0.008	0.439**	0.448**
Mn	$Y_{Mn} (\text{mg kg}^{-1}) = 32.3 + 0.012 X_{Mn} (\text{mg kg}^{-1}) - 4.14 \text{ pH}$	0.006	0.515**	0.521**

Significant at \**P* < 0.05 and \*\**P* < 0.01, respectively

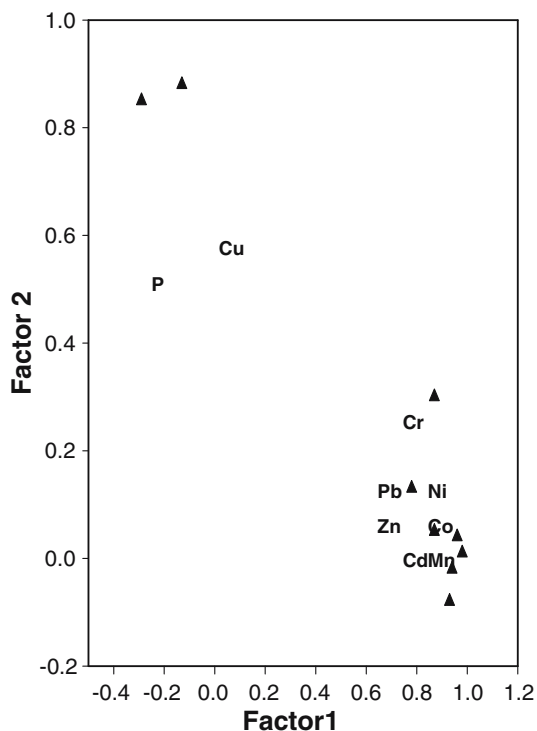
They were significantly higher in the upper layers and had a definite tendency of decreasing toward the bottom of the core regardless of the sampling locations. The water-soluble P concentration in the upper 75 cm ranged from 2.0 to 12.3 mg kg<sup>-1</sup>, whereas the concentration of water-soluble P in the lower layers was generally less than 2.0 mg kg<sup>-1</sup>. The water-soluble Cu concentrations in the upper 50 cm ranged from 80 to 935 μg kg<sup>-1</sup>, whereas the concentrations of water-sol-

uble Cu in the lower layers were mostly below 60 μg kg<sup>-1</sup>. These results indicated that recently deposited sediments had greater release potential of P and Cu, and may pose a significant effect on water quality, as compared with the old sediments.

In contrast, the concentrations of water-soluble Pb, Cd, Co, Zn, Cr, Ni, and Mn in the upper 90 cm sediments were 48–180, 0–18, 4–40, 193–800, 0–84, 4–86 μg kg<sup>-1</sup>, and 0.15–4.1 mg kg<sup>-1</sup>, respectively, which were generally lower than those of the sediments below 90 cm. The highest concentrations of water-soluble Pb, Cd, Co, Zn, Cr, Ni, and Mn occurred in the deeper layers where pH was low. Multiregression between water-soluble P and heavy metal concentration and their total content and pH indicates that water-soluble P and Cu level in the sediments were controlled mainly by their total concentrations while those of Cd, Co, Cr, Ni, Pb, Zn, and Mn were also affected by pH (Table 4).

The PCA based on data set of water-soluble P, Cd, Cr, Co, Cu, Ni, Pb, Zn, and Mn extracted two factors with eigen values > 1.0. The first and second factors accounted for 65.0 and 17.9%, respectively, of the total variance in the data. Factors grouped the variables (water-soluble P, Cd, Cr, Co, Cu, Ni, Pb, Zn, and Mn) into two narrow clusters (Fig. 6). Water-soluble Cd, Co, Cr, Ni, Pb, Zn, and Mn had high correlation with factor 1 (loadings ranged from 0.78 to 0.98), whereas water-soluble Cu and P had high correlation with factor 2 (loadings were 0.88 and 0.85).

There were significant differences in water-soluble P and heavy metal concentrations within each sampling location. For water-soluble Cd, Cr, Co, Ni, Zn, and Mn (factor 1), highest score occurred in the depths of 150–350 cm (Fig. 7). The difference within each location was the greatest in SF2 and the smallest in ME1. However, the highest score for water-soluble P and Cu (factor 2) was observed in the upper 50 cm except for SF2, where the sample from 375 to 390 cm also contained high water-soluble P and Cu (Fig. 8).



