Concentrations and solubility of heavy metals in muck sediments from the St. Lucie Estuary, U.S.A.

M.K. Zhang · Z.L. He · P.J. Stoffella · D.V. Calvert · X. Yang · P.L. Sime

Abstract To evaluate muck sediments as a potential soil amendment, total and Mehlich III-extractable concentrations of Cd, Cu, Cr, Ni, Pb, Zn, and Co in 59 muck sediment samples from the St. Lucie Estuary were analyzed. A seven-step chemical fractionation procedure was used to assess the potential mobility of heavy metals. Except for Cd, the average total concentrations of the metals are lower than the reported average concentrations of these elements in municipal composts in the U.S.A. The concentrations were also below critical levels for the safe use of wastes and byproducts in agriculture, as established by the United States Environmental Protection Agency. The Cd, Cu, Cr, Ni, Pb, Zn and Co in the sediments were predominantly associated with silicate minerals in the residual form. Most metals in the muck sediments occur predominantly in weakly mobile or nonbioavailable forms. Use of mucks in neutral pH upland soils should not pose any significant hazards or risk to the environment. However, Cd, Cu, Cr, Ni, Pb, Zn, and Co, especially Zn, Cu, and Pb, could be more readily released from the muck sediments under acidic soil conditions.

Keywords Concentration · Heavy metals · Muck sediment · Solubility · St. Lucie Estuary · Florida

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Introduction

The St. Lucie Estuary, in Martin and St. Lucie counties, Florida, has undergone significant changes over the last 200 years as development occurred along its shores and within the surrounding watersheds. 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 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. During the late 1800s and early 1900s, a series of drainage canals (C-44, C-23, and C-24) which discharge into the St. Lucie Estuary were constructed for urban and agricultural development. These canals increased the size of the watershed and are believed to have contributed to the accumulation of black, fine-grained organic sediment, commonly referred to as "muck", in the estuary. Muck layers range from nonexistent to >2 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 (Trefry 1996a; Marshall 1996, personal communication). The accumulation rate of muck in some locations ranges from 2 to 10 mm year^{-1} with higher loadings in tributary creeks (Trefry 1996b). Potential impacts from muck layers include alteration of benthic ecosystems, increased biological O_2 demand, enhanced buildup of nutrients and contaminants, increased turbidity, and adverse effect on seagrasses (Trefry 1996a). Muck removal, partnered with programs to reduce future muck accumulation, has been identified as an objective of the Indian River Lagoon Surface Water and Improvement Management Plan (SWIM) and the Comprehensive Everglades Restoration Plan (CERP; Trefry 1996a; Marshall 1996, personal communication). Generally, the muck from

the estuary contains organic matter, fine-grained aluminosilicates, and nutrients such as N and P (Haunert 1988; Trocine and Trefry 1993; Patel and Ericson 1996), which can be used to improve fertility of sandy soils. The sediments removed from canals or estuaries are often disposed of to land (Almeida and others 2001). Muck sediment amendments which are incorporated or surface-applied to soils have been reported to improve soil physico-chemical properties. However, land disposal of these dredged sediments may affect the surrounding environment due to the presence of contaminants (Singh and others 2000). Muck sediment, like other sediments, invariably contains measurable quantities of heavy metals. Toxic metals can be mobilized in soils by biogeochemical processes, causing water pollution or contamination of the food chain. The extent to which metals are solubilized depends on a variety of reactions involving the water, soil, and specific metal of interest (Padmalal and others 1995; Simpson and others 2002). Evaluation of total metal contents may be useful as a gross index of contamination but it provides minimal insight into the potential mobility of the metals under field conditions. Multistep sequential extraction schemes provide a more complete picture for predicting the heavy-metal distribution, mobility, and bioavailability in sediments, sludges, and waste-amended soils (Tessier and others 1979).

There are no data available regarding the chemical forms of metals in muck sediments, which are critically important for assessing mobility of heavy metals. The objectives of this research were to evaluate the total and Mehlich III-extractable contents as well as chemical fractionation of Cd, Cu, Cr, Ni, Pb, Zn, and Co in the muck sediments from the St. Lucie Estuary. The information generated from this study may be useful in assessing beneficial use of muck sediments in agriculture.

