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NICKEL, COPPER, ZINC AND CADMIUM FRACTIONATION IN MANGROVE SEDIMENTS, RED SEA, EGYPT

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ABSTRACT: Nickle (Ni), copper (Cu), zinc (Zn) and cadmium (Cd) in eight sediment samples from mangrove area, Red Sea, Egypt were fractionated using diethylenetriamine pentaacetic acid (DTPA) and a sequential extraction procedure (SEP). These sediment samples were collected horizontally from two locations (four samples from each site) based on different layer visual characterizations. Sediments were initially characterised using different analytical and statistical procedures. DTPA-extract table metal percent of the total metal content varies widely from 1.93 : 25.6% for Ni, from 3.86 : 18.2% for Cu from 0.6 to 4.1 for Zn and from 3.36 : 11.2% for Cd depending on soil characteristics. There no consistent trend of metal extracted by DTPA as a function of sediment depths although Cd_{DTPA} (%) was increased by increasing sediment depths in site 1 and in site 2. Moreover, metal extracted by DTPA showed no consistent correspondence with any single fraction of SEP. The metal extracted by DTPA showed reasonable correlation with the summation of exchangeable (F1) and carbonate (F2) fractions in both sites. So it may be reasonable to conclude that most 'available' metal is (presumably) surface-bound on $CaCO_3$, rather than occluded within $CaCO_3$ or present as a mixed solid-solution ($Ca_{1-x}M_xCO_3$). Approximately 84%, 30%, 70% and 95% of the variability in PTPA-extractable-Ni, Cu, Zn and Cd (mg kg^{-1}) values for a whole dataset, respectively were explained by the variation in soil pH, (%) SOM, (%) $CaCO_3$ and total metals content. Cd_{DTPA} showed the highest prediction performance while Cu showed the worst case of the regression model in which Cu availability is more likely controlled by either the source of Cu or other conditions rather than sediment properties.

Key words: Sequential and single extractions, heavy metals, mangrove sediment.

INTRODUCTION

It is now widely agreed that the toxicity and the mobility of metal pollutants, such as Ni, Cu, Zn and Cd depend strongly on their specific chemical forms and on their binding state (precipitated with either primary or secondary minerals, complexed by organic ligands, and so on (Mao *et al.,* 2014). Resolving metal fractionation and speciation in soils/sediments is vital to characterising the reactivity, bioavailability and mobility of metals and may serve as an aid to the development of successful metal remediation methods (Ahnstrom and Parker, 2001). Several techniques to determine the reactive pools of trace elements under such conditions have been developed, including: single and sequential extraction procedures (SEPs) (Li and Thornton, 2001). Chemical fractionation methods have been widely used to allocate trace metals into operationally defined pools of putatively distinct biogeochemical forms, classically designated as 'exchangeable', 'carbonate', 'organic', 'hydrous oxide', and 'residual' (Tack and Verloo, 1995). Generally, increasingly aggressive reagents are used, in sequence, to extract increasingly refractory forms of the target metals. However, the limitations of this procedure (and of other SEPs) have been addressed by several researchers

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(Tack and Verloo, 1995; Young *et al.,* 2005). These include the problem of achieving complete and selective dissolution and recovery of trace metals from specific phases in soils and sediments. In spite of these inherent limitations, SEPs are still considered a useful technique for characterizing (fractionating) trace metals in soils and sediments (Tack and Verloo, 1995; Arunachalam *et al.,* 1996) and, at worst, they provide a relative assessment of operationally defined soil and sediment metal fractions for comparative purposes.

A wide range of methods using single extraction steps have also been used to operationally define the fraction of metal that is potentially chemically reactive (Lindsay and Norvell, 1978; Meers *et al.,* 2007). Methods are based on the premise that labile metal is exhaustively solubilised using a single chemical extractant, whereas non-labile and inert metal is left in the solid phase. The DTPA extraction method is widely used, predominantly for the determination of extractable Cd, Cu, Fe and Mn (Laing, 2010). The DTPA method extracts less than the standard EDTA (NH_4OAc + EDTA) method. This may arise partly from the higher pH value of the DTPA extractant (7.3 vs. 5.5), lower concentration (0.005M vs. 0.05M), lower affinity of the DTPA than EDTA (Meers *et al.,* 2007) and lower liquid : solid ratio (2 : 1 vs. 5: 1). Although more sophisticated analytical methods have been developed to estimate the labile metal pool in soil/sediment, single extraction methods are still favoured because they are simple to apply, cost-effective and provide satisfactory results in many cases.

In the current study, we used well defined and characterised sediment samples, using different analytical procedures and multivariant analyses, collected from a highly diversative ecosystem close to Mangrove forest in Red Sea shoreline. The samples were analysed aiming to: (i) quantify the DTPA extraction as a measure of Ni, Cu, Zn and Cd reactivity; (ii) assess whether DTPA extractents in Mangrove sediments can be equated with specific metal fractions determined by a SEP and sediment characteristics; (iii) develop algebra regression model to predict metal lability from sediment properties.

MATERIALS AND METHODS

Sediment Sample Descriptions, Preparation and Characterization

Two sampling sites have been selected. The first site was located 17 km south Safaga at the end of valley Safaga (26° 37" 02' N, 34° 00" 43' E). The second site was located 46 km south Safaga and after the first site by 29 Km (26° 23" 54' N, 34° 07" 15' E). Both areas surrounding mangrove plants are a flatted plain gently sloping towards the sea. From each site, four Sediment samples were collected at different sediment depths depending on changing sediment colours (between 10 cm to 140 cm; May, 2013). Sediment samples were air-dried and sieved to 2 mm. Sediment pH was determined in sediment: water suspensions (1:2.5 ratio). Sediment organic carbon (SOC) concentrations were determined in HCl treated samples using CNS Analyzer (FlashEA® 1112). Sediment organic matter (SOM) were estimated by multiple SOC by the van Bemmelen's factor of 1.72 (Grybos *et al.,* 2007). Total sediment carbonate content was measured by the Collins' Calcimeter method (Piper, 1954). Samples of randomized particles were scanned using scanning electron microscope (SEM) JEOL-JSM-5600 equipped with an energy dispersive X-ray spectrometer (EDX) OXFORD Link-ISIS-300. Some selected samples were examined using X-Ray Diffraction (XRD) powder method utilizing Cu Ka radiation. Samples were scanned from 0 to 60 degrees 2θ. Finely ground sediment (200 mg) was digested using 2.5 ml hydrofluoric acid (HF; 40% AR), 2.0 ml HNO_3, 1.0 ml $HClO_4$ and 2.5 ml H_2O. Multi-element analysis including Ni, Cu, Zn, Cd, P, Na, Mg, Al, K, Ca, Fe, Mn, Co, As, Sr, Sb and U was carried out by ICP-MS (Model X-Series^{II}, Thermo-Fisher Scientific, Bremen, Germany) in diluted sediment digests. The certified reference material NIST 2711 (Montana soil) was used for quality assurance (average recovery for all elements was 96±4%); all analysis were run in triplicates.

