Chemistry Africa (2022) 5:731–744
https://doi.org/10.1007/s42250-022-00351-2

ORIGINAL ARTICLE

Comparative Study of Two Acid Digestion Protocols for Evaluating Potentially Toxic Elements in Surface Sediments Influenced by Sewage Discharge and Sand Mining Activity

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Received: 21 December 2021 / Accepted: 14 March 2022 / Published online: 11 April 2022

Abstract

The study aimed to compare two acid digestion techniques, the partial digestion (total-recoverable) protocol by USEPA 3051 (HNO_3) and total digestion (total-total) method by Hossner (Methods of soil analysis: Part 3. Chemical methods, SSSA and ASA, Madison, pp 49–64, 1996), to recommend an efficient method for evaluating ten potentially toxic elements (PTEs) (i.e., As, Pb, Cu, Cd, Mn, Zn, Cr, Ni, Co, and Fe) concentrations in surface sediments influenced by sewage discharge and sand mining activity. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyzed the PTEs after sample treatment and extraction. The hot plate Hossner method exhibited high PTEs extractability than the microwave-assisted USEPA 3051 method. Generally, As, Pb, Cu, Cd, Mn, Zn, and Cr extracted by both methods depicted sediment background concentrations. No significant differences in concentrations between the two digestion techniques for Ni, Co, and Fe were observed in all samples. Furthermore, lower negative biases were observed between the two digestion techniques for extracting Ni, Co, and Fe in all sediment samples. Also, positive correlations between the total-recovery protocol and the total-total method were observed for Ni, Co, and Fe concentrations in all study sites. This implied that both total-recoverable and total-total methods were efficiently extracted Ni, Co, and Fe in all sediment samples. In addition, the total-recoverable method partially extracted other PTEs in the sediment samples, unlike the total-total technique. The total-recoverable (USEPA 3051) method can be recommended for extracting PTEs in sediment samples originating from lithogenic sources on the condition of using a strong acid such as HF or strong acids combination. The study revealed that sediment physicochemical characteristics influence the extraction of PTEs in sediment. Therefore, sediment factors should be considered when selecting incomplete acid digestion methods for extracting PTEs.

Keywords Agona Abodom · Sediment · Potentially toxic elements · Hossner method · USEPA 3051 method

1 Introduction

Potentially toxic elements (PTEs) are generally the main contributors to environmental pollution. This can be accredited to the severe effect these PTEs have on the quality and purity of the ecology [1–4]. The environmental pollution by PTEs primarily originates from anthropogenic sources or human activities such as combustion of fossil fuel, disposal of leftovers (residues), numerous commercial operations like chemical and metallurgical operations, and mining activities [5]. The quantity of PTEs in soil/sediments may be attributed to biological and chemical weathering; however, Meuser [6] suggested that high contents of PTEs originate from anthropogenic activities. The fundamental phase in determining the likely environmental and human health impacts of PTEs availability in sediments is the measurement of their mass concentrations [7–9]. The quickness and effectiveness of analytical instrumentation for the accurate determination of PTEs in environmental samples have several digestion techniques adapted to estimate the total concentration of PTEs in sediment matrices, including several concentrated acids combinations. Presently, a feasible and accurate quantitating for PTEs levels in various environment

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partitions creates a serious question. Current research has indicated that a clean, simple, and efficient procedure could be an option for the open system complex method to extract PTEs from metals carrying media [10, 11]. The most extensively used digestion methods for extraction of PTEs in metal-containing materials such as soil, sediments, etc., for spectral analyses are conventional (open) acid digestion systems and microwave-assisted acid digestion systems. The conventional digestion techniques deal with the use of an open vessel. Heat is applied in a mixture of acids before the PTEs are extracted from the solid samples [11]. The merits of the conventional digestion system are; comparatively low-cost devices and instruments, requiring little or no advanced sample treatment. However, the conventional digestion methods are ordinarily time-consuming, strenuous, and frequently present a high propensity to contamination [11]. Chen and Ma [12] reported that because the conventional procedures are carried out in unenclosed system under heating, atmospheric contamination and the laboratory technician's health are at risk due to releasing of harmful gases.

On the contrary, the microwave-assisted digestion method is safe and quick with a 90 min maximum duration. Also, because it is a closed system method, it allows the usage of more pressure and temperature. Therefore, a successful dissolution of PTEs is assured. It also reduces loss of unstable compounds, contamination effects, acid consumption, and health risks of laboratory technicians [11, 13, 14]. Lo and Sakamoto [13] opined that several techniques of microwave-assisted digestion had been developed because of the demand for fast and accurate measure of PTEs levels in solid components of sediment, soil, or other media to give a productive breakdown and release of metals. These protocols are myriad and contingent on selecting chemicals and particular heating systems. In studies that employed advanced technology digestion instruments, high pressure has been used to the samples [4, 15, 16]. According to Kingston and Haswell [17], acid digestion by microwave is the most suitable technique for extracting PTEs from composite materials such as soil and sediment containing organic materials, oxides, and silicates. Data from the literature demonstrate that digestion techniques using a combination of acids, HNO_3, or Aqua regia yield approximately 100 percent of the total elemental concentrations depending on the composition of the environmental sample, except PTEs associated with silicates [11, 16]. Thus, the partial digestion techniques employing acids are suitable and efficient for pseudo-total analysis. However, they do undergo complete dissolution with silicates.

There is inadequate information to determine whether the above methods can be used on surface sediments collected from the tropical region influenced mainly by anthropogenic activities such as sewage discharge and sand mining activities. Therefore, this study aimed to compare two digestion techniques, the partial digestion (total-recovery) procedure by USEPA 3051 (HNO_3) [18] and total digestion (total-total) procedure by Hossner [19], for assessing the PTEs content in surface sediments collected from five different locations in Awobrew stream of Agona Abodom in the central part of Ghana, which is believed to be contaminated by sewage discharge and sand mining activities.

2 Methodologies

2.1 Reagents and Chemicals

All reagents and chemicals used were purchased from Merck, Darmstadt, Germany and they were analytical-grade.

2.2 Study Area and Sampling Process

The study area is located at Agona Abodom in the central region of Ghana. The stream is experiencing pollution due to liquid waste discharge from the nearby refuse damping site and dust particles from the illegal sand mining activities. The stream is located east of the town and covers approximately 0.82 hectares, and is 15 km long from the source. The stream coordinates are 5.5310° N; 0.8211° W (Fig. 1). Surface sediment samples from a depth of 0–10 cm were collected from five different locations using a grab sampler in January 2021. The surface sediment samples were subjected to air-dry at 25 °C and ground into a powdery form using mortar and pestle. Samples were sieved via a 3 mm stainless-steel screen and were placed in polyethylene bags at 25 °C for further analysis. The stainless-steel sieve was protected after sieving by plastic to prevent iron filings and other contaminants from settling on the surface and causing damage.

