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Speciation and stabilization of some heavy metals in the sediments from drains, Egypt

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ABSTRACT

Speciation has been used to indicate the chemical forms of metals and to measure their distribution in the sediment. Therefore, sequential extraction techniques were used to distinguish between different physicochemical states of metals and give detailed information on mobilization and their transportation. This work aimed to determine the total metals concentrations and their fractionation pattern (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in the sediment samples. Also, solidification/ stabilization processes were used to reduce the mobility of metal contaminants by the addition of an agent that solidifies and then immobilizes the metals. The data showed that metal fractionation is relatively stable under normal conditions except for Cd, Zn, and Mn, which were distributed mainly in the mobile fraction for all samples of Talkha drain, Egypt, while, in Rahway drain, Egypt, all heavy metals were found in the stable form bound to organic sulfide and residual fractions except for, Mn and Zn, which distributed mainly in the unstable form. The data showed that 50% of cement kiln dust was sufficient to reduce the mobility of metals by increasing their percentages in the stable forms.

Keywords: Sediment; Sequential extraction procedure; Stabilization; Cement kiln dust

1. Introduction

The environmental pollution due to developments in technology is one of the most significant problems in Egypt. Heavy metals are discharged into the environment through numerous industrial activities. The specific problem associated with heavy metals in the environment is their accumulation in the food chain and persistence in nature [1–4].

In the Nile delta region, there are several “hot spots” of pollution. One of these is due to wastewater discharged from Talkha nitrogen fertilizer factory into Damietta Branch. Another example is the severely polluted El-Rahawy drain, which discharges its water into the southern part of Rosetta Branch. This drain contains raw wastewater from industrial, domestic, and agricultural runoff collected from El-Giza district.

Sediments can act as both carriers and potential sources of contaminants in an aquatic environment [5–7]. Because the metals can be either adsorbed onto sediments or accumulated by benthic organisms to toxic levels, the bioavailability and subsequent toxicity of the metals have become the major research topic associated with sediments [8–10].

Consequently, identification of the geochemical phases of metals and the strength of bonds [7] are necessary to evaluate the availability and capacity of

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mobilization of heavy metals (i.e. the more mobile the metal is, the more risk associated with it) in sediment [11,12]. These kinds of studies have often gone into more depth by the use of sequential extractions [3].

Different sequential extraction schemes have been used by several authors [7,12–14] to provide information about the mobility, availability, and the fractions of metals in the different lattices of different types of sediments, namely, lake, river, coastal estuarine, and marine in comparison with the total metals content.

This study used the sequential extraction scheme of Tessier et al. [15] which was modified by Elsokkery and Müller [16], where metal ions in sediments are partitioned between the different phases, i.e. exchangeable (Fraction I), carbonates (Fraction II), iron and manganese oxides (Fraction III), organic sulfide (Fraction IV), and residual (Fraction V). In addition, metal ions are bounded with these solid phases by different mechanisms like ion exchange, outer- and inner-sphere surface complexation (adsorption), precipitation, or co-precipitation.

Many methods are implemented worldwide to remediate heavy metals in sediments, i.e. sequential extraction, pretreatment, physical separation processes, washing, thermal extraction, bioremediation, electro kinetics, solidification/stabilization, and vitrification [17]. The most important of which is Solidification/Stabilization (S/S) treatment that involves mixing a binding reagent into the contaminated media or waste [18]. Successful treatment is accomplished through physical changes in the waste form, and often, chemical changes to the hazardous constituents themselves.

According to USEPA [19], stabilization refers to techniques that chemically reduce the hazardous potential of a waste by converting the contaminants into less soluble forms, while solidification refers to techniques that encapsulate the waste, forming a solid material.

The objectives of this study are: (1) evaluating the total metal content and the different chemical forms of heavy metals in sediment, (2) investigating a suitable method for heavy metals remediation in contaminated sediment, and (3) evaluating the efficiency of stabilization methods for heavy metals in the contaminated sediments using sequential extraction procedure.

2. Materials and methods

Four samples (T1, T2, T3, and T4) were collected from the different points along the drain of wastewater disposal from Talkha nitrogen fertilizer factory which lies at 126 km north of Cairo after Talkha power station and finally discharges its water into Damietta branch. The locations of each sites according to the point of discharge (source of pollution) are shown in Fig. 1, where T1: in front of industrial discharge of Talkha Fertilizer, T2: 5 m downstream from the drainage of Talkha Fertilizer factory, T3: 10 km downstream from the drainage of Talkha Fertilizer factory, and T4: 15 km downstream from the drainage of Talkha Fertilizer factory. On the other hand, three samples (R1, R2, and R3) from El-Rahawy drain, which lies at 30 km north to Cairo at Al-Kanater and discharges its water into the southern part of Rosetta Branch, are shown in Fig. 2, where R1: at the beginning of Rahway drain, R2: almost in the middle of Rahway drain, and R3: at the end of Rahway drain. Sediment samples were collected using an Eckman sampling device.

Polyethylene scoops and cans used for sampling and storage of sediment samples were cleaned by rinsing with distilled water and kept in 0.1 M HNO_3 for several days before use. The collected samples were dried in an oven at 105˚C for 2 days, ground in an agate mortar. Finally, to normalize the variations in grain size distributions, the dried sediment samples were sieved to 0.2 mm.

All chemicals used were of analytical reagent grade from Merck, Fluka, or Aldrich Company. Freshly prepared daily-diluted solutions were prepared using distilled water and all glassware and plastic containers were washed with 15% nitric acid solution and rinsed thoroughly with distilled water.