Single and Sequential Extraction Procedures (SEPs)

Single extraction has been undertaken using DTPA. Triplicate samples (n = 24) of 4.0 g sediment (< 2 mm sieved) were suspended in 8 ml of 0.005 M DTPA (Lindsay and Norvell, 1978), and shaken on an end-over-end shaker, in Oak Ridge polypropylene centrifuge tubes, for 2 hours. Suspensions were then centrifuged at 2500 rpm for 15 min and the supernatant filtered (< 0.2 µm) into polyethylene tubes containing sufficient HNO_3 to produce 2% acid prior to multi-element analysis by ICP-MS. Sequential chemical extraction was carried out following the method described by Li and Thornton (2001) which was modified by Tessier *et al.* (1979). The extraction was carried out progressively using an initial sediment amount of 1.0 g. The sequence of fractions is nominally designated as 'Exchangeable' (F1), 'Carbonate' (F2), 'Fe/Mn oxides' (F3), 'Organic matter and Sulfides' (F4) and Residual (F5) (total n = 120). After each successive extraction, the supernatant solution was separated by centrifugation and filtration. The final extraction step (F5) was calculated by difference from the total metal content. The concentrations of metals in the filtered fractions were measured by ICP-MS.

Multiple Regression Model to Predict Metal Availability

Multiple regression models were used to predict the available metal pool (as M_{DTPA} extraction, mg kg^{-1}) from sediment pH, SOM (%), total sediment metal content (M_T) and $CaCO_3$ (%) contents (Eq 1).

$$M_{DTPA} = a + b(pH) + c\,(\%CaCO_3) + d\,(\%SOM) + e(M_T) \quad (1)$$

Where the regression coefficients (a, b, c, d and e., can be positive or negative), were optimised using the Solver function in Microsoft Excel 2016. The overall goodness fit for all measured and modelled metal availability was determined based on R^2 and the residual standard deviation (RSD) (Eq 2):

$$RSD = \sqrt{\frac{1}{n-c}\sum_{i=1}^{n}(M_i - P_i)^2} \quad (2)$$

Where M_i and P_i are the measured and predicted values of metal (mg kg^{-1}) using equation 2, n is the number of the observed values (n = 8) and c is the number of fitted coefficients in equation 2 (typically 5).

RESULTS AND DISCUSSION

General Sediment Characteristics

Sediment pH, $CaCO_3$, SOM (%) and multi-element concentrations in the sediment datasets are summarized in Table 1. Sediment samples had a narrow range of pH (7.81–8.39) with (%) SOM ranging from 0.893 to 3.84% where, in general, the least amount of organic matter was associated with relatively high sediment pH and *vice versa.* All sediments were calcareous in nature with carbonate contents (as (%) $CaCO_3$) ranging from 10.2 to 78.8%. Carbonates seems to be relatively increased as a function of sediment depths in both sites with exemption in P1-1 (sediment profile 1-layer 1) and P2-3 (sediment profile 2-layer3). All sediment samples were enriched by major cations (Na, Mg, Al, K, Mn and Fe) as affected by seawater continuous tidies from Red Sea shoreline (Table 1). The average element concentrations in site 1 were higher than those in site 2 with exception of Mg, Ca and Sr (Table 1). There are no clear trend in increasing or decreasing elements as a function of sediment depths. However, the majority of elements depict higher concentrations in layer 2 in site1 (such as Ni, Cu, Zn, Cd, Na, Al, K and Co). In site 1, the average total P, Na, K, Mn, Co and Sb concentrations, were approximately double than that of the site 2. The higher P concentration and associated elements found in Site 1 sediments is likely to be an outcome of a cumulative historical deposition of the raw materials of rock phosphate from sources linked to the nearby old phosphate trading harbour located at Quseir city (26° 41' 54.69" N, 33° 56' 19.34"E). The P results show that the average P concentration at the first profile depths (P = 875 mg kg^{-1}; 10 cm) was higher than that found in deeper subsamples (P = 460 mg kg^{-1}; > 10 cm) in site 1, showing a surface enrichment.

Significant correlations ($P < 0.02$) have been found between P and Ni (r = 0.82), Cu (r = 0.88), Zn (r = 0.78), Cd (r = 0.79), Fe (r = 0.93) and Co (r = 0.94) concentrations in both sites suggesting that the main source of these elements may be derived from a geogenic source (rock phosphate) or rock phosphate behave as adsorptive agent (Azzi *et al.,* 2017). Although multi

Table 1. Sediment pH, $CaCO_3$ (%), SOM (%) and sediment acid digest total element concentrations (mg kg^{-1}) for studied locations as a function of sediment depth (cm)