2.3 Physicochemical Parameters

The protocol for determining the particle size distribution was the hydrometer method adapted by Gee and Bauder [20]. An electrical conductivity meter (Model 1152) was used to evaluate the electrical conductivity of the sediment samples. A glass electrode in water suspension in a ratio of 1:4 (sediment/water) was the protocol used to determine sediment's pH. The method formulated by Gupta [21] was used to determine the proportions of carbonate ion (CO_3^{2-}) and hydro carbonate ion (HCO_3^-). This was achieved by titrating with 0.05 mol dm^{-3} sulfuric acid. The calcium carbonate ($CaCO_3$) contents in sediment samples were evaluated using a calcimeter [22]. The turbid metric method (turbidity meter PCE-TUM 50) determined the sulfate ion (SO_4^{2-}) presence in sediment samples, while portable turbidity meter (Model TN480) evaluated turbidity [21]. A flame

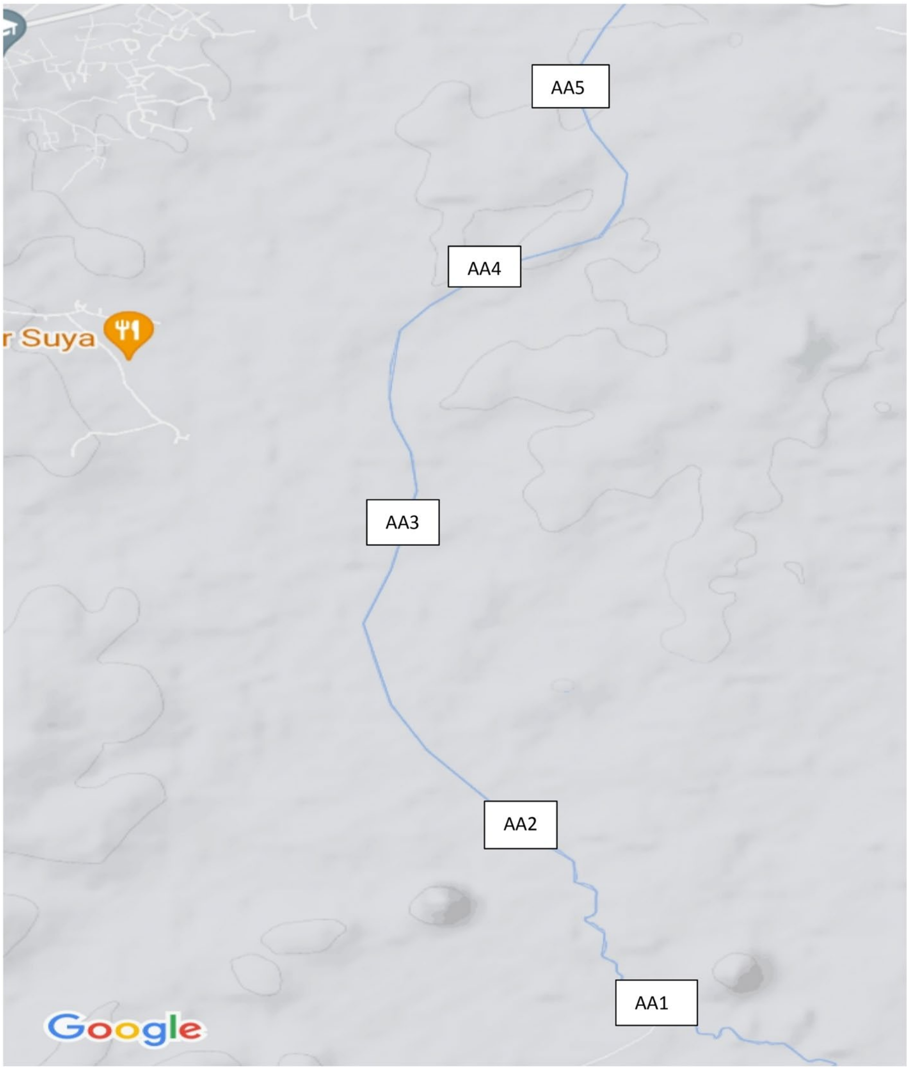

Fig. 1 Study site showing sampling positions (Google map data © 2021)

photometer (Model 410-Sherwood Scientific) was used to measure the soluble Na^+ and K^+ contents in the samples. Soluble Ca^{2+} and Mg^{2+} contents were assessed by titration with ethylene-diamine-tetra-acetic acid (EDTA) 0.01 N, a suitable indicator. The organic carbon component of sediment was evaluated by Gupta [21] procedure using back titration. The sodium acetate ($C_2H_3NaO_2$) method was used to quantify cation exchange capacity (CEC) [22].

2.4 Extraction of PTEs from the Surface Sediments

The total PTE concentrations in surface sediments were extracted by the total-total digestion procedure [19] and the total-recoverable (USEPA 3051) method.

2.4.1 Hossner (HF-H_2SO_4-$HClO_4$) Method

About 0.5 g of sediment sample was placed in a 40 mL crucible, and a few drops of H_2SO_4, 18 M (98%), were added. Then, 6 mL of HF 29 M (55%) and 1.0 mL of $HClO_4$ 15 M (85%) were added. The crucible with mixture content was heated on a hot plate (Model sx-a13) until the $HClO_4$ fumes were depleted. The crucible was removed from the hot plate and allowed to cool. About 7 mL of HF was added to the content in the crucible and then placed in a muffle furnace (Model sx-5-12) at 250 °C for heating until dry. The addition of acids was repeated when the content in the crucible was not clear after cooling and still had organic matter until a clear solution was obtained. After cooling and obtaining a clear solution, 7 mL of HCl 8 M (98%) and 10 mL ultrapure water was added to the content in the crucible and heated until boiling. Subsequently, the crucible with the solution was removed from the hot plate to cool. Filtration via Whatman No. 42 filter paper followed, and after filtration, the filtrate was transferred quantitatively to a 30 mL volumetric flask by topping up with ultrapure water. The solution was kept in a 50 mL calibrated plastic bottle at 6 °C. The filtered solutions were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Perkin elmer optima 3000 ICP-OES, Model: 3000, S/N: 149091). The operating conditions of ICP-OES include; RF is 1100 W, view height is 5 mm, gas used is argon 99.999%, plasma gas is 0.6 L/min, Auxiliary gas is 10 L/min, nebulizer gas is 0.65 L/min, sample is 2 mL/min, aspiration rate read is on-peak, 3 s, and number of replicates was 5.

2.4.2 USEPA 3051 Method

Approximately 0.5 g of a representative sample of a sample site was transferred into a Teflon microwave digestion vessel (Model 4781, 23 mL). 14 mL of concentrated HNO_3 was introduced to the content in Teflon. The sample vessels were placed into a microwave digestion unit (MARS). Suitable software was employed to heat the content to 170 °C for 15 min. The supernatant was collected after the content was digested, followed by filtration using Whatman No. 42 filter paper. The filtrate was diluted to 30 mL using ultrapure water and stored at 6 °C until analysis. ICP-OES was used to analyze the samples for the various PTEs of interest.

2.5 Geo-accumulation Index

The geo-accumulation index (I_{geo}) can be used to evaluate PTE contamination status in sediment. The I_{geo} was computed by the equation (Eq. 1) formulated by Muller [23]:

$$I_{geo} = \log_2\{C_n/(\sqrt{}2.25)B_n\} \quad (1)$$

where C_n denotes the concentration of PTEs detected in the surface sediment, B_n represents geochemical background values for the PTEs (n), and ($\sqrt{}2.25$) is the background matrix correction factor due to lithogenic impacts. Table 1 shows the I*geo* classes and their environmental risk grade.

Table 1 Geo-accumulation index classifications and their environmental risk grade

I_{geo}	Value	Environmental risk grade
	> 5	Very highly polluted
	4–5	Highly polluted
	3–4	Moderately to highly polluted
	2–3	Moderately
	1–2	Moderately to unpolluted
	< 1	Unpolluted

2.6 Quality Assurance and Quality Control (QA/QC)

The limit of detection and limit of quantification (LoD and LoQ) for PTEs were calculated over 10 quantitation's of the blank for each analysis, as $\sqrt{}11*(U_{blank}/s)$ and $\sqrt{}100*(U_{blank}/s)$ respectively, U represents the standard deviation of the blank and s is the sensitivity of calibration curve [3, 8]. The estimated limit of detection (LOD) of various PTEs were; As (0.052 mg/kg), Pb (0.004 mg/kg), Cu (0.051 mg/kg), Cd (0.081 mg/kg), Mn (0.091 mg/kg), Zn (0.036 mg/kg), Cr (0.051 mg/kg), Ni (0.041 mg/kg), Co (0.052 mg/kg), and Fe (0.071 mg/kg). The computed limit of quantification for PTEs As, Pb, Cu, Cd, Mn, Zn, Cr, Ni, Co, and Fe were as follows: 0.158 mg/kg, 0.012 mg/kg, 0.270 mg/kg, 0.246 mg/kg, 0.276 mg/kg, 0.109 mg/kg, 0.155 mg/kg, 0.124 mg/kg, 0.158 mg/kg, and 0.215 mg/kg, respectively.