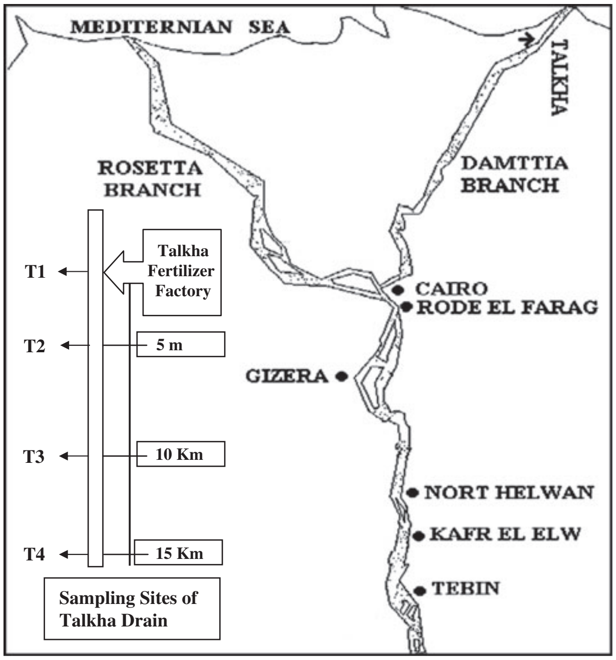

Fig. 1. Sites of sediment samples from Talkha drain.

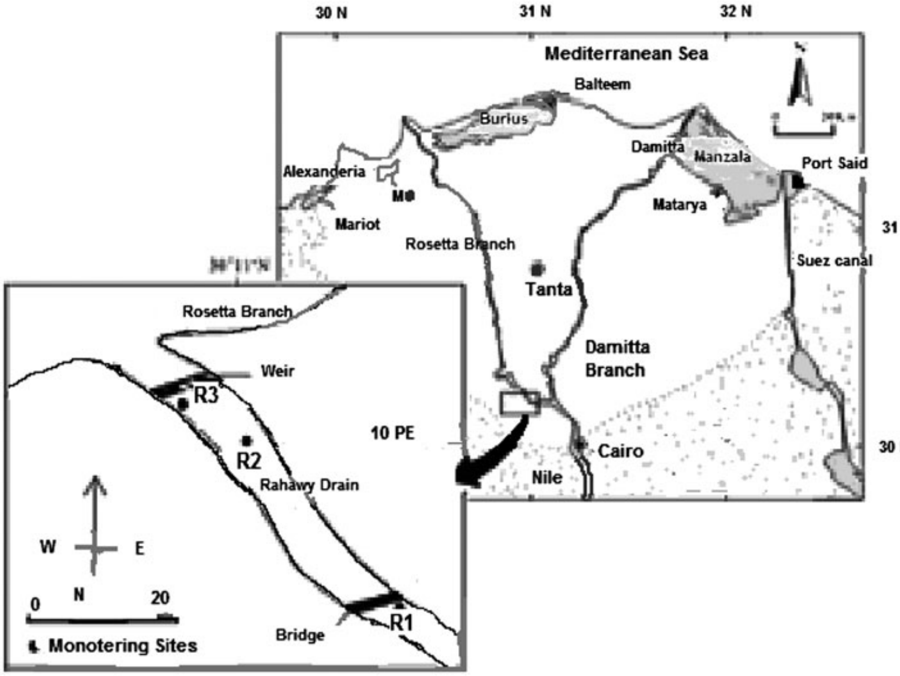

Fig. 2. Sites of sediment samples from Rahawy drain.

2.1. Experimental procedure for metals speciation in sediment

The metals speciation using sequential extraction scheme and procedure proposed by Tessier et al. [15] and modified by Elsokkery and Müller [16] was used to fractionate the metals into the following five operational steps:

Fraction I: Shaking one gram of dry sample with 8 ml of 1 M magnesium chloride-6 hydrate ($MgCl_2$ $6H_2O$) for 1 h at room temperature.

Fraction II: Shaking the residual solid from fraction I with 8 ml of 1 M sodium acetate anhydrous ($C_2H_3NaO_2$) and adjust pH to 5.0 using acetic acid (99.83% $C_2H_4O_2$) for 30 min at room temperature.

Fraction III: Shaking the residual solid from fraction II with 20 ml of 0.04 M Hydroxylamine hydrochloride ($H_3NO{\cdot}HCl$) in 25% acetic acid (99.83% $C_2H_4O_2$)·(v/v) at 85°C in water bath for 5 h.

Fraction IV: Shaking the residual solid from fraction III with 5 ml of hydrogen peroxide (30% H_2O_2) at 85°C in a water bath for 2 h. Adjust pH to 2 ± 0.2 using Nitric acid (0.02 M HNO_3). Add 3 ml of 30% H_2O_2 again and pH was monitored during the experiments. Then, shake at 85°C in a water bath for 3 h.

Fraction V: Finally, digesting the residual solid from Fraction IV with a mixture of HNO_3, HF, $HClO_4$, and HCl in (4:1:1:1) ratio, respectively for 3 h in a water bath.

The extractions were centrifuged at 2000 rpm for 30 min in each operational fraction step and the supernatant was filtered through filter paper (Whatman No. 4). The residue was washed with 8 ml of distilled water, shaken for 30 min, and centrifuged. The washing solution was combined with the supernatant of each step.

All the experiments were carried out in triplicate and the mean of the quantitative results were used for further calculations. The concentration of metals in all samples were determined according to APHA [20] using atomic absorption spectrometer (Varian SpectrAA (220)).

In order to minimize errors and control the good reliability of the speciation procedure, the percentages of the extracted metal were calculated in relation to the sum of metal fractions, Furthermore, there is relatively good agreement within 10% between the sum of the metal fractions and the total analysis. This is in agreement with Tack and Verlo [21].