Location	Site 1				Site 2			
Sediment depth cm	**10**	**60**	**90**	**140**	**10**	**60**	**90**	**140**
pH	8.23	7.88	8.04	8.06	8.39	8.34	7.81	7.98
$CaCO_3$	20	10.2	37	43.6	61.4	75.3	22.7	78.8
SOM	1.01	1.98	2.51	2.13	2.21	0.89	3.84	1.27
Na	19188	23709	19289	16401	11966	8124	19097	7044
Mg	7917	7942	10954	10480	15911	18093	11928	20238
Al	32639	39511	28483	22981	10921	6420	28381	5277
K	10561	12626	8391	7318	4344	2424	10390	1968
Ca	80172	40697	148263	174553	246061	301734	91052	315531
Mn	240	265	214	188	116	71	205	67
Fe	10241	14867	12510	7844	5607	3515	14906	4691
Co	3.44	5.66	3.74	3.28	1.78	1.14	5.38	1.11
As	4.16	8.53	17.7	9.39	4.47	3.27	6.98	13.4
Sr	966	527	1697	1780	2788	3271	1055	2937
Sb	0.33	1.02	1.46	1.17	0.249	0.125	0.776	0.621
U	2.10	4.64	11.5	14.6	3.48	2.82	4.48	11.8
P	875	723	511	460	301	253	631	188
Ni	8.71	16.1	10.1	8.06	4.41	3.39	16.9	6.05
Cu	3.97	6.74	4.59	4.14	2.55	1.57	6.72	1.54
Zn	21.3	31.7	21.6	18.3	15	11.8	42	8.05
Cd	0.086	0.161	0.131	0.128	0.071	0.047	0.144	0.054

element analysis have been measured in all sediment samples, in the current study we only focused on discussing the results related to Ni, Cu, Zn and Cd. Nickel, Cu Zn and Cd concentrations (mg kg^{-1}) ranged from 8.06 to 16.1 (average ± SD = 10.8 ± 3.68), 3.97 to 6.74 (4.86 ± 1.28), 18.3 to 31.7 (23.2 ± 5.82) and 0.086 to 0.16 (0.13 ± 0.03), respectively in site1 while from 3.39 to 16.9 (7.68 ± 6.23), 1.54 to 6.72 (3.09 ± 2.47), 8.05 to 42.0 (19.2 ± 15.4) and 0.047 to 0.144 (0.079 ± 0.044) in site 2, respectively (Table 1). Our results fell in the same concentration ranges measured by Mansour *et al.* (2013) in the same study area while, it gave lower values than those demonstrated by Dar (2002).

In attempt to correlate Ni, Cu, Zn and Cd concentrations with SOM, $CaCO_3$ and mineral oxides as potential sources of surface sorption activity, linear correlation coefficients (Pearson correlations) were calculated between total four metals and SOM (%), total concentration of Fe, Mn and Al. The results showed positive significant correlation values with Fe, Mn and Al ($r > 0.73$; $P < 0.05$) in both sites. However, significant negative correlation has been depicted for (%) $CaCO_3$ in both sites ($r > -0.83$; $P < 0.01$) which indicates that those metals accumulation decreased in sediments, while $CaCO_3$ deposition from marine increased.

Important information on trace element sources and pathways can be obtained from inter-element relationships (Manta *et al.,* 2002). Cobalt showed a very strong correlation ($P < 0.01$) with Ni, Cu, Zn and Cd (r = 0.96, 0.99, 0.93 and 0.95, respectively) which suggests a primary association arising from the isomorphous substitution of Co^{III} and tested metals in Fe/Mn hydrous oxides. This was confirmed from previous results that showed a strong correlation between oxides and tested metals. In addition, Zn was correlated with Cu ($r = 0.95$; $P<0.01$), confirming their probable common origin (sulphides), Cd ($r = 0.82$; $P < 0.05$), confirming their strong geochemical association (Cd occurs as a guest element in Zn sulphides), and Ni ($r = 0.93$; $P<0.01$), suggesting a common mineralogical source. Similar results were obtained by Martn *et al.* (2006) and Nan *et al.* (2002).

Cluster Analysis

To examine the strength of multiple elemental associations from the raw dataset, cluster analysis was undertaken. Fig. 1 shows a dendrogram illustrating possible associations within which it is possible to visually identify several clusters as suggested by Sparks (2003). Cluster (i) (Ni, Cu, Co, Fe, Zn, Cd and (%) SOM), could be indicative of either divalent cations held on SOM as exchangeable cations or (probably) on Fe oxide Also, Cu and Zn in this cluster may occur together in geochemical association (sulphides) (Marzouk *et al.,* 2013b). Cluster (ii) (P, K, Na, Al and Mn), suggests an association either with 2:1 alumino-silicates or Mn oxides. Cluster (iii). (As, Sb and U), again could signify a geochemical or anthropogenic correlation. Cluster (iv) ($CaCO_3$, Ca, Sr and Mg), strongly suggests a link through calcareous derived by marine wave actions as both Ca and Sr could be attributed from sea water.

Principal Component Analysis (PCA)

To study the relationship between numbers of variables and see the main component that may affect them, Principal Component Analysis (PCA) is often used (Halim *et al.,* 2009). Elemental associations in all sediment samples together were further examined by principal component analysis (PCA). All the elements were reasonably well represented by these two principal components (Fig. 2). Loading plots showed a positive value of PC1 probably identifies the influence of hydrous oxide or rock phosphate mineralogy and an association with key trace metals associated with either isomorphous substitution or strong adsorption (such as Ni, Cu, Zn and Cd). Sediment organic matter might play a significant role in adsorbing these elements as well The Sr, Ca and U and As seem to be representing the absence of oxide mineralogy (negative PC2 values) possibly reflecting a calcareous mineralogy. On the other hand, a very narrow range of sediment pH seems to have no influence on different metals existence as it has a separate positive value in PC2.

Electronic scanning microscope (SEM) with EDX and XRD

In attempt to qualitatively measured the main mineralogical fractions in the tested samples, SEM equipped with EDX was undertaken in the top and bottom sediment samples in both sites (at 10 and 140 cm). Fig. 3 shows that SEM image with EDX profile. The results showed that the common fraction was Si in all samples. In site 1, the top layer (P1-1) has almost 100% Silica (SiO_2) while in the bottom layer (P1-4) calcite ($CaCO_3$) exhibit 48%. The existence of Fe in the lower layer may represent a formation of pyrite under reducing conditions. On the other hand, in site2, the top layer (P2-1) showed a significant amount of calcium associated minerals (40%) as recommended by SEM-EDX software. Beside calcite, albite ($NaAlSi_3O_8$), silica, pyrite (FeS_2) and magnesia (MgO) were observed as seen in Fig. 4. In the bottom layer (P2-4), silica was the dominate fraction (56%). However, albite, magnesia, pyrite and alumina (Al_2O_3) were found as well.