Materials and methods

Sample collection and processing

Fifty-nine representative muck core samples were collected by the Army Corps of Engineers from the St. Lucie Estuary and delivered to the University of Florida, Indian River Research and Education Center. These samples were stored in a freezer at –4 °C after their arrival. Prior to chemical analysis, each sample was transferred from the sampling tube to a plastic bag, mixed thoroughly in the bag, air-dried, and ground to pass a 2-mm mesh sieve. These samples were directly used for measurement of pH and electrical conductivity (EC). Subsamples of the air-dried muck were further ground to pass a 0.15-mm mesh sieve and analyzed for total organic C, Al, Fe, Ca, Zn, Cu, Mn, Cd, Co, Cr, Pb, and Ni.

Characterization of physical and chemical properties

EC and pH were measured in water at solid:water ratios of 1:2 (for EC) and 1:1 (for pH) using a pH/ion/conductivity meter (Accumet Model 50, Fisher Scientific, Fair Lawn, NJ; Thomas 1996). The total concentrations of organic C in the muck samples were determined using a CNS Analyzer (NA 1500, Fisons Instruments Inc., Dearborn, MI). Particle composition of soil and sediment sample was determined following the micropipette method of Miller and Miller (1987).

Measurement of total concentrations of heavy metals

For determination of total concentration of macro- and micro-elements in the muck, the <0.15 mm ground samples (each 0.5 g) were weighed into a 50-ml Teflon pressure digestion vessel, and 9 ml concentrated HNO_3, 3 ml 50% (v/v) HF and 0.5 ml concentrated HCl were then added. Samples and reagents were well mixed, sealed, and digested using a microwave digestion system (O·I·Analytical, College Station, TX) following USEPA method 3052 (USEPA 1995). The digestion solution was brought to a final volume of 50 ml with deionized water following filtration (Whatman #42). The concentrations of Ca, Al, Fe, Mn, Zn, Cu, Co, Cr, Cd, and Ni in the acid digests were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Ultima, JY Horiba Inc., Edison, NJ). Lead was determined using a flame atomic absorption spectrometer (Perkin Elmer, Simaa 6000, Boston, MA).

Sequential fractionation

To understand more complete fractions of the heavy metals in the mucks, a modified procedure of Amacher (1996) was employed to fractionate heavy metals in the muck sediment. A deionized water extraction step (shaking 1 h) was included for insight into water solubility of these elements. As the muck samples contained relative low amounts of heavy metals, two grams of each sample were used in the sequential extractions to replace the 0.5-g sample for the original method. The sequential fractionation consists of (1) water soluble, (2) exchangeable by 0.1 mol l^{-1} $Mg(NO_3)_2$, (3) carbonate-associated (1 mol l^{-1} Na acetate at pH 5), (4) Mn oxide-associated (0.1 mol l^{-1} $NH_2OH \cdot HCl$ at pH 2), (5) Fe oxide-associated (0.2 mol l^{-1} ammonium oxalate + 0.2 mol l^{-1} oxalic acid + 0.1 mol l^{-1} ascorbic acid at pH 3.3), (6) organic matter-associated (30% v/v H_2O_2 at pH 2), and (7) residual. After each successive extraction, the supernatant solution was separated by centrifuging the suspension at 7,500×g rcf for 30 min and filtering through Whatman #42 filter paper. The concentrations of Cd, Co, Cr, Cu, Ni, Pb, and Zn in the solution were determined using the ICP-AES. The residual fraction for each metal was calculated by subtracting the sum of the above six types of extractable metal from the total metal content in the sample. The detection limits of the ICP-AES are 0.22, 0.52, 0.42, 2.50, 0.61, 1.96 and 0.60 μg l^{-1} for Cd, Co, Cr, Cu, Ni, Pb, and Zn, respectively. Standard stock solutions of 1,000 mg l^{-1} Ca, Al, Fe, Mn, Zn, Cu, Co, Cr, Cd, and Ni were obtained from Spex Industries (Edison, NJ). Nitric acid, HCl, and HF of trace-metal

grade were obtained from Fisher Scientific. 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 ±5%.