The percentage of leaching metals for dry samples was calculated as mentioned elsewhere [22,23] as following:

$$\text{Percentage of leaching metals} = (V_{\mathrm{F}}/DI) \times 100 \tag{1}$$

where D: 1 g dry solids sediment; V_{f}: final volume after dilution to 25 ml; F: concentration of metal in filtrate mg/l; and I: concentration of metal in initial dry solid sample mg/kg.

2.2. *Experimental procedure for metal remediation in sediment*

The processing for solidification and stabilization method involved the following steps:

1. The contaminated sediment samples (T1 and R2) and cement kiln dust which was obtained locally from a cement plant (National Cement Company) were dried in an oven at 105℃ for 24 h, ground, and sieved to 0.2 mm.
2. Mixing the sediment samples with cement kiln dust manually in proportion of 50% (dry weight basis) by adding few drops of distilled water to facilitate curing using a bowl and a rubber spatula.
3. Drying the cured samples in an oven at 105℃ for 24 h and then ground to pass through 0.2 mm sieve.

Select sequential extraction procedure to identify the changes associated with metal speciation and the transformations in the chemical forms of heavy metals in stabilized sediment samples [24,25].

3. Results and discussion

3.1. *Total metal concentrations*

Table 1 represents the average of total metal concentrations and pH of sediment samples from Talkha and Rahawy drains. For Talkha drain, the pH of sediment samples ranged from 7.7 to 9.4 and from 6.8 to 8.0 for Rahawy drain. The neutral pH of the sediment samples collected from the different sampling sites indicated that there is no source of pollution which affects the sediment mineralogy. However, the low and high pH affect sediment mineralogy and also, many biological processes, such as reproduction, cannot function [11].

Also, the highest total metal concentrations of Talkha drain were observed at T1 site and decreased its downstream. The results showed that Talkha drain sediments are enriched with cadmium, copper, iron, manganese, and zinc. In addition, by comparing the total metals concentration at the different sites from Rahawy drain, the results show that sediment at R2 site is relatively enriched with copper (100 mg/kg), iron (23,050 mg/kg), nickel (240 mg/kg), and zinc (440 mg/kg).

3.2. *Metal speciation*

The speciation of metals for different sites along the Talkha drain sediment (T1, T2, T3, and T4) is shown in Table 2. The results showed that Cd, Zn, and Mn mostly occur in the first two fractions (Exchangeable and Carbonate). For Cd, the sum of these fractions were 59.42, 80.01, 50.6, and 30.79% for T1, T2, T3, and T4, respectively, those for Zn were 29.77, 62.04, 22.09, and 15.79 for T1, T2, T3, and T4, respectively, and those for Mn were 38.51, 78.25, 36.89, and 58.1%, respectively. Therefore, Cd, Zn, and Mn can be exchanged easily which means that Talkha drain was exposed to pollution risks from Cd, Zn, and Mn. Overall, the speciation of these metals in the sediments from the four sites exhibited high bioavailability and consequently, these metals posed a high ecological risk. This conclusion is consistent with literature data, which reported that the unstable metal forms are the most important cause of metal contamination in the discharge of industrial wastewater [4,26,27].

Table 3 represents the percentages of metal concentrations at each extraction step in the sediment samples at different sites of Rahawy drain (R1, R2, and R3). For the sediment samples from sites R1 and R3, the results show that all metals (except Mn) were

Table 1
Total metal concentrations and pH in sediment samples of Talkha and Rahawy drains

Sample site	pH	Total metals concentration (mg/kg)							
		Cd	Cu	Cr	Fe	Pb	Mn	Ni	Zn
Talkha T1	9.0	236 ± 18	229 ± 13.5	36 ± 1.33	31,250 ± 2,500	24 ± 1.26	3,675 ± 45.0	28 ± 2.5	2,888 ± 262
T2	9.4	216 ± 9.3	62 ± 2.8	42 ± 0.50	31,590 ± 1907	13 ± 2.4	2,346 ± 80.0	29 ± 1.5	2,250 ± 191
T3	9.1	40 ± 1.16	62 ± 2.0	34 ± 2.1	18,750 ± 1,573	9 ± 1.0	1,151 ± 47.5	33 ± 2.5	1,090 ± 20
T4	7.7	11 ± 0.5	37 ± 1.3	24.5 ± 2.6	12,520 ± 368	5.5 ± 0.28	1,132 ± 45.7	30 ± 1.7	706 ± 20.0
Rahawy R1	6.9	2.37 ± 0.03	63 ± 1.8	53 ± 2.0	54,620 ± 2,290	11.3 ± 0.76	494 ± 4.8	79 ± 18	111 ± 13.0
R2	8.0	3.8 ± 0.45	100 ± 3.4	42 ± 6.7	23,050 ± 902	60 ± 5.0	389 ± 37	240 ± 18	440 ± 18
R3	6.8	2.37 ± 0.08	60 ± 2.6	51 ± 2.1	51,370 ± 2,133	11 ± 1.3	500 ± 28	78 ± 7.3	105 ± 2

Note: Data are represented as means of triplicate samples ± standard deviation.