In addition, XRD analysis was undertaken for P1-1 and P1-1 as a representative of site 1 and 2, respectively. Marked deficiencies of carbonate mineral was observed in P1-1 (Fig. 4) in consistent with SEM-EDX results (Fig. 3). However, carbonates in the same layer in site 2 (P2-1) showed significant amount as calcite and Mg-calcite. Both minerals were formed either through diagenetic processes and/or ecological environments that prevailed in the study area (Okbah *et al.,* 2005). The silicates included quartz and feldspars in both sites with different distributions as seen from Fig. 4 but with less amounts in P2-1. The dominance of silicate and the marked deficiency of the carbonates in P1-1 (Fig. 4) might suggest either fluviomarine or detritus-origin of the sediments in site 1.

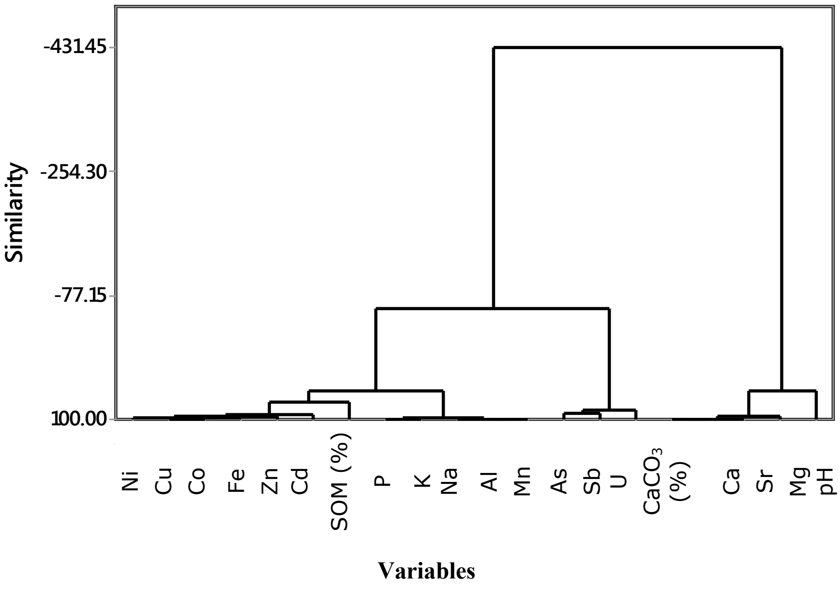


Fig. 1. Dendrogram of elemental analysis on tested sediments. Sediments from two sites and at different depth intervals are included as a single dataset

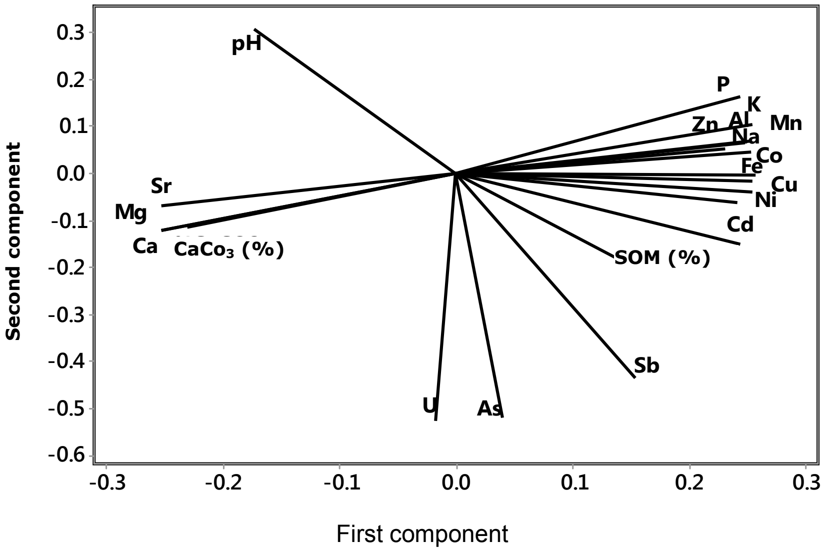
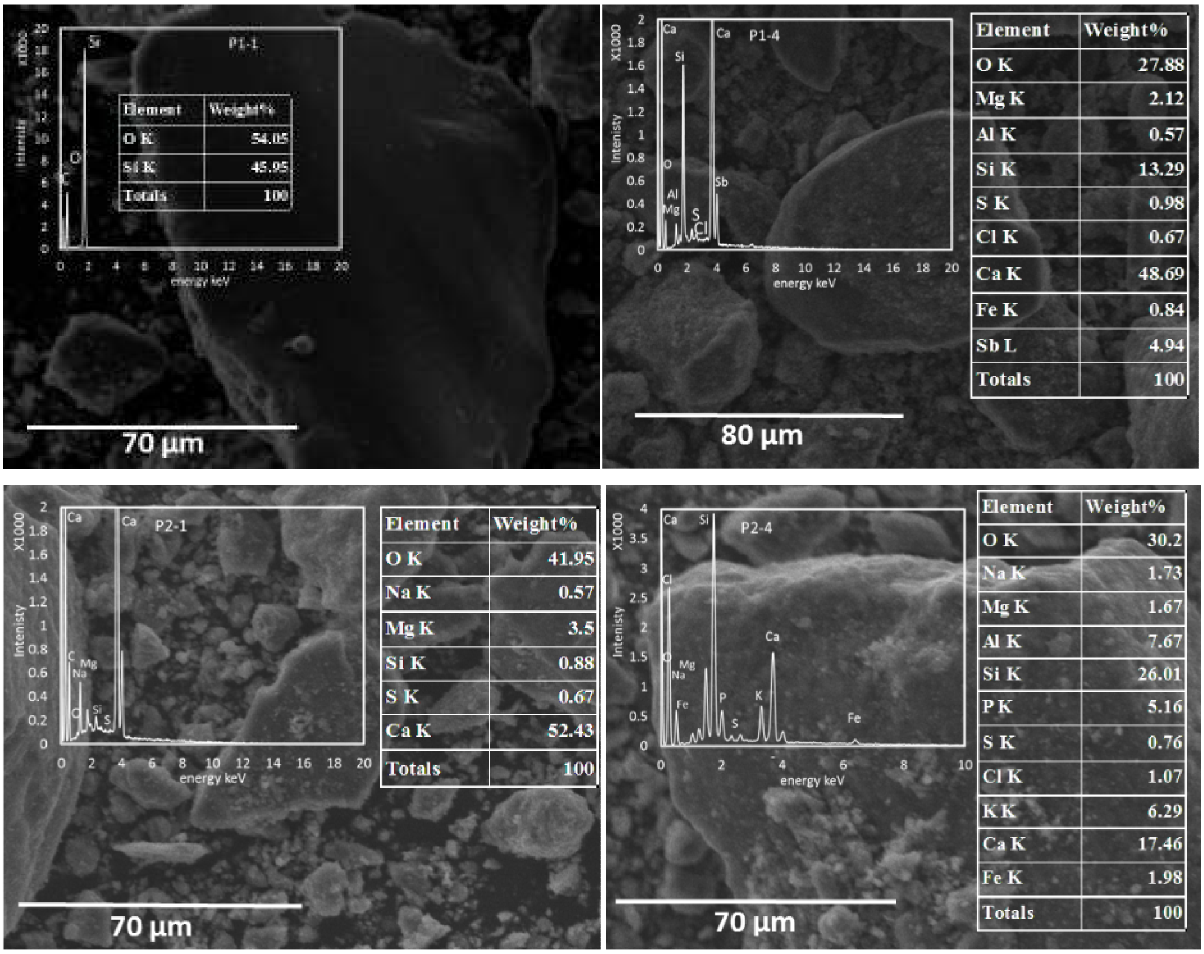