**Fig. 6** Variable loadings on the first two factors from a principal component analysis (PCA) of water-soluble nutrients and heavy metals

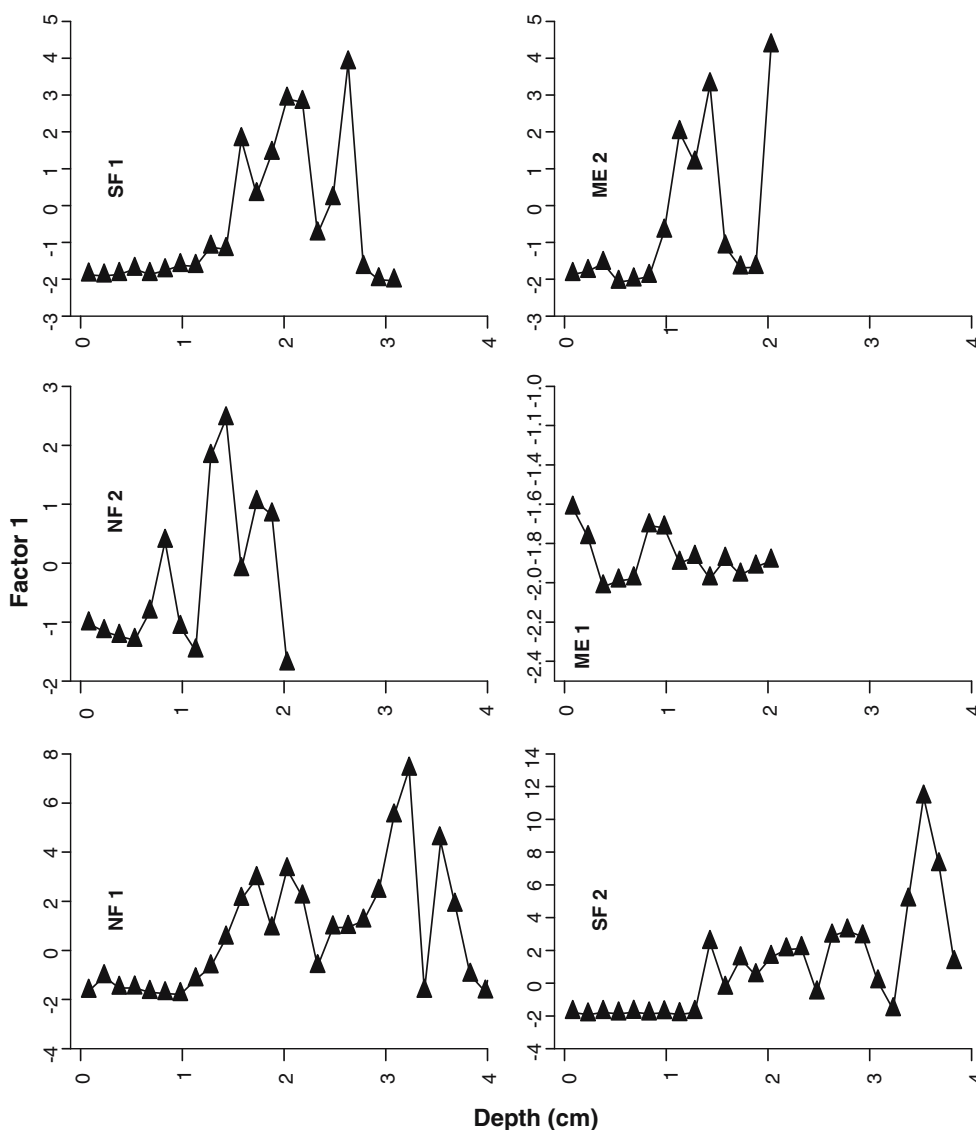


## General discussion

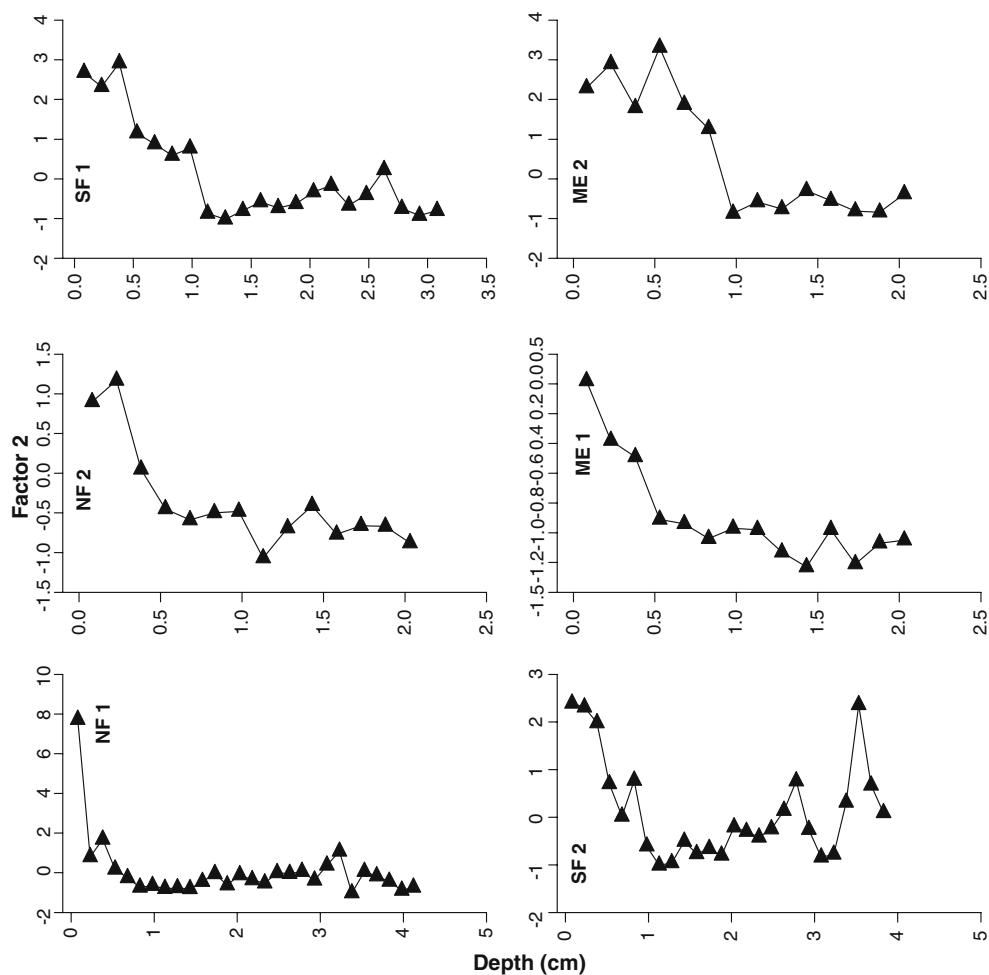
The accumulation of P and Cu in the surface layers of sediment in the St. Lucie Estuary was also observed in previous study (He et al. 2001) and reported by Haunert (1988). Among other factors, transport of P and Cu from agricultural production systems may contribute to the increase of these elements in the sediment. The St. Lucie watershed is dominated with flatwood sandy soils. More than 90–95% of sand in the surface layers (0–60 cm) is underlain with an argillic horizon, which is relatively impermeable (USDA and SCS 1980). Citrus and vegetables are the major crops in this watershed, with approximately 150–200 years' production history. Water table is very close to soil surface and bedding is necessary to sustain root

aeration and subsequently crop yield (Tucker et al. 1995). Repeated application of fertilizers is required to achieve desired crop yields because of a small holding capacity of the sandy soils for nutrients, and nutrients (especially P), which are not taken up by the crop plants, are readily subjected to losses through surface runoff, and which are eventually drained to the Estuary through a canal network (He et al. 2003). The transport of Cu from agricultural land to the Estuary through surface runoff was related to the accumulation of this metal in the soils growing citrus or vegetable crops. Cu-containing fungicides have been used in these production systems for many years (Zhang et al. 2003a, b). Copper forms complexes with organic matter, which are more water-soluble and readily transported to the receiving waters by surface runoff.