Table 2
Speciation of heavy metals in sediments of Talkha Drain

Sample site	Heavy metals	Summed total mg/kgm	Exchangeable mg/kgm	%	Carbonate mg/kgm	%	Fe/Mn-oxide mg/kgm	%	Organic-sulfide mg/kgm	%	Residual mg/kgm	%
T1	Cd	222 ± 12.6	28.21 ± 2	12.7	103.7 ± 3	46.7		24.5	25.83 ± 2.5	11.64	9.93 ± 0.4	4.5
	Cu	204 ± 8.7	9.35 ± 1.09	4.6	13.6 ± 1.28	6.6	54.32 ± 5	4.65	50.1 ± 3	24.56	121.5 ± 15.5	59.6
	Cr	31.9 ± 2.4	n.d.	0.0	0.41 ± 0.05	1.3	9.49 ± 0.25	39.25	7.7 ± 0.7	24.14	11.27 ± 0.05	35.3
	Fe	30,747 ± 1,197	240.9 ± 15.6	0.8	214.2 ± 11.8	0.7	12.52 ± 1.4	1.21	622.3 ± 17.8	2.02	29,298 ± 1,112	95.3
	Pb	23.8 ± 0.85	0.88 ± 0.15	3.7	0.88 ± 0.15	3.7	371.66 ± 47.2	22.61	0.79 ± 0.1	3.32	15.87 ± 1.74	67.3
	Mn	3,406 ± 317.5	100 ± 18.7	2.9	1,211 ± 118	35.6	5.38 ± 0.15	34.99	573.3 ± 111	16.83	329.45 ± 39	9.7
	Ni	27.9 ± 2.4	n.d.	0.0	0.64 ± 0.25	2.3	1191.8 ± 124	6.24	9.66 ± 0.15	34.62	15.86 ± 1.74	56.9
	Zn	2734.13 ± 78	11.27 ± 1.67	0.4	802.79 ± 30	29.4	1.74 ± 0.16	23.84	536.9 ± 36.8	19.64	731.44 ± 45	26.8
T2	Cd	202.08 ± 33	10.18 ± 1.48	5.0	151.5 ± 13.3	74.97	651.7 ± 33	16.79	1.94 ± 0.09	0.96	4.525 ± 0.4	2.2
	Cu	61.03 ± 6.9	0.984 ± 0.13	1.6	3.43 ± 0.43	5.6	33.93 ± 2.3	6.47	22.6 ± 3.55	37.00	30.085 ± 5.5	49.3
	Cr	37.33 ± 4.7	n.d.	0.0	0.93 ± 0.25	2.5	3.95 ± 0.13	5.81	6.1 ± 0.25	16.34	28.135 ± 3.1	75.4
	Fe	31588.7 ± 1,760	177.95 ± 14.3	0.6	499.9 ± 26.8	1.6	2.168 ± 0.14	6.09	2,973 ± 221	9.41	26,013 ± 100	82.4
	Pb	13.29 ± 0.99	n.d.	0.0	0.5 ± 0.01	3.8	1924.3 ± 186	26.64	1.75 ± 0.25	13.17	7.5 ± 0.75	56.4
	Mn	2364.3 ± 210	69.76 ± 1.43	2.8	1784.3 ± 99	75.5	3.54 ± 0.2	17.65	13.88 ± 1.93	0.59	79.08 ± 11.3	3.34
	Ni	26.535 ± 33.9	n.d.	0.0	1.28 ± 0.6	4.8	417.25 ± 25.3	19.97	3.24 ± 0.19	12.21	16.72 ± 1.3	63.0
	Zn	2075.73 ± 233	123.375 ± 14.5	5.9	1164.5 ± 117	56.1	5.3 ± 0.46	33.14	35.31 ± 2.5	1.70	64.67 ± 9.5	3.12
T3	Cd	38.92 ± 4.9	5.142 ± 0.66	13.2	14.55 ± 1.45	37.4	687.88 ± 79.5	39.06	1.08 ± 0.03	2.76	2.952 ± 0.1	7.58
	Cu	59.23 ± 6.2	1.44 ± 0.25	2.4	2.86 ± 0.4	4.8	15.2 ± 3.2	6.50	35.51 ± 2.9	59.95	15.57 ± 1.33	26.3
	Cr	30.68 ± 5.7	n.d.	0.0	n.d.	0.0	3.85 ± 0.2	45.57	6.43 ± 0.25	20.96	10.27 ± 1.34	33.5
	Fe	18219.9 ± 1,189	486.86 ± 44.5	2.7	1,442 ± 141	7.9	13.983 ± 0.4	28.31	589.8 ± 62	3.24	10,544 ± 925	57.9
	Pb	9.13 ± 0.97	n.d.	0.0	0.75 ± 0.01	8.2	5157.3 ± 346	6.57	2.75 ± 0.25	30.12	5.03 ± 0.5	55.1
	Mn	1150.48 ± 112	40.79 ± 3.4	3.6	383.5 ± 45	33.3	0.6 ± 0.05	56.42	31.64 ± 3	2.75	45.37 ± 5.3	3.94
	Ni	33.07 ± 6.9	n.d.	0.0	2.87 ± 0.4	8.7	649.14 ± 89	26.43	4.41 ± 0.3	13.34	17.05 ± 1.1	51.6
	Zn	1097.86 ± 117	33.4 ± 2.5	3.0	209 ± 24.7	19.1	8.74 ± 1.3	66.37	63.53 ± 8.4	5.79	63.22 ± 7.4	5.76
T4	Cd	10.37 ± 1.3	0.443 ± 0.09	4.3	2.75 ± 0.3	26.5	728.6 ± 100	31.82	1.06 ± 0.05	10.20	2.82 ± 0.2	27.2
	Cu	34.55 ± 6.6	0.97 ± 0.1	2.8	1.9 ± 0.18	5.4	3.3 ± 0.11	21.42	5.6 ± 0.37	16.21	18.7 ± 1.1	54.1
	Cr	21.62 ± 2.9	n.d.	0.0	0.15 ± 0.024	0.7	7.4 ± 0.12	22.27	1.13 ± 0.07	5.20	15.53 ± 10.4	71.8
	Fe	12515.61±1,090	107.5 ± 14	0.9	95.9 ± 14	0.8	4.816 ± 0.51	18.26	1,328 ± 138	10.61	8698.3 ± 421	69.5
	Pb	5.33 ± 0.46	n.d.	0.0	n.d.	0.0	2285.6 ± 1,084	10.88	0.75 ± 0.14	14.07	4 ± 0.25	75.05
	Mn	1172.5 ± 133	66 ± 5.9	5.6	615 ± 75	52.5	0.58 ± 0.14	28.72	51.12 ± 1.3	4.36	103.4 ± 11.5	8.82
	Ni	31.985 ± 6.1	n.d.	0.0	0.78 ± 0.15	2.4	336.8 ± 19.6	6.22	5.27 ± 0.6	16.48	23.95 ± 2.5	74.9
	Zn	702.74 ± 169	34.6 ± 4.7	4.9	76.4 ± 4.5	10.9	1.99 ± 0.77	69.13	52.45 ± 2.4	7.46	53.47 ± 7.2	7.61