The sequential fractionation is based on solubility of individual solid-phase components and on selectivity and specificity of chemical reagents. The procedure provides a gradient for chemical association strength between heavy metals and solid; the fractions on each step of the sequential extraction procedure are operationally defined and may not correspond exactly to what they are being called. Although sequential procedures vary in the number of fractions evaluated (Tessier and others 1979; Shuman 1985), it is conceptually convenient to consider two broad categories, i.e., nondetrital and detrital metals, distinguished by whether solid-associated dissolution is required to release the metals. Nondetrital metals include water-soluble and exchangeable fractions. The detrital fraction includes metals present as precipitates with Fe or Al oxides, carbonate, fixed within the silicate matrix, or associated with hydrous oxides through occlusion, chemisorption, co-precipitation or associated with organic matter. The detrital metals are generally not significantly mobilized within the short-term under normal soil conditions.

Extraction of available metals

Available metals in the muck sediment were determined by extracting the soil with Mehlich III solution (0.2 mol l^{-1} CH_3COOH + 0.25 mol l^{-1} NH_4NO_3 + 0.015 mol l^{-1} NH_4F + 0.013 mol l^{-1} HNO_3 + 0.001 mol l^{-1} EDTA, pH 2.0) and measuring the metal concentrations in the extracts using the ICP-AES (Mehlich 1984). Briefly, 2.5 g air-dried soil sample was placed in a 50-ml polystyrene centrifuge tube, and 25 ml Mehlich III extractant was added. The suspension was shaken for 5 min and filtered through Whatman #42 filter paper. Concentrations of extractable metals in the filtrate were analyzed using the ICP-AES.

All measurements were performed on duplicate samples. Data analyses were conducted using SAS program procedures (SAS Institute 1998). Arithmetic mean, minimum and maximum values, and the coefficient of variation (C.V.) were calculated for each measured parameter.

Results and discussion

General characterization

Muck pH values ranged from 5.2 to 8.2, with a mean of 7.2. Approximately 85% of the samples had pH values ranging from 6.0–8.0, close to a neutral condition, suggesting that muck pH may not pose any critical impact on soil reactions. The muck contained 2.6 to 109 g kg^{-1} of organic C, with a mean value of 44 g kg^{-1}. The muck contained significant amounts of Ca, Fe, Al and clay (Table 1) and may influence retention and solubility of heavy metals in the muck sediments.

Table 1
Ranges and mean values of physical and chemical properties, and total heavy-metal concentrations of the muck sediments (n=59)

Properties	Range	Mean
pH	5.2–8.2	7.2
EC (dS m^{-1})	1.51–2.29	2.03
Clay (g kg^{-1})	18.6–511	182
Organic C (g kg^{-1})	2.6–109	44
Total Al (g kg^{-1})	4.2–60	30
Total Fe (g kg^{-1})	1.6–37	17
Total Ca (g kg^{-1})	0.96–40	19
Total Mn (mg kg^{-1})	23–223	117
Cd (mg kg^{-1})	4.9–23	14
Co (mg kg^{-1})	7.8–29	19
Cr (mg kg^{-1})	5.2–91	40
Cu (mg kg^{-1})	3.1–72	26
Ni (mg kg^{-1})	13–55	36
Pb (mg kg^{-1})	2.8–23	10
Zn (mg kg^{-1})	3.4–127	40

Total amounts of heavy metals in muck sediments

The total concentration ranges of the heavy metals in the sediments are given in Table 1. The concentrations were within the normal concentration range of these elements in most agricultural soils, except for Cd. According to the reviews by Lindsay (1979), Kabata-Pendias and Pendias (1992), and Alloway (1995), normal concentration ranges of these elements in soils are 0.01–0.7 mg kg^{-1} for Cd, 1–1,000 mg kg^{-1} for Cr, 2–250 mg kg^{-1} for Cu, 0.4–1,000 mg kg^{-1} for Ni, 2–200 mg kg^{-1} for Pb, and 1–900 mg kg^{-1} for Zn. Mean concentrations of Cu, Zn, Cr, Pb, and Cd in solid-waste composts were reported to be 463, 725, 40, 106, and 7 mg kg^{-1} in the U.S.A. (USEPA 1990). In comparison, the concentrations of heavy metals including Co, Cr, Ni, Zn, Cu, and Pb in these muck samples were generally lower than those found in most biosolids or municipal solid-waste composts. The mean concentration (14 mg kg^{-1}) of Cd in the muck samples was higher than the mean value of Cd in the municipal composts in the U.S.A. However, the concentrations of the measured heavy metals, including Cd, in the muck samples were below critical level for those elements for acceptable utilization of wastes and byproducts in agriculture as established by the United States Environmental Protection Agency (pollutant limits for land-applied biosolids of Cd, Zn, Cu, Ni, Pb, and Cr in USEPA Part 503 are 39, 2,800, 1,500, 420, and 300 mg kg^{-1}; Harrison and others 1999; Walker 2001).