Fig. 2. Principal component analysis loading plots for elemental analysis of tested sediments. Sediments from two sites and at different depth intervals are included as a single dataset



P1-1

Element	Weight%
O K	54.05
Si K	45.95
Totals	100

P1-4

Element	Weight%
O K	27.88
Mg K	2.12
Al K	0.57
Si K	13.29
S K	0.98
Cl K	0.67
Ca K	48.69
Fe K	0.84
Sb L	4.94
Totals	100

P2-1

Element	Weight%
O K	41.95
Na K	0.57
Mg K	3.5
Si K	0.88
S K	0.67
Ca K	52.43
Totals	100

P2-4

Element	Weight%
O K	30.2
Na K	1.73
Mg K	1.67
Al K	7.67
Si K	26.01
P K	5.16
S K	0.76
Cl K	1.07
K K	6.29
Ca K	17.46
Fe K	1.98
Totals	100

Fig. 3. Scanning electronic microscope (SEM) with EDX peaks for selected samples from site 1 and 2. P1 refers to profile 1 in site 1 and the followed number refers to the sediment layer

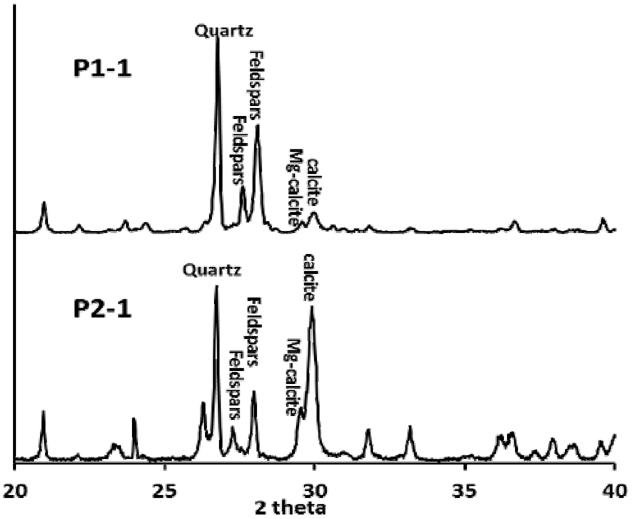


Fig. 4. X-ray diffraction patterns of the sediments of the top layer in site 1 and 2

Fractionations of Ni, Cu, Zn and Cd in Sediment Extracted by DTPA and SEP

DTPA extractable metal from eight sediment samples (under study) ranged from 0.0.31 to 0.87 mg Ni kg^{-1}, 0.19 to 0.33 mg Cu kg^{-1}, 0.14 to 0.57 mg Zn kg^{-1} and 0.0018 to 0.0091 mg Cd kg^{-1}. Mean ± SD values (mg kg^{-1}) were 0.60 ± 0.21, 0.26 ± 0.05, 0.29 ± 0.15 and 0.0061 ± 0.0033 for Ni, Cu, Zn and Cd, respectively. With the DTPA extractability expressed as a proportion of total sediment metal content (%), showed a narrow range across the sediment samples collected from the two sites. In this context, Fig 5 showed Ni_{DTPA}, Cu_{DTPA}, Zn_{DTPA} and Cd_{DTPA} (% of the total metal content) as a function of sediment depth in site 1 and 2.

The results showed that (%) Ni_{DTPA} decreased from 9.07% at 10 cm to 1.92% at 60 cm then increased afterward but it did not reach the proportion exhibited at the top layer in site 1. However, there is no consistent trend for (%) Ni_{DTPA} in site 2 where the highest proportion was found at 60 cm (25.6%). On the other hand, (%) Cu_{DTPA} decreased from 8.35% at 10 cm to 3.86% at 10 cm then increased with increasing sediment depth till 6.81 at 140 cm in site 1. In contrast, (%) Cu_{DTPA} showed no consistent trend in site 2 and behave as (%) Ni_{DTPA} in the same site. For (%) Zn_{DTPA}, the highest proportion was observed in the top layer in site 1 (2.67%) while behave the same trend as (%) Ni_{DTPA} and (%) Cu_{DTPA} in site 2. A clear trend was observed for (%) Cd_{DTPA} as it increased with increasing the sediment depth in site 1 and 2 as seen in Fig. 5. The DTPA extractions seems to be sediment properties dependent. Coloration coefficient analysis for the whole dataset showed that a significant coloration between (%) $CaCO_3$ and the proportion of metal extracted by DTPA for Ni ($r = 0.72$), Cu ($r = 0.82$) and Zn (0.66) while small nonsignificant coloration value was observed with (%) Cd_{DTPA} ($r = 0.28$). this might explain fluctuation of DTPA extraction values for Ni, Cu and Zn as they related to $CaCO_3$ content in the sediments. Moreover, the highest $CaCO_3$ was observed in layer 2 (60 cm) in site 2 which coincide with the highest values of Ni, Cu and Zn as well. The DTPA method was originally developed for diagnosing trace metal nutrient deficiency in calcareous soils (Hooda, 2010). Therefore, it was not intended to simply dissolve all metals present as carbonates. Perhaps for this reason it gives the highest extraction amount with highest $CaCO_3$ content in the sediment samples.