Table 3
Speciation of heavy metals in sediments of Rahawy drain

Sample site	Heavy metals	Summed total mg/Kgm	Exchangeable mg/Kgm	%	Carbonate mg/Kgm	%	FelMn-oxide mg/kgm	%	Organic-sulfide mg/kgm	%	Residual mg/kgm	%
R1	Cd	2.437 ± 0.26	n.d.	0.0	n.d.	0.0	0.117 ± 0.038	4.80	0.47 ± 0.014	19.29	1.85 ± 0.05	75.91
	Cu	62.28 ± 4.9	2.575 ± 0.63	4.1	4.88± 0.2	7.83	3.142 ± 0.26	5.04	15.57 ± 1.54	25.00	36.12 ± 6.43	57.99
	Cr	50.28 ± 8.1	0.26 ± 0.017	0.5	n.d.	0.0	2.83 ± 0.26	5.63	8.46 ± 0.04	16.82	38.73 ± 5.85	77.03
	Fe	52,893 ± 2,609	50.67 ± 6.2	0.1	82.7 ± 10.3	0.16	1964.4 ± 115	3.71	2414.8 ± 312	4.57	48,380 ± 1,631	91.47
	Pb	11.18 ± 0.58	n.d.	0.0	n.d.	0.0	1.583 ± 0.14	14.16	4.1 ± 0.29	36.66	5.5 ± 1.3	49.18
	Mn	481.3 ± 29	72 ± 9.6	14.9	95 ± 10.3	19.74	112.4 ± 12.3	23.35	63.1 ± 0.8	13.11	138.8 ± 16.7	28.84
	Ni	77.3 ± 6.87	7.391 ± 2.8	9.6	n.d.	0.0	6.12 ± 0.26	7.92	18.92 ± 3.87	24.48	44.87 ± 5.86	58.05
	Zn	103.27 ± 9.9	3 ± 0.63	2.9	3.43 ± 0.2	3.32	7.2 ± 0.5	6.97	17.34 ± 2.5	16.79	72.3 ± 9.3	70.01
R2	Cd	3.74 ± 0.32	0.43 ± 0.19	11.5	0.78 ± 0.1	20.73	0.392 ± 0.1	10.5	0.44 ± 0.16	11.82	1.7 ± 0.1	45.5
	Cu	95.85 ± 3.7	3.3 ± 0.13	3.51	5.2 ± 0.7	5.43	4.35 ± 0.33	4.54	52 ± 6.2	54.25	31 ± 5.0	32.3
	Cr	39.15 ± 4.1	n.d.	0.0	1.37 ± 0.1	3.50	2.85 ± 0.57	7.28	8 ± 2.89	20.43	26.9 ± 7.6	68.8
	Fe	23,052 ± 2,500	34.2 ± 5.3	0.15	36.2 ± 9.3	0.16	2,763 ± 158	11.99	3,463 ± 295	15.02	16,756 ± 1,297	72.7
	Pb	55.8 ± 9.1	2 ± 0.25	3.58	4.33 ± 1.3	7.76	12.3 ± 1.15	22.40	28.17 ± 3.6	50.48	9 ± 1.7	16.13
	Mn	385.3 ± 63	48.3 ± 2	12.5	92.8 ± 6.7	24.09	116 ± 7.8	30.13	36.8 ± 4.7	9.55	91.4 ± 10.2	23.71
	Ni	238.91 ± 39	15.6 ± 1.3	6.53	7.4 ± 0.44	3.10	21.5 ± 3.84	9.00	28.66 ± 5.6	12.00	165.8 ± 14.75	69.38
	Zn	437.18 ± 47	41 ± 2.6	9.38	61.4 ± 7.3	14.05	142 ± 14.3	32.48	102.98 ± 19.9	23.56	89.8 ± 15.7	20.54
R3	Cd	2.34 ± 0.11	n.d.	0.0	n.d.	0.0	0.083 ± 0.018	3.54	0.41 ± 0.014	17.50	1.85 ± 0.05	78.96
	Cu	58.31 ± 6.7	2.65 ± 0.21	4.54	4.5 ± 0.36	7.72	2.96 ± 0.1	5.08	13.5 ± 1.7	23.15	34.7 ± 2.5	59.51
	Cr	49.63 ± 7	n.d.	0.0	n.d.	0.0	2.5 ± 0.2	5.04	6.63 ± 0.43	13.36	40.5 ± 18.8	81.60
	Fe	51362.5 ± 2003	49.49 ± 9.3	0.10	76.2 ± 9.4	0.15	1796.7 ± 122	3.50	2333.3 ± 112	4.54	47,107 ± 2,799	91.71
	Pb	10.58 ± 0.34	n.d.	0.0	n.d.	0.0	1 ± 0.2	9.45	2.58 ± 0.29	24.39	7 ± 0.5	66.16
	Mn	499.5 ± 28.9	68.4 ± 9.8	13.7	72.6 ± 10.9	14.53	145.5 ± 19.9	29.13	71.1 ± 9.5	14.23	141.9 ± 7.9	28.41
	Ni	74.26 ± 5.6	5.8 ± 0.3	7.81	n.d.	0.0	6.3 ± 0.18	8.48	17.66 ± 3.5	23.78	44.5 ± 7.9	59.92
	Zn	102.6 ± 11	1.8 ± 0.14	1.75	4.5 ± 0.85	4.39	6.8 ± 1.28	6.63	15.4 ± 3.27	15.01	74.1 ± 10.3	72.22

mainly associated with the residual fraction that can be considered as the environmentally safest component. The high metal concentrations in the residual may indicate that these metals are immobile. This finding is confirmed by some authors [28–30] who reported that the residual fraction is an important carrier for heavy metals in sediments.