Except for Cu, heavy-metal concentrations in the muck sediments were higher than those in soils near the St. Lucie Estuary. Mean Cu, Zn, Cd, Co, Cr, Ni, and Pb concentrations in the soils near the St. Lucie Estuary were 54, 27, 0.17, 0.32, 8.0, and 4.1 mg kg^{-1} for vegetable land, and 4.1, 6.6, 0.15, 0.31, 1.8, 0.68, and 4.5 for forestland (Zhang and others 2002, unpublished data). Copper, Co, Cr, Ni, Pb, and Zn concentrations in the muck sediments in this study were less or close to those reported by Perez and others (1991), Menon and others (1997), and Chen and others (2000), whereas Cd concentration in the muck was higher than those in the sediments from the Yangtze estuary

(Chen and others 2000), and less or close to those in sediments from the Hudson River estuary (Menon and others 1997) and the Tinto-Odiel junction (Perez and others 1991).

Zinc, Ni, Pb, Cd, Co, and Cr concentrations in this study were all significantly correlated ($p<0.01$) with Fe and Al concentrations in the mucks, except for Pb which had no significant relationship with Fe concentration. All the metals, except for Ni, were also closely correlated with organic C ($p<0.05$). Copper was different from other heavy metals – it was negatively related to Al and positively related with Ca ($p<0.05$). These results imply that most heavy metals in the mucks may be associated with Fe and Al oxides or $CaCO_3$ or chelated by organic matter.

Chemical fractionation

Chemical fractionation data of Cd, Co, Cr, Cu, Ni, Pb, and Zn by sequential extraction are presented in Table 2. A small percentage of the total metals in these muck sediments was measured as labile (water-soluble and exchangeable fractions; Table 2). Except for water-soluble Pb and exchangeable Cu, only 1% or less, on the average, of the total metals in these sediments was water soluble and exchangeable. The sum of the water-soluble and exchangeable fractions can be used to reflect the maximum

availability of metals in contaminated soils or sediments. On the basis of the relative amount of each element released from the first two extractions (Table 2), Cu and Pb in the muck had relatively higher mobility than other heavy metals in the sediment–water systems. In water-soluble fractions, only Pb accounted for a considerable proportion of the total concentration (1.1%; Table 2). However, water-soluble Pb concentration was low because of its very low total concentration (Table 2). The percentages of water-soluble and exchangeable fractions in the total for all metals were less than 1.5%. The carbonate-associated fraction accounted for 4.49–11.02% of the total for Cu, Pb, and Zn, and the corresponding values for the other metals were $\leq 2\%$.

The manganese oxide-associated fraction was generally low (<3.5%) for all metals because of the low content of Mn in the muck sediments. The iron oxide-associated fraction accounted for >10% of the total of Cu, Zn, Pb, and Cr in the muck. The close association of Pb, Zn and Cu with Fe oxides has been reported on several soils (Kuo and others 1982; Ma and Rao 1997). The heavy metals associated with Mn and Fe oxides may be remobilized under reducing condition (Boyle 2001). However, the fractions are stable in upland with high redox potential. The amounts of metals found in the organic matter-associated

Table 2
Concentrations and percentages in the total for various fractions of Cd, Co, Cr, Cu, Ni, Pb, and Zn in muck sediments ($n=59$). *C.V.* Coefficient of variation