Each sediment sample was digested and analyzed in 5 replicates (n = 5). The accuracy of PTEs ascertainment by ICP-OES technique was checked by analyzing certified reference material (CRM), sewage sludge amended soil, standardized by BCR 149-R obtained from the Community Bureau of Reference in Belgium. The CRM was prepared for five determinations (n = 5) and air-dried based on Community Bureau of References specifications. The CRM samples were stirred thoroughly to get a homogenous mixture before further analysis. Table 2 shows the results obtained for the analysis of CRM of soil. The percentage recovery obtained for each metal is within the acceptable range (80–110%), according to Carril et al. [24].

2.7 Statistical Analysis

The statistical analysis of data was achieved using the statistical software Statistica for Windows [25]. Minimum, maximum, and average concentrations of PTEs and their standard deviations were calculated. The correlation of two

Table 2 Detected PTEs concentrations (mg/kg d w) in CRM sewage sludge amended soil, standardized by BCR (Community Bureau of Reference) by ICP-OES

Reference material	Certified value ± U^m	Measured value ± U^m (n = 5)	% Recovery ± U^m (%)
As	45.7 ± 0.91	45.29^n	99.10
Pb	165.3 ± 7.4	162.3 ± 1.11	98.19 ± 0.67
Cu	114.7 ± 8.1	115.5 ± 0.98	100.70 ± 0.59
Cd	71.2 ± 2.9	70.68 ± 0.67	99.27 ± 0.94
Mn	98.9 ± 3.4	97.6 ± 0.85	98.69 ± 0.86
Zn	209.3 ± 8.5	206.6 ± 2.04	98.71 ± 0.96
Cr	312.6 ± 14.2	310.3 ± 3.22	99.26 ± 1.03
Ni	53.4 ± 3.3	52.61^n	98.52
Co	55.2 ± 2.8	54.6^n	98.91
Fe	2609.4 ± 40.9	2601.1 ± 3.51	99.68 ± 0.14

^{m}Expanded uncertainty for 95% confidence interval

^{n}Measured value's without uncertainty due to insufficient CRM sample measurement repetitions variables was evaluated with Spearman's rho and Pearson's correlation coefficient.

3 Results and Discussion

3.1 Physicochemical Sediment Characteristics

The physicochemical properties of sediments influence PTEs availability, movement (mobility), and eco-toxicological effects [26]. The study revealed that the sediment texture in samples at study sites AA1, AA2, AA3, and AA4 was sandy loam, while the sediment texture in the sample at study site AA5 was sand (Table 3). The average pH values obtained from the sediment samples were in the range of 7.59 ± 0.08 to 8.30 ± 0.05, suggesting alkaline conditions. Alsaleh et al. reported that a pH value between 6.5 and 7.0 is viewed as a compost indicator where decomposition of organic matter occurs [11]. The obtained results for the EC varied from 0.64 ± 0.01 to 2.13 ± 0.02 µS/m. Sediment samples collected from five study sites in Awobrew stream showed low CEC values (i.e., 6.41 ± 0.04–8.13 ± 0.02 $\text{cmol}_{(+)}$/kg). The major indicator for assessing salinity in sediment is electrical conductivity (EC) [17]. The level of salt in sediment water (salinity) significantly increases sediment EC measurements [11]. Moisture is the primary means to conduct electricity in the sediment but other factors also exist and influence sediment EC evaluations. Some of these factors include; water content—water contains ions that can conduct electricity [17]. Thus, a wet sediment has higher EC than a dry sediment. Porosity can also impact the conduction of electrical current in the sediment by providing more space for water. Therefore, higher porosity increases the potential of conducting electricity when wet. High clay content has higher EC values than sandy soils due to moisture retention [11]. Sediment compaction tend to increase soil EC. A particle that has a high surface area and more pore space tends to have a higher conductivity and directly influencing yields potential. This is why clay generally have a higher conductivity than sandy soils. Mineral soil containing high levels of organic matter (humus) and/or 2:1 clay mineral such as montmorillonite, illite or vermiculite have a high ability to retain positively charged ions (such as Ca, Mg, K, Na, or H). The presence of these ions in the moisture-filled soil pores enhance soil EC as salinity does. Sediment temperature can directly affect EC measurements too but mainly around or below freezing temperatures. Sediment EC measurements decrease as the soil temperature nears the freezing point of water. Below freezing, sediment pores become increasingly insulated from each other and overall soil EC declines rapidly [15]. For $CaCO_3$, samples collected at sample sites AA2, AA3, AA4, and AA5 have high $CaCO_3$ content, with averages of 8.51 ± 0.04%, 15.24 ± 0.06%, 9.33 ± 0.01%, and 6.16 ± 0.03%, respectively while low

Table 3 Physicochemical features of the investigated surface sediment samples at each sample site (n = 5)

Parameters/location	AA1	AA2	AA3	AA4	AA5
Sediment textural characteristics					
Sand	68 ± 0.65	74 ± 1.39	73 ± 4.02	69 ± 2.04	81 ± 4.36
Clay	12 ± 0.30	5.9 ± 0.21	2.3 ± 0.03	6.1 ± 0.16	6 ± 0.11
Silt	20 ± 0.29	20.2 ± 0.46	25 ± 1.06	25 ± 0.44	13 ± 0.21
pH	7.94 ± 0.03	8.30 ± 0.05	7.68 ± 0.05	7.59 ± 0.08	8 ± 0.03
EC µs/m	0.64 ± 0.01	2.13 ± 0.02	2.29 ± 0.01	1.83 ± 0.02	2 ± 0.01
Soluble anions (mmol/L)					
CO_3^{2-}	–	–	0.01	0.05	–
HCO_3^-	0.37 ± 0.01	0.53 ± 0.02	0.89 ± 0.01	0.64 ± 0.01	1.21 ± 0.01
Cl^-	0.15 ± 0.01	0.31 ± 0.07	0.28 ± 0.03	0.25 ± 0.06	3.51 ± 0.02
SO_4^{2-}	4.11 ± 0.02	5.21 ± 0.01	1.94 ± 0.02	9.66 ± 0.03	2.97 ± 0.01
Soluble cations (mmol/L)					
Na	2.06 ± 0.20	1.79 ± 0.09	1.83 ± 0.13	3.02 ± 0.01	3.31 ± 0.30
K	0.93 ± 0.01	0.51 ± 0.04	0.97 ± 0.03	0.35 ± 0.03	0.26 ± 0.07
Ca	2.93 ± 0.41	3.01 ± 0.09	2.66 ± 0.22	2.04 ± 0.05	1.33 ± 0.32
Mg	3.26 ± 0.61	1.09 ± 0.44	1.28 ± 0.52	1.55 ± 0.34	2.07 ± 0.53
Moisture content %	0.83 ± 0.01	1.02 ± 0.01	0.63 ± 0.02	0.67 ± 0.01	0.89 ± 0.02
OM (g/kg)	0.61 ± 0.01	0.84 ± 0.01	0.44 ± 0.03	0.75 ± 0.02	0.41 ± 0.03
Ash content %	89 ± 2.05	87 ± 2.63	91 ± 1.92	89 ± 2.02	91 ± 4.02
CEC ($\text{cmol}_{(+)}$/kg)	8.13 ± 0.02	8.02 ± 0.21	6.41 ± 0.04	7.81 ± 0.02	6.69 ± 0.02
Gypsum %	0.31 ± 0.07	0.18 ± 0.03	0.15 ± 0.03	0.26 ± 0.02	0.51 ± 0.04
$CaCO_3$%	0.81 ± 0.01	8.51 ± 0.04	15 ± 0.06	9.33 ± 0.01	6.16 ± 0.03

content of $CaCO_3$ was recorded in sediment sample at study site AA1 (0.81 ± 0.01%).