Speciation studies showed that Mn was found primarily in the first three fractions for all samples of Rahawy drain. The sum of these fractions was 58.05, 66.76, and 57.35%, for R1, R2, and R3, respectively. This indicates that Mn is in an available form for the environment, which means that Rahawy drain has Mn pollution risk that mostly resulted from anthropogenic activities (industrial and agricultural activities) as mentioned elsewhere [27].

Furthermore, speciation studies of Zn showed that high percentage of Zn (55.91%) was found in the first three fractions of site R2. This indicates that Zn is present in an unstable form therefore, it can be exchanged easily and the most important cause of the Zn contamination is the industrial wastes. On the other hand, Zn is found mainly in residual, organic, and sulfide fractions of site R1 (86.8%) and R3 (87.23%). This is consistent with other reported findings [31].

For site R2, total concentration of Ni is 239.91 mg/kg. From the speciation studies, the percent distribution of Ni fractions was found primarily

Table 4
Percentage of metals speciation in solidified/stabilized (S/S) sediments of Talkha (T1) and Rahawy (R2) using 50% of cement kiln dust

Heavy metals	Sample	Exchangeable %	Carbonate %	Fe/Mn-oxide %	Organic-sulfide %	Residual %
Cd	T1	12.7	46.71	24.47	11.64	4.47
	S/ST1	9.6	19.48	62.04	1.70	7.19
	R2	11.5	20.72	10.48	11.82	45.45
	S/SR2	0.0	0,0	46.32	5.89	48.42
Cu	T1	4.6	6.64	4.65	24.56	59.56
	S/ST1	1.4	4.96	3.76	22.16	67.76
	R2	3.51	5.43	4.54	54.25	32.34
	S/SR2	1.64	3.92	5.98	24.87	63.59
Cr	T1	0.0	1.29	39.25	24.14	35.33
	S/ST1	0.0	1.6	40.33	19.3	38.8
	R2	0.0	3.5	7.28	20.43	68.79
	S/SR2	0.0	4.2	9.26	19.54	67.00
Fe	T1	0.78	0.7	1.21	2.02	95.29
	S/ST1	0.58	0.64	2.36	1.54	94.88
	R2	0.15	0.16	11.99	15.02	72.67
	S/SR2	0.17	0.27	13.44	12.38	73.64
Pb	T1	3.7	3.7	22.61	3.32	66.68
	S/ST1	0.9	2.11	25.6	1.67	69.72
	R2	3.58	7.76	22.4	50.48	16.31
	S/SR2	1.43	9.48	44.46	20.88	23.75
Mn	T1	2.94	35.57	34.99	16.83	9.67
	S/ST1	1.00	11.85	62.87	3.09	31.19
	R2	12.54	24.09	30.15	9.55	23.71
	S/SR2	2.87	8.75	40.19	7.28	40.91
Ni	T1	0.41	29.36	23.84	19.64	26.75
	S/ST1	0.39	6.80	60.38	6.32	26.11
	R2	9.38	14.05	32.48	23.56	20.54
	S/SR2	1.32	9.74	40.84	16.03	32.08
Zn	T1	0.0	2.29	6.24	34.62	56.85
	S/ST1	0.0	0.0	9.16	20.81	70.02
	R2	6.53	3.10	9.00	12.00	69.38
	S/SR2	0.0	0.0	11.73	12.94	75.29

T1: the sample of T1 before mixing with 50% of cement kiln dust, R2: the sample of R2 before mixing with 50% of cement kiln dust, S/ST1: stabilized sample of T1 with 50% of cement kiln dust, S/SR2: stabilized sample of R2 with 50% of cement kiln dust.

in the last two fractions (81.38%) and only 6.53% of the 238.91 mg/kg is found in an exchangeable form. Although there is a high value of total Ni concentration, the speciation studies revealed that there is low pollution risk. This finding is confirmed by several authors [32–35] who mentioned that the availability of metals is closely related to their chemical forms rather than the total concentration i.e. the high total concentrations of heavy metals in sediments may not necessarily indicate anthropogenic contaminations. In addition, the natural occurrence and chemical speciation of metals can complicate the evaluation of potentially polluted aquatic sediment.

3.3. Metal stabilization

At present, there is an urgent importance to find a simple and inexpensive method for the stabilization of heavy metals in sediment samples. Where, there is no consensus between the results obtained through the application of cement or cement kiln dust, the last was chosen for the subsequent studies because it has high cementation properties and is economically cheap [36–38]. From previous studies, it was found that a ratio of 50% of cement kiln dust is efficient to stabilize metals in contaminant sediment [38]. Table 4 represents the results of metals speciation for T1 and R2 before and after stabilization with 50% of cement kiln dust as stabilizer material. The data show that the sum of the percentages for the immobilized forms of metals in the stabilized sample of Talkha (T1) was 70.93% of Cd, 93.68% of Cu, 98.43% of Cr, 98.78% of Fe, 96.99% of Pb, 97.15% of Mn, 100% of Ni, and 93.29% of Zn. Therefore, the order of preferential metals for stabilization by 50% of cement kiln dust was found to be: $\mathrm{Cd} < \mathrm{Cu} < \mathrm{Zn} < \mathrm{pb} < \mathrm{Mn} < \mathrm{Fe} < \mathrm{Ni}$.