Fractions		Concentrations (mg kg^{-1})							Extracted percentages in the total (%)						
		Cd	Co	Cr	Cu	Ni	Pb	Zn	Cd	Co	Cr	Cu	Ni	Pb	Zn
Water-soluble	Maximum	0.15	0.26	0.16	0.20	0.43	0.24	0.78	1.1	1.0	1.8	4.3	0.92	3.7	5.0
	Minimum	0.01	0.01	0.02	0.00	0.02	0.01	0.07	0.05	0.04	0.06	0.01	0.07	0.11	0.14
	Mean	0.06	0.07	0.06	0.07	0.14	0.10	0.19	0.41	0.37	0.21	0.42	0.39	1.1	0.61
	C.V. (%)	54	69	49	80	56	51	67	50	58	117	163	51	62	119
Exchangeable	Maximum	0.30	0.35	0.36	0.57	0.67	0.79	0.70	1.8	1.2	3.1	4.9	1.6	1.7	2.6
	Minimum	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00
	Mean	0.10	0.13	0.07	0.23	0.21	0.15	0.19	0.71	0.65	0.23	1.01	0.57	0.30	0.57
	C.V. (%)	66	64	137	58	66	124	74	58	49	199	77	56	123	96
Carbonate-associated	Maximum	0.73	0.88	1.3	16.8	1.7	1.4	8.9	6.1	4.7	4.9	53.2	5.8	12.3	33.3
	Minimum	0.07	0.09	0.16	0.06	0.24	0.05	0.96	0.71	0.46	0.73	0.33	0.58	0.34	1.4
	Mean	0.34	0.38	0.59	2.8	0.77	0.48	2.8	2.7	2.1	1.8	11.0	2.4	4.9	7.7
	C.V. (%)	41	46	40	137	40	64	70	51	52	55	116	53	56	75
Mn oxide-associated	Maximum	0.36	0.45	0.60	0.58	0.87	0.61	2.2	6.5	5.0	6.6	2.3	4.6	19.1	28.7
	Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.68
	Mean	0.11	0.14	0.18	0.11	0.30	0.20	1.0	0.89	0.70	0.83	0.43	0.82	2.4	3.4
	C.V. (%)	97	106	110	134	92	93	29	123	127	164	136	104	142	108
Fe oxide-associated	Maximum	6.8	2.8	17.1	14.6	6.0	2.5	39.9	42.0	13.3	52.6	47.2	15.6	27.7	61.7
	Minimum	0.29	0.20	1.0	0.66	0.60	0.19	2.6	2.8	1.3	8.2	5.6	1.8	1.8	2.6
	Mean	1.2	0.97	6.7	5.7	2.1	1.2	9.9	8.7	5.1	17.4	22.2	6.1	12.4	25.9
	C.V. (%)	75	52	55	56	49	49	71	62	49	42	39	46	49	54
Organic matter-associated	Maximum	12.6	5.4	23.4	16.2	13.5	6.2	19.2	80.4	28.6	31.1	48.1	39.2	74.9	42.2
	Minimum	0.45	0.28	0.81	0.83	0.58	0.25	0.00	4.3	1.6	6.7	3.3	1.6	3.7	0.0
	Mean	3.7	1.9	6.4	4.1	4.7	2.1	4.8	26.6	10.6	15.4	17.5	13.9	23.0	11.4
	C.V. (%)	62	50	67	60	53	54	92	53	56	30	52	59	62	80
Residual	Maximum	14.5	23.8	61.4	50.0	44.8	16.6	118	89.4	94.2	80.9	71.4	93.1	90.4	92.7
	Minimum	1.40	5.2	1.4	0.61	7.4	2.0	0.00	8.9	63.7	27.2	4.9	52.5	10.4	0.0
	Mean	8.2	15.5	26.4	13.5	27.7	6.4	21.3	60.0	80.4	64.1	47.4	75.8	55.9	50.4
	C.V. (%)	39	30	53	67	34	70	77	25	9.4	16	34	13	41	43
Sum of water-soluble and exchangeable	Maximum	0.44	0.57	0.49	0.65	0.89	0.89	1.39	2.2	1.9	4.9	7.3	1.8	4.8	7.6
	Minimum	0.02	0.03	0.02	0.13	0.09	0.05	0.13	0.18	0.16	0.07	0.49	0.26	0.20	0.31
	Mean	0.15	0.20	0.13	0.30	0.35	0.30	0.37	1.1	1.0	0.45	1.4	0.96	1.4	1.2
	C.V. (%)	53	55	84	40	51	67	54	40	37	156	82	28	66	95