The dominant anion identified in the sediment samples was SO4^{2-} and this may be due to the control of tailings derived from the anthropogenic sources such as sewage and sand mining activities that increased its role in sediment contamination [27, 28]. Conversely, the predominant anion was Cl^- and was detected in a sediment sample at study site AA5, attributed to the leaching of salts from the sewage area into the water.

3.2 PTEs and Contamination Levels

Tables 4 and 5 showed the concentrations of total-total (Hossner procedure) and total-recoverable (USEPA 3051 method) (mg/kg d.w) of PTEs, respectively. The results are average concentrations and standard deviations of five determinations (n = 5). PTEs digested by both techniques exhibited significant differences among sediment samples collected from different sample sites. Overall, the PTE concentrations except for Cu and Cr in a sediment sample AA5 near the sand mining activities were noticeably higher than those in the sediment samples polluted by sewage and other sources. The PTEs extracted by the total-total protocol except for Cd and Zn in all sediment samples were lower than the average common range values in soil according to Lindsay [29], as highlighted in Table 4. According to the average shale values by Turekian and Wedepohl [30] for sedimentary rock, the As concentration at sample site AA5 was higher while the concentrations of As in other sites extracted by the total-total protocol were below the average shale values. The concentration of Zn and Cu extracted by

Table 4 PTEs concentrations (mg/kg d.w) extracted by total-total (Hossner) protocol in selected study sites (n = 5)

Location/PTEs	As	Pb	Cu	Cd	Mn	Zn	Cr	Ni	Co	Fe
AA1										
Min	3.45	11	89	3.08	107	155	15	19	2.51	1984
Max	5.78	17	102	9.82	139	199	20	39	9.91	2177
Mean	4.62	14	95	6.45	123	177	17	29	6.21	2081
SD	± 0.48	± 1.25	± 3.09	± 0.61	± 9.06	± 7.28	± 1.94	± 2.11	± 0.69	± 16.51
AA2										
Min	2.99	17	75	1.09	128	139	10	12	1.38	1683
Max	6.07	23	94	3.31	152	208	25	26	4.55	1911
Mean	4.53	20	85	2.20	140	174	18	19	2.97	1797
SD	± 0.82	± 2.41	± 4.17	± 0.04	± 7.93	± 8.16	± 1.83	± 1.03	± 0.12	± 11.04
AA3										
Min	6.01	7	95	–	136	101	5	20	–	1988
Max	17.04	16	133	–	150	152	13	28	–	2504
Mean	11.53	12	114	–	143	127	9	24	–	2246
SD	± 0.92	± 1.06	± 3.41	–	± 9.10	± 6.22	± 0.52	± 1.58	–	± 15.92
AA4										
Min	4.06	5	84	–	163	98	8	21	1.09	1406
Max	5.64	6	258	–	319	142	11	31	3.27	1831
Mean	4.85	5	173	–	241	120	9	26	2.18	1619
SD	± 0.31	± 0.45	± 3.90	–	± 3.02	± 2.24	± 0.42	± 1.51	± 0.38	± 15.11
AA5										
Min	11.19	19	79	3.57	198	165	4	25	4.05	2989
Max	19.09	29	126	5.02	236	206	12	35	6.74	3120
Mean	15.14	24	103	4.30	217	186	8	30	5.40	3055
SD	± 0.59	± 0.57	± 2.11	± 0.41	± 6.48	± 4.37	± 0.61	± 1.64	± 0.31	± 17.56
Common range										
Min	–	2.00	2	0.01	20	10	1	5	1.00	7000
Max	–	200.00	100	0.70	3000	300	1000	500	40.00	55,000
Mean	–	10.00	30	0.06	600	50	100	40	8.00	38,000
Average shale value										
	13.00	20.00	45	0.30	850	95	90	68	19.00	47,200

SD standard deviation, *Min* minimum, *Max* maximum

[a]Lindsay [29]. [b]Turekian and Wedepohl [30]

Table 5 PTEs concentrations (mg/kg d.w) extracted by total-recoverable (USEPA 3051) method in selected sites (n = 5)

Location/PTEs	As	Pb	Cu	Cd	Mn	Zn	Cr	Ni	Co	Fe
AA1										
Min	0.45	0.07	7	0.10	52	71	0.29	17	3.12	1652
Max	0.78	0.12	10	0.24	64	98	0.31	37	6.17	2031
Mean	0.62	0.10	9	0.17	58	85	0.30	27	4.65	1841
SD	±0.11	±0.08	±0.34	±0.04	±1.98	±2.49	±0.04	±0.31	±0.03	±16
AA2										
Min	0.51	0.15	4	0.32	53	64	0.45	14	1.09	1277
Max	0.93	0.29	6	0.49	57	66	0.67	16	3.24	1809
Mean	0.72	0.22	5	0.41	55	65	0.56	15	2.17	1543
SD	±0.09	±0.02	±0.51	±0.07	±2.17	±1.07	±0.09	±0.27	±0.06	±13
AA3										
Min	0.29	0.15	6	–	48	26	0.29	15	–	1812
Max	0.68	0.24	13	–	52	38	0.82	26		2105
Mean	0.49	0.20	9	–	50	32	0.56	20		1959
SD	±0.09	±0.11	±0.62	–	±1.03	±1.05	±0.06	±0.49		±19
AA4										
Min	0.15	0.13	9	–	21	38	0.41	14	2.24	1073
Max	0.58	0.26	13	–	43	49	0.84	31	7.39	1920
Mean	0.37	0.20	11	–	32	43	0.63	23	4.82	1497
SD	±0.16	±0.04	±0.61	–	±2.26	±2.53	±0.09	±0.47	±0.05	±11
AA5										
Min	1.92	1.11	6	2.16	43	89	0.41	23	4.18	2869
Max	2.98	2.19	9	3.59	50	103	0.57	33	6.25	2904
Mean	2.45	1.65	8	2.88	47	101	0.49	28	5.22	2887
SD	±0.31	±0.24	±0.29	±0.49	±2.58	±2.51	±0.09	±0.27	±0.09	±10

SD standard deviation, *Min* minimum, *Max* maximum

the total-total procedure were higher than average shale values in all sediment samples. The average concentrations of Cd extracted by the total-total method at sample sites AA1, AA2, and AA5 were higher than their average shale values.

The PTE concentrations extracted by the total-recoverable method in sediment samples at study sites AA1, AA2, AA3, AA4, and AA5 were 0.62, 0.72, 0.49, 0.37, and 2.45 for As, 0.10, 0.22, 0.20, 0.20, and 1.65 for Pb, respectively. 8.60, 5.05, 9.36, 11.04, and 7.55 for Cu, respectively. 58, 55, 50, 32, and 47 for Mn respectively. 85, 65, 32, 43, and 101 for Zn, respectively. 0.30, 0.56, 0.56, 0.63, and 0.49 for Cr, respectively. 1591, 1193, 1708, 997, and 1887 for Fe, respectively, 0.17, 0.41, not detected, not detected, and 2.88 for Cd, respectively. 0.15, 0.17, not detected, 0.32, and 3.22 for Co, respectively (Table 5). Cd levels were not detectable in sediment samples AA3 and AA4, while Co content was not detectable in a sediment sample at study site AA3 by both digestion methods.