Furthermore, the sum of the percentages for the immobilized forms of metals in stabilized sample of Rahawy (R2) was 100% of Cd, 95.8% of Cu, 95.8% of Cr, 99.46% of Fe, 89.09% of Pb, 88.38% of Mn, 100% of Ni, and 88.95% of Zn. The preferential order of metals for stabilization by 50% of cement kiln dust was found to be: $\mathrm{Mn} \approx \mathrm{Zn} < \mathrm{pb} < \mathrm{Cu} < \mathrm{Fe} < \mathrm{Cd} = \mathrm{Ni}$.

The results demonstrated a very good immobilization of metals in sediment samples. The fixing degree of contaminant metals by mixing with a ratio of 50% of cement kiln dust is very efficient. The percentages of Fe–Mn oxide and residual forms increased for all metals, except for Cr and Fe. Our results are in agreement with those reported by several authors [39–41]. Accordingly, it appears that cement kiln dust may hold promise for commercial S/S treatment pending more comprehensive evaluations with contaminated sediments. This would allow for the development of potentially more cost-effective S/S approaches, while, at the same time, increasing the beneficial use of cement kiln dust.

4. Conclusions

Since the mobility of heavy metals is closely related to their chemical form rather than to the total metal concentration, it is important to relate the degree of mobility with risks assessment. Therefore, metal speciation in sediments can indicate potential harm to the environment. Sequential extraction scheme provides valuable information on the mobility of metals in sediment and helps in the prediction of their behavior, where the mobility of metals decrease in the order of extracted fractions from readily exchangeable to residual. All heavy metals at the different sites of Talkha drain are relatively stable under normal conditions, except for Cd, Zn, and Mn, which are distributed mainly in the unstable forms. Therefore, they can be exchanged easily which means that Talkha drain has Cd, Zn, and Mn pollution risk. In addition, all heavy metals at the different sites of Rahawy drain are relatively stable under normal conditions except for Mn and Zn which are distributed mainly in the unstable form. This means that Rahawy drain has Mn and Zn pollution risk and mostly resulted from anthropogenic activities. Finally, cement kiln dust is uniquely suited for use as a stabilizer material for metal contamination in sediments, where it reduces the mobility of metals by increasing the percentages of metal forms in the Fe/Mn-oxide and residual fractions.

References

[1] O. Akoto, T.N. Bruce, G. Darko, Heavy metals pollution profiles in streams serving the Owabi reservoir, Afr. J. Environ. Sci. Technol. 2 (2008) 354–359.

[2] H.S. Lim, J.S. Lee, H.T. Chon, M. Sager, Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea, J. Geochem. Explor. 96 (2008) 223–230.

[3] L. Medici, J. Bellanova, C. Belviso, F. Cavalcante, A. Lettino, P. Pasquale, R.S. Fiore, Trace metals speciation in sediments of the Basento River (Italy), Appl. Clay Sci. 53(2) (2010) 414–442.

[4] Z. Yang, Y. Wang, Z. Shen, J. Niu, Z. Tang, Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, Chin. J. Hazard. Mater. 166 (2009) 1186–1194.

[5] W. Calmano, W. Ahlf, U. Forstner, in: J.A.C. Broekaert, Ş. Güçer, F.Adams (Eds.), Metal Speciation in the Environment. NATO ASI Series, vol. G 23. Springer-Verlag, Berlin, 1990, pp. 503–522.

[6] M. Soylak, S. Yilmaz, Heavy metal levels in sediment samples from lake Palas, Kayseri – Turkey, Fresenius Environ. Bull. 15 (2006) 340–344.

[7] A. Naji, A. Ismail, A.R. Ismail, Chemical speciation and contamination assessment of Zn and Cd by seuential extraction in surface sediment of Klang River Malaysia, Microchem. J. 95 (2010) 285–292.