fraction were 10–27% for all the metals. As the organic matter-associated forms include some forms of sulfur-associated heavy metals, oxidation reaction may result in acidification after upland disposal of dredged sediments (Singh and others 2000). However, the previous incubation experiment of soil (pH 5.5) amendment with 46 muck samples at two rates (150 and 300 g kg^{-1} soil) indicated that application of muck sediments slightly increased soil pH, and the pH increased with increasing muck rates. The increase was due to the high water-soluble Na/(Ca+Mg+K) ratio and the presence of carbonates in the muck sediments which could buffer against a decrease in pH (Zhang and others 2002). The residual fraction accounted for more than 45% of the total concentrations in the muck for all the metals (Table 2). The metals tended to be associated with solid components such as silicates, hydrous Fe oxides, and organic matter. The co-precipitation and strong adsorption of heavy metals by Al and Fe oxides and clay minerals have been demonstrated in many studies (Forbes and others 1976; Tiller and others 1984; Harrington and others 1998). These studies indicated that Al and Fe oxides and clay minerals play a major role in the immobilization of heavy metals in soils and aquatic sediments. Limited proportions of available metals, including Cd (water-soluble and exchangeable fractions), in the mucks suggest that the use of the mucks in normal soil conditions may not pose any significant hazards or risk to the environment. Low proportions of nondetrital metals, including water-soluble and exchangeable fractions, in the estuary sediments were also observed by several previous researchers (Allen and others 1990; Surija and Branica 1995; Jones and Turki 1997).

All water-soluble and exchangeable heavy metals (except for exchangeable Cu and Zn) in the muck were significantly correlated with the muck pH ($p<0.01$), suggesting that the water solubilities of these elements increase at a decreased pH. Muck pH may have an important role in controlling the solubility of the heavy metals. However, the positive correlation between exchangeable Cu and pH ($p<0.01$) indicated that exchangeable Cu in the muck was mainly associated with organic matter, as organic matter dissolution was enhanced at elevated pH. Clay content had no significant effects on the water-soluble and exchangeable fractions for all the heavy metals. The water-soluble and exchangeable fractions of the heavy metals were also affected by the total contents in the muck sediment. Water-soluble Cd, Co, Cr and Ni ($r=0.51**$, $0.47**$, $0.40**$, $0.41**$), and exchangeable Cd, Co, Cu, Ni and Pb ($r=0.71**$, $0.71**$, $0.43**$, $0.67**$, and $0.26*$) were positively correlated with their total contents.

Mehlich III-extractable heavy metals

The Mehlich III method was originally developed to evaluate plant-availability of macro- and micro-nutrients in soils (Mehlich 1984; Reed and Martens 1996). The concentrations of Mehlich III-extractable Cd, Co, Cr, Cu, Ni, Pb, and Zn in the muck varied greatly (Fig. 1). Zinc was the most readily extractable, with concentrations ranging from 1.2 to 16.8 mg kg^{-1}. The second most extractable element was Cu with concentrations ranging
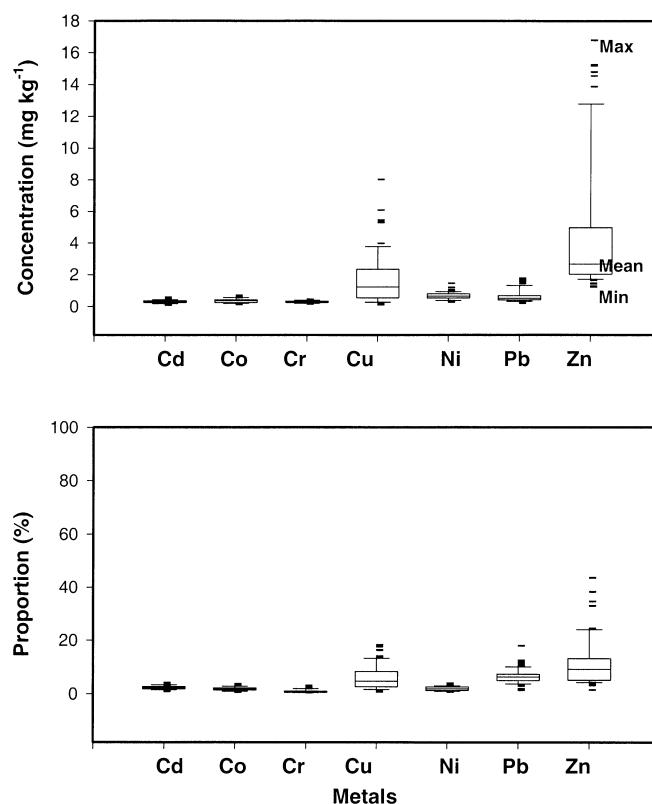