3.3 Geo-accumulation Index Evaluation

The geo-accumulation index values for sediment samples in selected study sites are presented in Table 6. It has been stated that the geo-accumulation index (*Igeo*) can be used efficiently and more significantly in assessing the sediment quality [23]. Based on the obtained *Igeo* values, only Cu was moderately polluted in all sediment samples extracted by the Hossner method. However, the *Igeo* values for Cu in all sediment samples using USEPA 3051 method were < 0, suggesting background concentrations. Based on the obtained *Igeo* values, the concentration of Cd extracted by the Hossner digested method in sediment samples at study sites AA1, AA2, and AA5 showed moderate to highly contamination. The *Igeo* values for Zn extracted by the Hossner method suggested moderately pollution in sediment samples collected from the study sites AA1, AA2, and AA5.

In general, the obtained I*geo* values for PTEs digested using USEPA3051 protocol showed background concentrations in all sediment samples. The *Igeo* values for As, Pb, Cr, Ni, Mn, Co, and Fe extracted by the Hossner method and USEPA protocol exhibited no or low pollution in all sediment samples. This means that As, Pb, Cr, Ni, Mn, Co, and Fe was originated from lithogenic sources and was primarily influenced by sediment-forming factors. However, anthropogenic inputs such mining may contribute to their presence in sediment samples. Several studies have reported

Table 6 Obtained geo-accumulation index values in various sampling sites

	As	Pb	Cu	Cd	Mn	Zn	Cr	Ni	Co	Fe
Location AA1										
Hossner	– 2.08	– 1.08	0.50	3.84	– 3.37	0.32	– 2.97	– 1.81	– 2.20	– 5.09
USEPA 3051	– 4.98	– 8.23	– 2.98	– 1.40	– 4.47	– 0.92	– 8.82	– 1.93	– 2.62	– 5.27
Location AA2										
Hossner	– 2.11	– 0.60	0.33	2.29	– 3.19	0.26	– 2.96	– 2.43	– 3.26	– 5.3
USEPA 3051	– 4.76	– 7.09	– 3.74	– 0.13	– 4.53	– 1.13	– 7.70	– 2.75	– 3.72	– 5.52
Location AA3										
Hossner	– 0.76	– 1.36	0.76	–	– 3.15	– 0.17	– 3.85	– 2.09	–	– 5.00
USEPA 3051	– 1.99	– 7.23	– 2.85	–	– 4.67	– 2.16	– 7.90	– 2.32	–	– 5.17
Location AA4										
Hossner	– 1.43	– 1.88	1.36	–	– 2.40	– 0.25	– 0.56	– 1.98	– 2.39	– 5.45
USEPA 3051	– 5.73	– 7.23	– 2.61	–	– 5.31	– 1.71	– 7.73	– 2.17	– 2.45	– 5.56
Location AA5										
Hossner	– 0.36	– 0.33	0.60	3.26	– 2.55	0.39	– 4.10	– 1.76	– 2.40	– 4.54
USEPA 3051	– 2.99	– 4.18	– 3.07	– 2.68	– 4.77	– 0.50	– 8.12	– 1.86	– 2.45	– 4.62

high contents of PTEs in plants and soil in sites close to the mining centres [11, 31, 32]. Al-Farraj and Al-Wabel reported that urban soils circumvention of the Mahd AD'Dahab mine in Saudi Arabia experiences high PTEs such as Pb, Cd, As, Zn, and Cu, mainly due to mining operation [29]. Alsaleh et al. reported high Zn, Cu, Pb, and Cd concentrations in soil samples from Mahd AD'Dahab [11]. They concluded that the high concentrations of PTEs in the study sites were originated from mining activities. Thus, in this study, high obtained *Igeo* values for Cu, Zn, and Cd in sediment samples could be attributed to illegal sand mining activities near the stream as well as sewage discharge from the nearby refuse damping site. Although, the obtained *Igeo* values for all PTEs extracted by USEPA 3051 method showed background concentrations in all sample sites. However, looking at the obtained *Igeo* values carefully for PTEs extracted by the two methods showed that they have equal potential for extracting PTEs in sediment to ascertain their contamination levels.

3.4 Hossner Method and USEPA 3051 Method Comparison

Spearman coefficient (r_s), regression statistic, and percent biases between two digestion techniques for PTEs are shown in Table 7. The biases were computed as a percentage by the difference between the concentrations of PTEs extracted by the two digestion techniques over the concentration of PTE extracted by the hot plate Hossner procedure [12]. The obtained negative bias values suggested that the concentration of PTEs extracted by the USEPA 3051 technique was lesser than the obtained PTE concentrations extracted by the hot plate Hossner technique (Table 7). Higher negative biases were observed between the two techniques for As, Pb, Cu, Cd, Mn, Zn, and Cr in all sediment samples. In the case of Co and Fe, the percent biases were − 25.12% and − 11.51%, respectively, suggesting moderate biases between the two techniques in sediment sample AA1.

In comparison, the percent bias of Ni was − 8.22%, indicating a lower bias between the two extraction protocols (Table 7). For sediment samples AA2, AA3, and AA4, moderate biases were recorded for Ni, Co, and Fe between the two extraction methods. In contrast, lower negative biases were observed for Ni, Co, and Fe between the two extraction protocols in sediment sample AA5. The lower negative biases showed that Ni, Co, and Fe were extracted satisfactorily using the USEPA 3051 method. Significant negative biases between the two extraction methods for PTEs suggested that USEPA 3051 method was not fully extractable of the selected PTEs in sediment samples. The considerable differences between the two digestion protocols may be attributed to the differences in sediment properties. Chen and Ma [12] suggested that soil/sediment properties are essential to evaluate metal recovery during digestion. Natural and anthropogenic inputs, including the affinity of extractants for PTEs differing in their soft nature, could be the reason for substantial negative biases between the two methods [33]. The obtained results showed significant differences between the two digestion protocols for As, Pb, Cu, Cd, Mn, Zn, and Cr in all study sites.

Concerning the Spearman correlation coefficients, significant differences between total-recoverable and total-total methods were observed for Cu ($r_s = 0.99$, < 0.05) in sediment sample AA1, As ($r_s = 0.99$, < 0.05) in sediment sample AA2, Cd ($r_s = 0.99$, < 0.01) in sediment sample AA2, Cr ($r_s = 0.99$, < 0.05) in sediment sample AA4, Cu ($r_s = 0.99$, < 0.01) in sediment sample AA5, and Zn ($r_s = 0.99$, < 0.01) in sediment sample AA5 (Table 6). Strong positive correlations between the total-recoverable digestion method

Table 7 Spearman coefficient (r_s), regression statistic and percent biases between PTEs concentrations extracted by two digestion methods