[8] W.J. Berry, D.J. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin, W.S. Boothman, Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulfide and interstitial water normalizations, Environ. Toxicol. Chem. 15 (1996) 2067–2079.
[9] O.I. Davutluoglu, G. Seckın, D.G. Kalat, T. Yılmaz, C.B. Ersu, Speciation and implications of heavy metal content in surface sediments of Akyatan Lagoon–Turkey, Desalination 260 (2010) 199–210.
[10] S.K. Sundaraya, D.B.B. Nayakb, S. Lina, D. Bhattac, Geochemical speciation and assessment of heavy metals in the river estuarine sediments—A case study: Mahanadi basin, India, J. Hazard. Mater. 186 (2011) 1837–1846.
[11] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Remediation technologies for metal-contaminated soils and groundwater. An evaluation, Eng. Geol. 60 (2001) 193–207.
[12] C. Ianni, E. Magi, F. Soggia, P. Rivaro, R. Frache, Trace metal speciation in coastal and off-shore sediments from Ross Sea (Antarctica), Microchem. J. 96 (2010) 203–212.
[13] P. Svete, R. Milacic, B. Pihlar, Partitioning of Zn, Pb and Cd in river sediments from a lead and zinc mining area using the BCR three-step sequential extraction procedure, J. Environ. Monit. 3 (2001) 586–590.
[14] P. Chakraborty, Speciation of Co, Ni and Cu in the coastal and estuarine sediments: Some fundamental characteristics, J. Geochem. Explor. 115 (2012) 13–23.
[15] A. Tessier, P.G.C. Campbell, M. Bission, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51(7) (1979) 844.
[16] I.H. Elsokkary, G. Muller, Assessment and speciation of chromium, nickel, lead, and cadmium in the sediments of the river Nile, Egypt, Sci. Total Environ. 97/98 (1990) 455–463, doi: 10.1016/0048-9697(90) 90256-T
[17] J-f. Peng, Y-H. Song, p. Yuan, X-y. Cui, G-l. Qiu, The remediation of heavy metals contaminated sediment, J. Hazard. Mater. 161 (2009) 633–640.
[18] T.T. Lim, J. Chu, M.H. Goi, Effects of cement on redistribution of trace metals and dissolution of organics in sewage sludge and its inorganic waste-amended products, Waste Manage. 26 (2006) 1294–1304.
[19] USEPA (United States Environmental Protection Agency), Solidification/Stabilization Resource Guide. EPA/542-B-99-002, Office of Solid Waste and Emergency Response, Washington, DC, 1999.
[20] APHA, Standard Methods for the Examination of Water and Wastewater, 21th ed., American Public Health Association, Washington, DC, 2005.
[21] F.M.G. Tack, M.G. Verloo, Leaching behaviour and solid phase fractionation of selected metals as affected by thermal treatment of a polluted sediment, Int. J. Environ. Anal. Chem. 51 (1993) 167–175.
[22] R.L. Jenkins, B.J. Scheybeler, M.L. Smith, R. Baird, M.P. Lo, R. T. Haug, Metals removal and recovery from municipal sludge, J. Water Pollut. Control Fed. 53 (1981) 25–32.
[23] K.S.L. Lo, Y.H. Chen, Extracting heavy metals from municipal and industrial sludges, Sci. Total Environ. 90 (1990) 99–116.
[24] P.N. Soltanpour, Determination of nutrient availability and elemental toxicity by AB-DTPA soil tests and ICPS, Adv. Soil Sci. 16 (1991) 165–189.
[25] X.L. Qiao, Y.M. Luo, P. Christie, M.H. Wong, Chemical speciation and extractability of Zn, Cu and Cd in two contrasting biosolids-amended clay soils, Chemosphere 50 (2003) 823–829.
[26] K.A. Hudson-Edwards, M.G. Macklin, C.D. Curtis, D. Vaughan, Processes of formation and distribution of Pb-, Zn-, Cd-, and Cu-bearing minerals in the Tyne Basin, northeast England: Implications for metal-contaminated river systems, Environ. Sci. Technol. 30 (1996) 72–80.
[27] H. Akcay, A. Oguz, C. Karapirec, Study of heavy metal pollution and speciation in BuyakMenderes and Gediz river sediments, Water Res. 37 (2003) 813–822.
[28] M. Stone, I.G. Droppo, Distribution of lead, copper and zinc in size-fractionated river bed sediment in two agricultural catchments of southern Ontario Canada, Environ. Pollut. 93 (3) (1996) 353–362.
[29] K.S. Murry, D. Cauvet, M. Lybeer, J.C. Thonas, Particle size and chemical control of heavy metals in bed sediment from the Rouge River, southeast Michigan, Environ. Sci. Technol. 33 (1999) 987–992.
[30] Y. Xiujuan, Y. Yan, W. Wen-Xiong, The distribution and speciation of trace metals in surface sediments from the Pearl River Estuary and the Daya Bay Southern China, Mar. Pollut. Bull. 60 (2010) 1364–1371.
[31] C. Yuan, J. Shi, B. He, J. Liu, L. Liang, G. Jiang, Application of chemometrics methods the estimation of heavy metals contamination in river sediments, Environ Intern. 30 (2004) 769–783.
[32] O. Abollino, M. Aceto, C. Sarzanini, E. Mentasti, The retention of metal species by different solid sorbents. Mechanisms for heavy metal speciation by sequential three-column uptake, Anal. Chim. Acta 411 (2000) 223–237.
[33] W.X. Liu, X.D. Li, Z.G. Shen, D.C. Wang, O.W.H. Wai, Y.S. Li, Multivariate statistical study of heavy metal enrichment in sediments of the Pearl river, Environ. pollut. 121 (2003) 377–388.
[34] J. Hlavay, T. Prohaska, M. Weisz, W.W. Wenzel, G.J. Stingeder, Determination of trace elements bounds to soils and sediment fractions (IUPAC Technical report), Pure Appl. Chem. 76 (2004) 415–442.
[35] U.O. Mingbiao, L.I. Jianqiang, C.A.O. Weipeng, W.A.N.G. Maolan, Study of heavy metal speciation in branch sediments of Poyang Lake, J. Environ. Sci. 20 (2008) 161–166.
[36] H. A. Todres, A. Mishulovich, I. Ahmad, Cement Kiln Dust Management: Permeability, Research and Development Bulletin RD103T, Portland Cement Association, Skokie, Illinois, USA, 1992.
[37] J. Duchesne, G. Laforest, Evaluation of the degree of Cr ions immobilization by different binders, Cem. Concrete Res. 34 (2004) 1173–1177.
[38] M.R. Lasheen, N.S. Ammar, Assessment of metals speciation in sewage sludge and stabilize sludge from different Wastewater Treatment Plants, Greater Cairo, Egypt, J. Hazard. Mater. 164 (2009) 740–749.
[39] C.M. Wilk; Stabilization of Heavy Metals with Portland Cement: Research Synopsis, IS007, Portland Cement Association, Skokie, IL, 1997.
[40] A. Adaska, Solidification and Stabilization of Wastes Using Portland Cement. EB071, second ed., Portland Cement Association, Skokie, IL, 1998.
[41] A. Bhatty, Stabilization of Heavy Metals in Portland Cement, Silica Fume/Portland Cement and Masonry Cement Matrices. RP348, Portland Cement Association, Skokie, IL, 1999.