Fig. 1
Range and mean of Mehlich III-extractable heavy-metal concentrations and their proportion in the total contents in the muck sediments ($n=59$)

from 0.11 to 8.0 mg kg^{-1}. Extractable concentrations of Pb ranged from 0.21 to 1.8 mg kg^{-1}, and Ni from 0.28 to 1.5 mg kg^{-1}. Extractable concentrations of Cd, Co and Cr were generally <0.7 mg kg^{-1}. The proportions of the Mehlich III-extractable contents in the total concentrations varied greatly among the Cd, Co, Cr, Cu, Ni, Pb, and Zn. The proportions of Zn, Cu and Pb were relatively high, averaging 12.5, 6.2, and 6.5%, respectively (Fig. 1). This was due to the high concentration of these elements in the carbonate-associated fraction (Table 2). The proportions of Cd, Co, Cr and Ni were <4%, with averages of 2.3, 1.9, 0.93, and 2.0%, respectively. The Mehlich III-extractable amounts of all the heavy metals except for Ni were positively correlated with the respective total concentrations ($r=0.66**$, $0.44**$, $0.73**$, $0.50**$, $0.62**$, and $0.36**$ for Cd, Co, Cr, Cu, Pb, and Zn, respectively). Multiple linear regression equations between the Mehlich III-extractable heavy metals and individual metal fractions obtained from the sequential extractions are presented in the Table 3. Combinations of the metal fractions contributing to Mehlich III-extractable metals varied with metal types. However, the carbonate-associated fraction was consistently correlated with the Mehlich III-extractable metals with the exception of Ni, indicating that the Mehlich III-extractable heavy metals in the muck sediments appeared to be partially from the carbonate-associated fraction, which is readily dissolved in the acid extractant (pH=2). This suggests that Cd, Cu,

Table 3
Regression equations for Mehlich III-extractable heavy-metal concentrations as related to their concentrations in various fractions estimated by the sequential extraction procedure ($n=59$). ** Significant at the 0.01 probability level

Metals	Regression equations[a]	r^2
Cd	$Cd_{M3}=0.070+1.43F_1+0.44F_2+0.33F_3$	0.73**
Co	$Co_{M3}=0.05+0.63F_2+0.27F_3+0.059F_6$	0.62**
Cr	$Cr_{M3}=0.17+0.052F_3+0.013F_5$	0.71**
Cu	$Cu_{M3}=0.18+0.16F_3+0.34F_5$	0.49**
Ni	$Ni_{M3}=0.25+0.85F_1+0.077F_5+0.029F_6$	0.52**
Pb	$Pb_{M3}=0.30+4.56F_3+0.14F_6$	0.72**
Zn	$Zn_{M3}=0.70+1.77F_3-2.95F_4+0.19F_5$	0.92**

[a]F_1, water-soluble; F_2, exchangeable, F_3, carbonate-associated; F_4, Mn oxide-associated; F_5, Fe oxide-associated; F_6, organic matter-associated

Cr, Ni, Pb, Zn, and Co, especially Zn, Cu and Pb, in the muck sediments are potentially more mobile under acidic soil conditions.

Conclusions

Mean total concentrations of Cd, Cu, Cr, Ni, Pb, Zn and Co in the 59 muck sediment samples from the St. Lucie Estuary were 14, 26, 40, 36, 10, 40, and 19 mg kg^{-1}, respectively, which are below critical levels for safe use of solid wastes and industry byproducts in agriculture, as established by the United States Environmental Protection Agency. However, total Cd is higher than the reported average concentrations of the element in municipal composts in the U.S.A. Fortunately, only a small portion of total Cd, Cu, Cr, Ni, Pb, Zn, and Co in the muck sediment was in water-soluble and exchangeable form, whereas the organically associated, carbonate-associated and iron Fe oxide-associated fractions constituted the majority of the nonresidual forms. Obviously, most heavy metals in the muck sediments predominantly occur in weakly mobile or nonbioavailable forms under neutral or slightly alkaline, upland soil conditions. Therefore, use of these materials in normal soils should not pose any significant hazards or risk to the environment. However, both fractionation and Mehlich III extraction analysis indicated that the mobility of Cd, Cu, Cr, Ni, Pb, Zn, and Co, especially Zn, Cu and Pb, in the muck sediments may increase under more acidic soil conditions.

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