The SEP protocol shows in Figure 6 the proportion (%) of sediment Ni, Cu Zn and Cd in each SEP fraction as average values through all sediment layers. The SEP results indicate that the residual pool (F5) was clearly the largest single fraction for all sediments. Nickel is mainly associated with residual (F5) and Fe-Mn oxide (F3) fractions making up 67.2% and 17.4% for site 1 and 58% and 17.9 for site 2, respectively (Fig. 6). Exchangeable (F1) is the lowest, only accounting for 0.49% and 0.62 for site 1 and 2, respectively. The percentage of organic (F4) and carbonate (F2) were 6.81% and 7.98% for site 1 and 12.3% and 10.9% for site 2, respectively. The average proportion of Ni fractions follows the order as residual > Fe-Mn oxides > carbonate > organic > exchangeable for sites 1 and residual > Fe-Mn oxides > organic > carbonate >exchangeable for sites 2.

The average percentage of the sediment Cu in exchangeable (F1), carbonate (F2), Fe-Mn oxides (F3) and organic (F4) fractions were 3.05, 2.19, 1.60 and 14.1%, respectively, in site 1 while the most of the Cu which is 79.0% presented in the residual fraction (Fig. 6; site 1). The average percentage of the sediment Cu in F1, F2, F3 and F4 fractions were 5.48, 4.33, 6.90 and 11.8%, respectively in site 2 while the most of the Cu which is 71.4% presented in the residual fraction (Fig. 6; site 2). The average amount of Cu in each fraction follows the order residual > organic > exchangeable > carbonate > Fe-Mn oxide and residual > organic > Fe-Mn oxide > exchangeable > carbonate in site 1 and 2, respectively.

Zinc exhibited approximately the same profile in both sites. The highest contents of Zn associated with residual (F5) fraction 96.2% and 94.3% for site 1 and 2, respectively (Fig. 6). The lowest Zn fraction was associated with exchangeable (F1) 0.22% and 0.56% for site 1 and 2, respectively. A further small amount (2.06% for site 1 and 3.37% for site 2) appears in carbonate (F2), about 0.85% and 1.02% present in organic (F4) for site 1 and 2, respectively, and only 0.67% (site 1) and 0.79 (site 2) in Mn and Fe oxides (F3). The percentage of Zn fraction follows the order residual > carbonate > organic > Fe-Mn oxide > exchangeable for both sites.

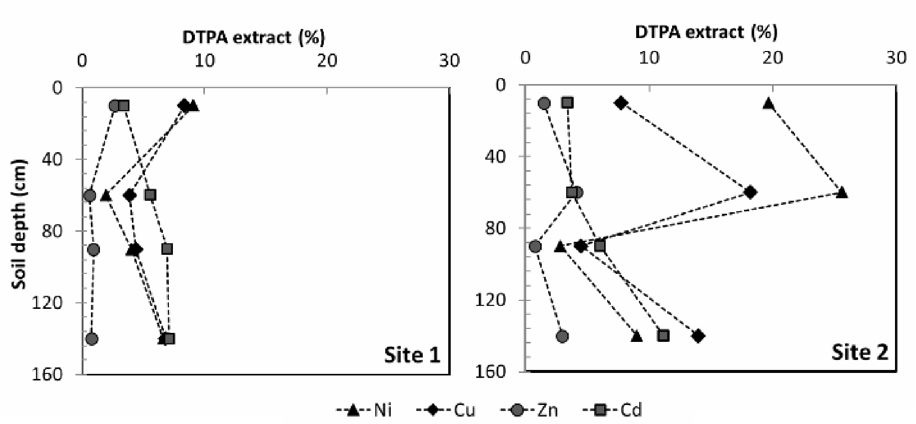


Fig. 5. Nickle, Cu, Zn and Cd extracted by DTPA (% of the total metal content) as a function of sediment depth (cm)

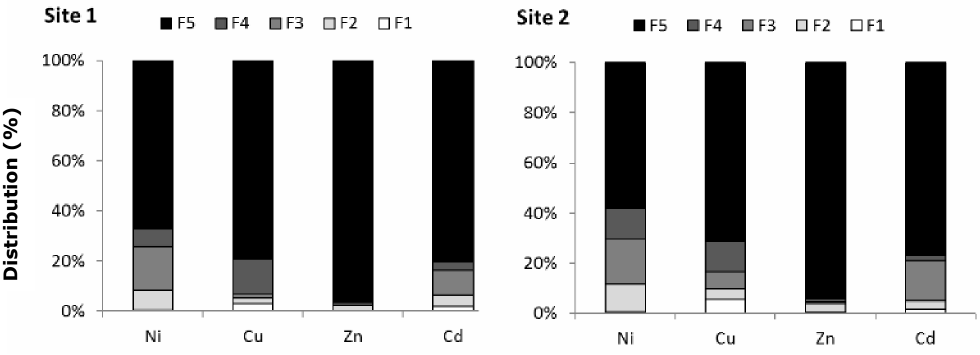


Fig. 6. Average distribution of sediment Ni, Cu, Zn and Cd fractions (%), measured by sequential extraction procedure (F1 = 'exchangeable', F2 = 'carbonate', F3 = 'oxides', F4 = 'organic matter and sulfide' and F5 = 'residual')

Finally, average Cd is mainly associated with residual (F5) fraction making up 80.3% and 76.9% followed by Fe-Mn oxide (F3) as 9.89 and 16.2% for site1 and 2, respectively (Fig. 6). Average exchangeable fraction (F1) is the lowest, only accounting for 1.97 and 1.53% for site1 and 2, respectively. The average percentage of carbonate (F2) and organic (F4) were 4.58% and 3.41% as well as 3.18 and 1.88% for site 1 and 2, respectively. The average proportion of Cd fractions follows the order as residual > Fe-Mn oxide > carbonate > organic > exchangeable for both sites.