PTEs	r_s	Regression statistic		Percent biases	
		Equation	Rp	Mean	±SE
AA1					
As	0.99	Total-recoverable = − 0.1066 + 0.1564(total-total)	0.99	− 87	39
Pb	0.79	Total-recoverable = 0.0359 + 0.0042(total-total)	0.79	− 99	47
Cu	0.99*	Total-recoverable = − 12.596 + 0.2225(total-total)	0.99	− 91	45
Cd	0.87	Total-recoverable = 0.0845 + 0.0133(total-total)	0.87	− 97	47
Mn	0.96	Total-recoverable = 22.932 + 0.2842(total-total)	0.96	− 53	39
Zn	0.95	Total-recoverable = 5.9788 + 0.4432(total-total)	0.95	− 52	33
Cr	0.66	Total-recoverable = 0.2713 + 0.0017(total-total)	0.66	− 98	49
Ni	0.99	Total-recoverable = 1.9803 + 0.085(total-total)	0.99	− 8	43
Co	0.99	Total-recoverable = 2.2167 + 0.391(total-total)	0.99	− 25	48
Fe	0.85	Total-recoverable = − 277 + 1.0181(total-total)	0.85	− 12	2
AA2					
As	0.99*	Total-recoverable = 0.1643 + 0.1227(total-total)	0.99	− 84	45
Pb	0.11	Total-recoverable = 0.2777 – 0.0029(total-total)	0.11	− 99	50
Cu	0.99	Total-recoverable = − 3.0033 + 0.0952(total-total)	0.99	− 94	44
Cd	0.99**	Total-recoverable = 0.2228 + 0.0828(total-total)	0.99	− 81	38
Mn	0.99	Total-recoverable = 28.424 + 0.1903(total-total)	0.99	− 61	36
Zn	0.95	Total-recoverable = 55.367 + 0.0562(total-total)	0.95	− 63	43
Cr	0.99	Total-recoverable = − 0.1246 + 0.69451(total-total)	0.99	− 97	48
Ni	0.97	Total-recoverable = 11.12 + 0.212(total-total)	0.97	− 20	37
Co	0.99	Total-recoverable = 0.1083 + 0.6919(total-total)	0.99	− 27	25
Fe	0.94	Total-recoverable = − 1324.6 + 1.596(total-total)	0.94	− 14	7
AA3					
As	0.99	Total-recoverable = 0.0868 + 0.0345(total-total)	0.99	− 96	45
Pb	0.95	Total-recoverable = 0.0663 + 0.011(total-total)	0.95	− 98	45
Cu	0.99	Total-recoverable = − 11.174 + 0.1802(total-total)	0.99	− 92	37
Cd	–	–	–	–	–
Mn	0.99	Total-recoverable = 6.7781 + 0.3019(total-total)	0.99	− 65	44
Zn	0.99	Total-recoverable = − 2.9592 + 0.2775(total-total)	0.99	− 75	42
Cr	0.99	Total-recoverable = − 0.0148 + 0.0609(total-total)	0.99	− 94	44
Ni	0.99	Total-recoverable = − 12.992 + 1.3907(total-total)	0.99	− 15	35
Co	–	–	–	–	–
Fe	0.97	Total-recoverable = 222.82 + 0.7729(total-total)	0.97	− 13	10
AA4					
As	0.99	Total-recoverable = − 0.9745 + 0.2762(total-total)	0.99	− 95	24
Pb	0.98	Total-recoverable = − 0.1717 + 0.0676(total-total)	0.98	− 98	46
Cu	0.99	Total-recoverable = 6.9954 + 0.0237(total-total)	0.99	− 94	42
Cd	–	–	–	–	–
Mn	0.99	Total-recoverable = -1.3373 + 0.1385(total-total)	0.99	− 87	13
Zn	0.99	Total-recoverable = 11.639 + 0.2646(total-total)	0.99	− 64	7
Cr	0.99*	Total-recoverable = − 0.5313 + 0.1269(total-total)	0.99	− 93	39
Ni	0.99	Total-recoverable = − 18.891 + 1.6065(total-total)	0.99	− 12	34
Co	0.99	Total-recoverable = − 0.2168 + 2.3082(total-total)	0.99	− 11	43
Fe	0.99	Total-recoverable = − 1681.7 + 1.9636(total-total)	0.99	− 8	14
AA5					
As	0.98	Total-recoverable = 0.1331 + 0.153(total-total)	0.98	− 84	24
Pb	0.99	Total-recoverable = − 1.2579 + 0.1212(total-total)	0.99	− 93	29
Cu	0.99**	Total-recoverable = 1.3995 + 0.0599(total-total)	0.99	− 93	43
Cd	0.98	Total recoverable = − 0.7586 + 0.846(total-total)	0.98	− 33	10

Table 7 (continued)

PTEs	r_s	Regression statistic		Percent biases	
		Equation	Rp	Mean	± SE
Mn	0.95	Total recoverable = 15.837 + 0.1419(total-total)	0.95	– 79	30
Zn	0.99**	Total recoverable = 43.97 + 0.301(total-total)	0.99	– 46	21
Cr	0.99	Total recoverable = 0.3305 + 0.0203(total-total)	0.99	– 94	43
Ni	0.99	Total recoverable = 0.0709 + 0.9297(total-total)	0.99	– 7	42
Co	0.99	Total recoverable = 1.1005 + 0.7627(total-total)	0.99	– 3	36
Fe	0.30	Total recoverable = 3192.3 – 0.1(total-total)	0.30	– 6	21

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

and the total-total digestion method for all selected PTEs were observed in all sample sites except Fe. A weak positive correlation ($r_s = 0.30$) was observed between the total-recoverable technique and the total-total digestion method for Fe concentration in sediment sample AA5. This observation indicated that the USEPA 3051 protocol and Hossner method have similar extraction potential for Ni, Co, and Fe in sediment samples influenced by sewage discharges and sand mining activities since their percent biases were lower than other PTEs biases (Table 7). Thus, instead of the Hossner method, it is suggested that the USEPA 3051 protocol can be used as a recommended method in making a general judgment for assessing the concentration of Ni, Co, and Fe in sediments of Africa and other tropical regions. da Silva et al. [14] conducted a study to collate USEPA digestion techniques to extract PTEs in polluted soils; their study concluded that the USEPA 3051A was more efficient for extracting Ni, Zn, Cd, Cu, and Pb as compared to other USEPA protocols. They recommended that microwave closed system procedure is applicable for extracting PTEs on an extensive range of soils with several characteristics. They also suggested that the microwave-assisted digestion method reduces loss of PTEs via volatilization than the open digestion method. In this study, higher concentrations of PTEs were obtained by the extraction of hot plate Hossner method than the microwave-assisted USEPA 3051 method. This implied that a fraction of PTEs remains intact in the sediment samples during total-recoverable digestion [11, 31]. With this scenario, the microwave-assisted acid digestion USEPA 3051 protocol may not be feasible to digest the total concentrations of selected PTEs in sediments under the influence of anthropogenic inputs. It has been acknowledged that the "total-recoverable" digestion protocol such as 3051A, 3051, and 3050 do not retrieve the total concentration of PTEs in soil/sediment [14, 33]. This study confirms the observations of da Silva et al. [14] and Sawhney and Stilwell's study. Violante et al. suggested that a greater quantity of Cr, Fe, Mn, Co, and Ni might remain in alumina-silicate complexes when using microwave-assisted digestion USEPA methods [34]. It has been reported that total-recovery methods, for instance, USEPA 3051 method, cannot wholly digest PTEs but may need strong acid such as HF or acids combination before it can completely digest PTEs [35].

Furthermore, it has been extensively stated that HF in combination with H_2SO_4–$HClO_4$ is needed to extract PTEs completely from silicate structures [36]. In light of the above reasons, the more realistic procedure for pseudo-total analysis and assessing the potentially available fractions for PTEs is the USEPA 3051 method. Even though the USEPA 3051 protocol cannot extract PTEs bound to silicates, it may be feasible to extract PTEs bound to potential sediment fractions, such as organic matter, calcium carbonate, and efficiently reducible Fe/Mn. It can be deduced that Ni, Co, and Fe were efficiently extracted using microwave-assisted USEPA 3051 protocol or hot plate Hossner method in sediment. Additionally, it has been reported that HNO_3 can dissolve the PTEs portion corresponding to the labile forms of soil/sediment-containing metals [11]. Similar to the findings of this study, Szakova et al. [37] stated that dilute HNO_3 could be recommended for use when extracting total PTEs content in sediment, especially in sediment polluted by anthropogenic inputs such as mining and sewage discharge.