**Fig. 7** Vertical distributions of scores on the first factor from a principal component analysis (PCA) of water-soluble nutrients and heavy metals



**Fig. 8** Vertical distributions of scores on the second factor from a principal component analysis (PCA) of water-soluble nutrients and heavy metals



## Conclusions

Total P, Cd, Co, Cr, Cu, Ni, Mn, Pb, and Zn concentrations in the sediments varied widely, and ranged from 0.01 to 1.44 g kg<sup>-1</sup>, 0.07 to 2.38, 0.37 to 8.11, 0.84 to 87.26, 7.58 to 277, 0.10 to 19.67, 7.51 to 244, 1.75 to 28.8 mg kg<sup>-1</sup>, respectively. The differences with depths at the same location were greater than those with the locations at the same depth. The PCA of total contaminants and minerals resulted in two factors (contaminants of P, Cd, Co, Cr, Ni, Pb, Zn, and Mn and accumulation of Fe and Al oxides), they accounted for 61.7 and 17.2%, respectively, of the total variation in all variables. The first factor could be used for assessing overall contamination of P and heavy metals, and was much higher in the upper 45–90 cm than the lower depths for each core. These

results indicate that the overall contamination of P and heavy metals in recent sediments is significantly higher than older sediments. In addition, principal analysis of water-soluble contaminants developed two factors (Cd–Co–Cr–Ni–Pb–Zn–Mn and Cu–P factors). The second factor (Cu–P) was higher in the upper sediment, while the highest score of first factor (Cd–Co–Cr–Ni–Pb–Zn–Mn) occurred below 100 cm. The water-soluble Cu and P concentrations were mainly dependent on their total concentrations in the sediments, whereas the water-soluble Cd, Co, Cr, Ni, Pb, Zn, and Mn concentrations were controlled mainly by sediment pH.