In identifying the pollution source and potential for contamination, total metal concentration is useful (Marzouk, 2012). However, rather than total element concentrations, mobility and bioavailability of metals strongly depend on their different binding form or specific chemical speciation (Marzouk *et al.,* 2011). Accordingly, knowledge of metal partitioning between different geochemical phases was necessary to assess the bio-available fraction. Exchangeable, carbonate bound, Fe and Mn oxide-bound, organic-bound, and residual forms were usually distinguished as the chemical species of sediment heavy metals (Lu *et al.,* 2003). Generally, the solubility and bioavailability decreases in the order exchangeable > carbonate-bound > Fe–Mn oxide-bound> Organic bound > residual (Lu *et al.,* 2003).

In general, Ni, Zn and Cd and cadmium show a relatively similar distribution across the range of studied sediments. There is a tiny exchangeable pool and surprisingly little in the carbonate pool, which has definitely dissolved. A substantial proportion of the potentially available metal (non-residual phase) is present in the reducible fraction (F3). A smaller proportion is bound to humus (F4); as expected this is greatest for Cu which is more strongly bound to humus than the other three metals (Lu *et al.,* 2003). The results of this study does not agree with the findings of Okbah *et al.* (2005) who revealed that Cu and Zn were strongly associated with carbonate, Fe-Mn oxides in the Red Sea sediments. In general however, it is clear that neither humus nor $CaCO_3$ seem to act as the major adsorption sites for trace metals. In most cases the major proportion of the trace metals are bound into primary minerals and appear in the residual phase (F5).

Comparing DTPA Extraction with SEP

Regarding comparing DTPA with SEP, in this section we will show the correlation with different fractions of SEP and DTPA extarctents. For the different metal ions as well as the binding strength of the sediments for these ions, extraction of cations from sediments depends upon the binding strength of DTPA. DTPA was intended at the same time, to avoid too much dissolution of $CaCO_3$ with the release of occluded metals, which are normally not available for absorption by Mangrove roots. By compare, during sequential extraction the release of this occluded metal pool is intended. Thus, they are less appropriate for estimating metal availability, while sequential extractions may provide helpful indications on the chemical association of metals. Suitable single reagent leaching tests are more reliable for assessing short term metal availability, such as DTPA extraction (Tack and Verloo, 1995).

It is clear that no corresponding values have been found between Ni- Cu- Zn or Cd-DTPA and any single fraction of SEP. it may either over- or underestimate the DTPA extraction. For example, oxide-bound Ni and Cd (Ni_{OX} and Cd_{OX}) is far greater than the Ni_{DTPA} and Cd_{DTPA} suggesting that most of the Ni_{ox} and Cd_{OX} are occluded within Mn oxides. Marzouk *et al.* (2013a) did not obtain significant correlation for Cd extracted by DTPA and Cd extracted by sequential extraction (Cd_{ox}). The most coherent trend shown is DTPA extracts against the sum of F1 and F2 (F1+F2) (r = 0.94 for Ni, 0.90 for Cu, 0.99 for Zn and 0.91 for Cd; see Fig. 7) and so it may be reasonable to conclude that most 'available' metal is (presumably) surface-bound on $CaCO_3$, rather than occluded within $CaCO_3$ or present as a mixed solid-solution (*e.g.* $Ca_{1-x}Zn_xCO_3$).

By contrast the correlation between Cu_{DTPA} against F4 (humus) shows considerably less values and the results show that $Cu_{hum} > Cu_{DTPA}$ suggesting strong organic binding in such high pH soils which resists DTPA extraction, or possibly exhaustion of the DTPA extractant by Ca. In general Cd_{DTPA} and Cu_{DTPA} are slightly greater than F2 and so the overall conclusion is that the DTPA extractent dissolves most Cd and Cu from (the surface of) a Ca-carbonate phase and also dissolves a proportion of humus-bound metal (eg. Cu). DTPA is used at a fairly low concentration compared to the popular EDTA extractant and it would be expected that mainly 'surface adsorbed' metal would be solubilised by DTPA.

Multiple Regression Model to Predict Metal Lability Measured by DTPA

Multiple regression models were used to predict the Ni-, Cu-, Zn- and Cd-DTPA (mg kg^{-1}) from soil properties (Equation 1). Approximately 84%, 30%, 70% and 95% of the variability in measured metals (mg kg^{-1}) values for Red Sea sediments as a whole dataset for Ni, Cu, Zn and Cd extracted by DTPA, respectively, were explained by the differences in soil pH, (%) SOM, (%) $CaCO_3$ and total metals contents (Table 2). Results showed that the predicted DTPA metal fractions were in reasonable agreement with the measured values particularly for Ni ($r = 0.95$; $P < 0.001$), Zn ($r = 0.94$; $P< 0.01$) and Cd ($r = 0.97$; $P< 0.01$). Cd_{DTPA} showed the highest model performance with lowest RSD (0.0011; Equation 2) and highest R^2 (Table 2). The lowest model performance was observed with Cu_{DTPA} ($R^2 = 0.30$ and RSD = 0.064) in which Cu availability is more likely controlled by the source of Cu rather than sediment properties. However, sediments under the study conditions may be subjected to redox reactions due to the fluctuate tides within a day. Redox potential is not the core of this study and the samples were air dried before undertaken the analytical procedures. Some studies has shown the prediction of metal availability in soils. For example, Mao *et al.* (2014) used basic soil properties

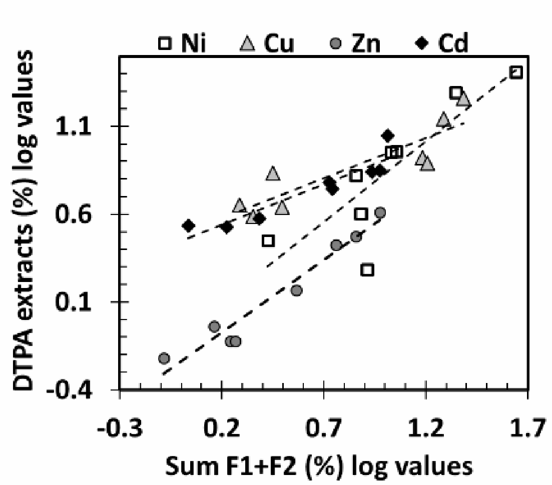


Fig.7. Log-log values show correlation between the summation of F1 and F2 and Ni, Cu, Zn and Cd DTPA extractions