3.5 Relationship Between Total-Recoverable PTEs Contents and Sediment Controlling Factors

To foretell whether sediment factors influence extraction of PTEs in sediments using the total-recoverable protocol, the Pearson correlation coefficients (r) between PTEs concentrations extracted by total-recoverable method and selected sediment properties such as sediment texture, OM, pH, $CaCO_3$, gypsum, and CEC were evaluated (Table 8). Positive correlations between PTEs concentrations extracted by the total-recoverable method and CEC were observed in sediment sample AA1. For sediment sample AA2, the PTEs concentrations extracted by total-recoverable protocol were negatively correlated with CEC except for Pb, which showed a strong positive correlation with CEC ($r_s = 0.71$). Although As and Fe concentrations showed positive correlations with CEC but the relationships were weak and insignificant

Table 8 Pearson's correlation coefficients (r) between PTEs concentrations extracted by total-recoverable (USEPA 3051) protocol and sediment properties

PTE	Sediment properties							
	Sand	Clay	Silt	pH	OM	$CaCO_3$	Gypsum	CEC
AA1								
As	0.71	− 0.77	− 0.71	− 0.78	0.84	0.71	− 0.32	0.84
Pb	0.59	− 0.54	− 0.59	− 0.52	0.91	0.59	− 0.26	0.91
Cu	− 0.01	− 0.63	0.01	0.01	0.47	− 0.01	0.37	0.47
Cd	0.62	− 0.59	− 0.62	− 0.57	0.91	0.62	− 0.28	0.91
Mn	0.69	− 0.73	− 0.69	− 0.74	0.88	0.69	− 0.31	0.88
Zn	0.69	− 0.72	− 0.69	− 0.72	0.89	0.69	− 0.31	0.89
Cr	0.50	− 0.42	0.50	− 0.38	0.87	0.50	− 0.22	0.86
Ni	0.70	− 0.76	− 0.77	− 0.77	0.86	0.70	− 0.31	0.86
Co	0.71	− 0.78	− 0.71	− 0.80	0.83	0.71	− 0.32	0.83
Fe	0.67	− 0.67	− 0.67	− 0.66	0.91	0.67	− 0.30	0.91
AA2								
As	− 0.71	0.95	0.51	− 0.60	− 0.44	0.08	0.89	0.05
Pb	0.05	− 0.06	0.59	− 0.16	− 0.38	0.99**	− 0.06	0.71
Cu	− 0.71	0.95	− 0.82	− 0.58	− 0.39	− 0.04	0.89	− 0.03
Cd	− 0.70	0.94	− 0.85	− 0.57	− 0.36	− 0.11	0.89	− 0.07
Mn	− 0.69	0.93	− 0.89	− 0.54	− 0.32	− 0.20	0.88	− 0.14
Zn	− 0.67	0.86	− 0.95*	− 0.45	− 0.19	− 0.43	0.81	− 0.31
Cr	− 0.71	0.95	− 0.82	− 0.58	− 0.39	− 0.04	0.89	− 0.31
Ni	− 0.67	0.91	− 0.93	− 0.50	− 0.27	− 0.30	0.85	− 0.21
Co	− 0.71	0.95	− 0.81	− 0.59	− 0.41	− 0.01	0.89	− 0.01
Fe	− 0.69	0.92	− 0.66	− 0.62	− 0.49	− 0.23	0.87	0.16
AA3								
As	− 0.53	− 0.54	− 0.84	− 0.67	− 0.78	− 0.59	− 0.02	− 0.60
Pb	− 0.23	− 0.59	− 0.95	− 0.66	− 0.70	− 0.62	− 0.20	− 0.63
Cu	− 0.14	− 0.57	− 0.90	− 0.67	− 0.75	− 0.61	[a]	− 0.62
Mn	0.19	− 0.42	− 0.59	− 0.61	− 0.81	− 0.49	0.23	− 0.51
Zn	0.06	− 0.49	− 0.73	− 0.66	− 0.80	− 0.56	0.10	− 0.57
Cr	− 0.06	− 0.55	− 0.84	− 0.67	− 0.78	− 0.60	− 0.28	− 0.61
Ni	0.02	− 0.51	− 0.77	− 0.66	− 0.80	− 0.57	0.06	− 0.58
Fe	0.15	− 0.45	− 0.64	− 0.63	− 0.81	− 0.52	0.19	− 0.53
AA4								
As	0.99**	0.96*	0.87	0.91	0.99*	0.99*	− 0.44	− 0.74
Pb	0.97*	0.88	0.75	0.81	0.93	0.94	− 0.23	− 0.66
Cu	0.99**	0.95	0.84	0.89	0.98*	0.98*	− 0.40	− 0.73
Mn	0.99**	0.95	0.85	0.89	0.98*	0.98*	− 0.41	− 0.74
Zn	0.99**	0.95	0.85	0.89	0.98*	0.96*	− 0.41	− 0.73
Cr	1.00**	0.95	0.85	0.90	0.98*	0.98*	− 0.40	− 0.65
Ni	0.99**	0.95	0.85	0.89	0.98*	0.93*	− 0.41	− 0.73
Co	0.99**	0.95	0.85	0.89	0.98*	0.98*	− 0.40	− 0.73
Fe	0.99**	0.95	0.85	0.89	0.98*	0.98*	− 0.41	− 0.74
AA5								
As	− 0.73	0.95*	0.85	0.65	− 0.85	0.91	0.85	− 0.61
Pb	− 0.71	0.94	0.83	0.67	− 0.83	− 0.60	0.85	0.92
Cu	− 0.72	0.94	0.84	0.67	− 0.85	− 0.61	0.81	0.91
Cd	− 0.68	0.89	0.79	0.58	− 0.85	− 0.65	0.85	0.79
Mn	− 0.73	0.95*	0.83	0.65	− 0.80	− 0.86	0.51	0.91
Zn	− 0.64	0.86	0.84	0.35	− 0.74	− 0.63	0.78	0.43
Cr	− 0.71	0.41	0.83	0.65	− 0.85	0.84	0.84	0.72
Ni	− 0.71	0.94	0.83	0.58	− 0.67	− 0.60	0.63	0.21
Co	− 0.34	0.61	0.67	0.36	− 0.85	− 0.59	0.88	0.47
Fe	− 0.51	0.40	− 0.81	0.63	− 0.85	− 0.67	0.64	0.32

[*] Correlation is significant at the 0.05 level (2-tailed)

[**] Correlation is significant at the 0.01 level (2-tailed)

[a] Cannot be computed because at least one of the variables is constant

{As(r_s) = 0.05; Fe(r_s) = 0.16)}. Concerning study sites AA3 and AA4, the PTEs concentrations extracted by the total-recoverable technique were negatively correlated with CEC.

In contrast, the PTEs concentrations extracted by the total-recoverable method in sediment sample AA5 were positively correlated with CEC except As which showed a negative correlation with CEC ($r_s = -0.61$). It has been reported that CEC is directly associated with the ability of the sediment to retain PTEs by providing enough exchange sites on sediment minerals [38]. The positive and negative correlations between the PTEs concentrations extracted by the total-recoverable method and CEC indicated that PTE extraction using the total-recoverable method might rely not only on CEC but also on other amalgamated sediment metal-specific characteristics.