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## References

- Chen Z, Kostaschuk R, Yang M (2000) Heavy metals on tidal flats in the Yangtze estuary, China. *Environ Geol* 40:742–749
- Frankowski L, Bolalek J, Szostek A (2002) Phosphorus in bottom sediments of Pomeranian bay (Southern Baltic-Poland). *Estuar Coast Shelf S* 54:1027–1038
- Gibbs RJ (1987) Sources of estuarine sediments and their coagulation. In: *Proc. Sedimentation Control to Reduce Maintenance of Dredging of Navigational Facilities in Estuaries*. National Research Council, National Academy Press, Washington DC, USA, p32–52
- Hauert DE (1988) Muck characteristics and toxic substances in the St. Lucie Estuary. South Florida Water Management District Technical Pub, Florida, pp 88–10
- He ZL, Zhang MK, Stoffella PJ, Calvert DV, Wilson C (2001) Beneficial reuse of marine muck sediments—St. Lucie River. A final project report. South Florida Water Management District, West Palm Beach, FL, USA
- He ZL, Zhang MK, Stoffella PJ, Calvert DV, Li YC (2003) Loading of phosphorus in surface runoff in relation to management practices and soil properties. *Soil Crop Sci Fla Proc* 62:12–20
- Hossner LR (1996) Dissolution for total elemental analysis. In: Spark DL (ed) *Methods of soil analysis, Part 3: Chemical methods*. SSSA Book Series No 5, ASA-CSA-SSSA Inc. Madison, WI, USA
- Menon MG, Gibbs RJ, Phillips A (1997) Accumulation of muds and metals in the Hudson River estuary turbidity maximum. *Environ Geol* 34:214–222
- Miller WP, Miller DM (1987) A micropipette method for soil mechanical analysis. *Commun. Soil Sci Plant Anal* 18(1):1–15
- Presley BR (1994) The potential environmental impact of trace metals in the Arctic. *Arctic Res* 8:123–135
- Perez M, Usero J, Gracia I, Cabrera F (1991) Trace metals in sediments from the “Ria de Huelva”. *Toxicol Environ Chem* 31/32:275–283
- Ravichandran M, Baskaran M, Santchi PH, Bianchi TS (1995) History of trace metal pollution in Sabine-Neches estuary, Beaumont, Texas. *Environ Sci Technol* 29:1495–1503
- Statistical Analysis System Institute (2001) *SAS user’s guide*. SAS Inst., Cary, NC, USA
- Sigua GC, Steward JS Tweedale WA (2000) Water-quality monitoring and biological integrity assessment in the Indian River Lagoon, Florida: Status, Trend, and loadings (1988–1994). *Environ Manage* 25:199–209
- Singh M, Muller G, Singh IB (2002) Heavy metals in freshly deposited stream sediments of river associated with urbanization of the Ganga plain, India. *Water Air Soil Poll* 141:35–54
- Summers JE, Wade TL, Engle VD (1996) Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries* 19:581–594
- Trefy JH (1996a) Indian River Lagoon muck: characteristics, origins, distribution, and impacts. St. Johns River Water Management District, Palatka, FL, USA
- Trefy JH (1996b) Indian River Lagoon muck: Threat or potential source?. St. Johns River Water Management District, Palatka, FL, USA
- Tucker DPH, Alva AK, Jackson LK, Weaton TA (1995) Nutrition of Florida citrus trees. University of Florida cooperation Extension Service, SP169
- United States Department of Agriculture (USDA), Soil Conservation Service (SCS) (1980) *Soil Survey of St. Lucie County Area, Florida*. The Office of Soil Conservation Service, Fort Pierce, FL, USA
- Williams TM (1992) Diagenetic metal profiles in recent sediments of a Scottish freshwater loch. *Environ Geol Wat Sci* 20:117–123
- Zhang MK, He ZL, Calvert DV, Stoffella PJ, Yang XE, Lamb EM (2003a) Accumulation and partitioning of phosphorus and heavy metals in a sandy soil under long-term vegetable crop production. *J Environ Sci Health A* 38:1981–1995
- Zhang MK, He ZL, Calvert DV, Stoffella PJ, Yang XE (2003b) surface runoff losses of copper and zinc in sandy soils. *J Environ Qual* 32:909–915