Table 2. Linear regression coefficients (Eq 2), RSD (Eq 3) and R^2 values of individual equations for prediction model of Ni, Cu, Zn and Cd extracted by DTPA (mg kg^{-1})

Regression model	RSD	R^2
Ni_{DTPA}= -9.49 + 1.202 pH + 0.0034 %$CaCO_3$ - 0.0098 %SOM + 0.0256 Ni_T	0.134	0.84
Cu_{DTPA} = 0.32 + 0.003 pH - 0.00121 %$CaCO_3$ - 0.0171 %SOM - 0.0007 Cu_T	0.064	0.30
Zn_{DTPA} = -3.35 + 0.409 pH + 0.00424 %$CaCO_3$ - 0.2007 %SOM + 0.0258 Zn_T	0.128	0.70
Cd_{DTPA} = 0.049 - 0.0067 pH + 0.000078 %$CaCO_3$ - 0.00048 %SOM + 0.0866 Cd_T	0.0011	0.95

such as SOM (as (%) LOI (loss on ignition)), total metal content, pH, available P to predict Pb lability in a wide range of soils (n = 108). They found that 85 and 92% the variability in metal availability could be predicted by total metal content and pH, respectively. Marzouk *et al.* (2013b) found that 66% of the variability in the Pb, Zn and Cd labilities, was predicted by pH, (%) LOI and total metal content in contaminated soils (n = 246).

The general R^2 (0.94) and RSD (0.065) values show good agreement between measured and modelled all metal labilities grouped together (data not shown). A separate stepwise regression indicated that soil pH (82%) for Ni and pH (75%) and total metal content (71.6%) for Cd were the primary determinant of Ni_{DTPA} and Cd_{DTPA} (mg kg^{-1}) for the whole datasets and they were significant at probability < 0.01.

Conclusions

The sediments horizontally collected from two locations in Red Sea shoreline have been characterized by different analytical procedures and single and extraction procedures. Combined determinations of SEP fractionation and DTPA extraction have been used as a means of characterizing Ni, Cu, Zn and Cd in Mangrove sediments. The distribution of total Ni, Cu, Zn and Cd varied among the samples. The results showed that (%) metal-DTPA ranged from 0.06 to 25.6% in the whole datasets for all metals. A plausible explanation for this phenomenon is provided by the significant impact on metal fixation from different sediment components such as $CaCO_3$, SOM and oxides materials. In addition, a relatively no different pattern has been observed in SEP for all studied metals in both sites. No single extraction of SEP was corresponded with DTPA extraction. However, the summation of F1 and F2 represented a highly correlation relationship with all metals extracted by DTPA. Both sediment characteristics and source of metals affect its availability as measured by DTPA in all tested samples. Approximately 84%, 30%, 70% and 95% of the variability of the metal-DTPA concentrations identified in the whole dataset for Ni, Cu, Zn and Cd, respectively, could be explained by the variation in sediment pH, (%) SOM, (%) $CaCO_3$ and total metal content. This study demonstrated that sediment pH and metal contents were the primary determinant of Ni and Cd, respectively. The low effects of soil properties in predicting Cu_{DTPA} in both sites implies that the Cu availability is more likely controlled by the source of Cu or other conditions.

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تجزئة النيكل، النحاس، الزنك و الكادميوم فى رواسب المانجروف – البحر الاحمر – مصر

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تم تجزئة كلا من النيكل والنحاس والزنك والكادميوم فى ثمانية عينات من رواسب المانجروف بالبحر الأحمر – مصر باستخدام مركب داي إرثلين تراي اين بنتا استك أسد (DTPA) والاستخلاص المتعاقب (SEP)، تم اخذ ثمانية عينات رسوبية من قطاعين بناءً على اختلاف خواص الطبقات داخل القطاع الأرضي (أربع عينات من كل قطاع أرضى من ١٠ سم حتى ١٤٠ سم)، تم التوصيف الأولى للعينات باستخدام طرق تحليل مختلفة وتحليلات احصائية متعددة، أظهرت النتائج مجالا واسعا لمقدار العناصر المستخلصة بواسطة مركب DTPA (١,٩٣ إلى ٢٥% من العنصر الكلى بالرواسب) للنيكل و(٣,٨٦ إلى ١٨,٢%) للنحاس و(٠,٦ إلى ٤,١%) للزنك و(٣,٣٦ إلى ١١,٢%) للكادميوم اعتمادا على خواص الرواسب المختلفة، لم يتضح أى علاقة بين مستخلص الـ DTPA وأى جزء مستخلص منفردا من الـ SEP، العناصر المستخلصة بواسطة DTPA أظهرت علاقات معنوية مع مجموع الجزء المتبادل (F2) والكربونات (F2) فى كلا الموقعين. لذلك من المحتمل أن يكون هناك ادمصاص سطحى على كربونات الكالسيوم اكثر من تداخل العناصر فى التركيب البلوري لمعدن الكالسيت، تقريباً حوالى ٨٤% و٣٠% و٧٠% و ٩٥% من الاختلافات فى قياسات مستخلصات الـ DTPA لكل عينات الرواسب مجتمعة بالموقعين لكل من النيكل والنحاس والزنك والكادميوم على الترتيب تم تفسيرها باختلافات الخواص الكيميائية للرواسب مثل الرقم الهيدروجينى والمحتوى من المادة العضوية وكربونات الكالسيوم والتركيز الكلى من تلك العناصر، مستخلص الكادميوم أظهر أفضل تنبأ بينما مستخلص النحاس أظهر أقل أداء لنموذج التنبأ الرياضى حيث أن صلاحية عنصر النحاس على ما يبدوا أنها لا ترتبط بخواص الرواسب الكيميائية وإنما يتم التحكم فيها من المصدر الأساسي لعنصر النحاس أو خواص أخرى لم يتم دراستها.

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