For sediment sample AA1, $CaCO_3$ showed positive relationships with PTE concentrations extracted by the total-recoverable technique except for Cu, which showed a weak negative correlation ($r_s = -0.01$). PTEs concentrations extracted by the total-recoverable method showed negative relationships with $CaCO_3$ in sediment sample AA2 except for Pb, which showed a significant positive correlation with $CaCO_3$ ($r_s = 0.99$, < 0.01). Arsenic concentration extracted by the total-recoverable method in the sediment sample AA2 exhibited a weak positive correlation with $CaCO_3$ ($r_s = 0.08$). $CaCO_3$ negatively correlated with PTEs concentrations extracted by the total-recoverable method in sediment sample AA3. Positive correlation of $CaCO_3$ and As concentration extracted by the total-recoverable method in sediment sample AA5 was observed, while the other PTEs concentrations extracted by the total-recoverable technique were negatively correlated with $CaCO_3$ in sediment sample AA5. Surprisingly, $CaCO_3$ showed significant positive correlations with PTEs concentrations extracted by the total-recoverable protocol in sediment sample AA4 except for Pb concentration, which exhibited a strong positive relationship with $CaCO_3$ but insignificant ($r_s = 0.94$). It has been reported that $CaCO_3$ content is one of the most contributing factors influencing PTEs accumulation, mobility, and bioavailability in arid and tropical soils [39]. The positive and negative correlations between PTEs concentrations extracted by the total-recoverable protocol and $CaCO_3$ are an indication that the availability of $CaCO_3$ in the samples influences PTEs accumulation, bioavailability, and movement. Thus, this study attests to McLean and Bledsoe study [39].

PTEs concentrations extracted by the total-recoverable method negatively correlated with gypsum in sediment sample AA1 except for Cu, which showed a weak positive relationship with gypsum ($r_s = 0.37$). Gypsum exhibited positive relationships with PTE concentrations extracted by the total-recoverable protocol in sediment sample AA2 except for Pb, which showed a weak negative correlation with gypsum ($r_s = -0.06$). Weak negative correlations between other PTE concentrations extracted by the total-recoverable method and gypsum were observed in sediment sample AA3. Also, gypsum showed weak positive relationships with Mn, Zn, Ni, and Fe concentrations extracted by the total-recoverable technique in sediment sample AA3. PTE concentrations extracted by the total-recoverable method exhibited weak negative correlations with gypsum in sediment sample AA4.

In contrast, strong positive correlations were observed between gypsum and PTE concentrations extracted by the total-recoverable protocol in sediment sample AA5. It has been described that gypsum increases the retention of Pb, Cd, and Cu on solid components of the soil/sediment [40]. The strong and weak correlations between Pb and gypsum and Cu and gypsum in some of the study sites showed that gypsum influences the retention of PTEs on solid components of the soil/sediments.

Organic matter (OM) was positively correlated with PTE concentrations extracted by the total-recoverable protocol in sediment sample AA1 but negatively correlated with PTE concentrations extracted by the total-recoverable method in sediment samples AA2, AA3, and AA5. Significant positive correlations were noticed between OM and PTE concentrations extracted by the total-recoverable protocol in sediment sample AA4 except for Pb concentration, which showed a strong positive relationship with OM but not significant. The negative and positive associations of PTE concentrations extracted by the total-recoverable method and OM indicated that sediment organic matter influences PTEs availability and extractability. The strong positive correlations between OM and PTE concentrations extracted by incomplete digestion method using HNO_3 demonstrated that the total-recoverable method protocol can extract PTEs in sediment organic matter fractions.

Negative correlations between clay and PTE concentrations extracted by the total-recoverable method were observed in sediment samples AA1 and AA3. Furthermore, positive relationships of clay with PTE concentrations extracted by the total-recoverable technique were noticed in sediment sample AA2 except for Pb, which showed a weak negative correlation with clay ($r_s = -0.06$). Clay showed strong positive correlations with PTE concentrations extracted by the total-recoverable technique in sediment samples AA4 and AA5 except for As in sediment sample AA4, which showed a significant positive correlation with clay ($r_s = 0.96$, < 0.05). As and Mn concentration extracted by the total-recoverable method exhibited significant positive correlations with clay {As(r_s) = 0.95 < 0.05 and Mn(r_s) = 0.95 < 0.05} in sediment sample AA5. It has been detailed that clay minerals in surface sediment can influence the adsorption of PTEs [41]. Thus, the accumulation of PTEs in sediment is regulated by the granular composition of sediments. It can be deduced that the clay content in sediment influences the adsorption of PTE concentrations.

The clay content, OM, and CEC in sediment samples might contribute to the distribution of PTE concentrations in the selected study sites. It has been stated that fine fractions containing enough OM with high CEC could accumulate polluted organic and inorganic materials and are more eligible to be contaminated than coarse fractions [42].

Negative correlations between sediment pH and PTE concentrations extracted by the total-recoverable method were observed in sediment samples AA1, AA2, and AA3. In contrast, sediment pH was positively correlated with PTE concentrations extracted by the total-recoverable protocol in sediment samples AA4 and AA5. It has been stated that many adsorption sites in sediments are pH-dependent and include carbonates, OM, Fe, and Mn oxides, and clay minerals [39]. This means that sediment pH influences several mechanisms of PTEs retention in sediments. In this study, the correlations between PTE concentrations extracted by the total-recoverable protocol and sediment physicochemical characteristics indicated that several sediment physicochemical properties influence PTEs availability and extractability and thus should be considered when extracting PTEs using incomplete digestion methods.

4 Conclusion

Comparison of two digestion methods of total-total (hot plate Hossner) and total-recoverable (USEPA 3051 method) was investigated for systematic assessment of PTEs (i.e., As, Pb, Cu, Cd, Mn, Zn, Cr, Ni, Co, and Fe) concentrations in surface sediment collected from Awobrew stream in the central part of Ghana affected by sewage discharge and sand mining activity. It was observed that hot plate Hossner technique showed high PTEs extractability than microwave-assisted USEPA 3051. However, Ni, Co, and Fe were extracted satisfactorily using microwave-assisted USEPA 3051 or Hot plate Hossner protocol. The microwave-assisted USEPA 3051 method was noted to be feasible for extracting Ni, Co, and Fe in sediments influenced by sewage discharge and mining activity. Thus, microwave-assisted USEPA 3051 technique can be recommended for assessing PTEs in sediments influenced by lithogenic sources but on the condition of using a strong acid such as HF or acids combination. Sediment factors such as land use, soil types, lithologies and other chemical properties influence the extraction of PTEs in sediment. Microwave-assisted USEPA 3051 or Hot plate Hossner technique can be used to evaluate PTEs concentrations in surface sediments of Africa, other tropical regions and areas with similar anthropogenic influenced conditions. This research work also contributes to the evaluation of anthropogenic activities influence on streams in central part of Ghana and could be needed in establishing quality limits and planning alleviation programs.

Acknowledgements The authors would like to acknowledge the Ghana Environmental Protection Agency (Ghana EPA) and Ghana Food & Drugs Authority (GFDA) for non-financial supports.

Author Contributions The author is responsible for ensuring that the descriptions are accurate. Author contributed in multiple roles: Conceptualization, Methodology, Formal Analysis, Investigation, etc.

Funding The author received no financial support for this research, authorship, and/or publication of this article.

Data Availability The dataset used during this study is available from the corresponding author on reasonable request.

Declarations

Conflict of interest The author declared no potential conflict of interest concerning the research, authorship, and/or publication of this article.

Ethical approval and consent to participate Not applicable.

Consent for publication Not applicable.

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