Comparative assessment of chemical extractants for determining heavy metal mobility and potential risk in waste-impacted soils

Abstract

The use of suitable chemical extractants is essential in environmental and soil analyses. This study compared the concentrations of Pb, Cd, Cr, Ni, and V in soils affected by wastes using three chemical extractants: aqua regia (AR), nitric–perchloric acid (NP), and ethylenediamine tetraacetic acid (EDTA). The main goal was to compare extraction efficiencies and examine how the choice of extractant could influence contamination levels and data interpretation. Soil samples were collected from areas impacted by auto mechanic (A), paint processing (P), and abattoir (AB) wastes, and analyzed for Pb, Cd, Cr, Ni, and V using the three extractants. The metal concentrations obtained were compared to the respective regulatory limits based on established guidelines. The results showed significant differences in metal concentrations extracted by the three methods in the following order: AR>NP> EDTA. Concentrations of Pb extracted with AR, NP, and EDTA exceeded the FAO's permissible limits by 411%, 37%, and 267%, respectively, while Cd levels were higher by 1546%, 1,038%, and 534%. Vanadium concentrations extracted with AR, NP, and EDTA were below the regulatory limits by 1.73%, 15.17%, and 34.03%, respectively. Nickel levels extracted with AR exceeded limits by 5.87%, whereas Ni extracted with P and EDTA were below limits by 22.13% and 49.73%. This study highlights that using multiple extractants offers a more accurate assessment of soil contamination. Environmental monitoring and regulation programs should specify detailed extraction procedures and provide clear guidelines for data interpretation. Doing so will promote scientific accuracy and consistency, reduce data misinterpretation, facilitate comparison of studies, and minimize discrepancies in regulatory evaluations.

Keywords: Chemical extractants; Digestion methods; Heavy metals; Open dumpsites; Soil contamination; Extractant efficiency

INTRODUCTION

The contamination of soils by heavy metals resulting from urbanization, industrial activities, and indiscriminate waste disposal has become a major environmental concern (Zang et al. 2010;

Kaparwan et al. 2020; Wang et al. 2021; Udo et al. 2025a). Contaminated soils typically receive wastes that introduce potentially toxic elements into the environment (Umoh and Etim, 2013; Ojiego et al., 2022; Udo et al., 2026a). Soils contaminated by heavy metals have posed a serious ecological and human health risk as a result of the persistent, toxic, and bio-accumulative properties of the metals (Wuana and Okeimen, 2011; Sharma & Jain, 2020; Udo et al., 2026b). In the FAO's report of 2004, mercury, cadmium, lead, zinc, nickel, chromium, copper, and cobalt were listed among the top twenty dangerous substances. These elements are some of those released into the soils through various waste materials.

Heavy metals are toxic even at low levels (Wuana and Okeimen, 2011). Since life on earth owes its sustenance to certain elements derived from the earth's crust (Winegardner, 2019), soils contaminated by heavy metals cause unquantifiable damage to the entire ecosystem (Tóth et al., 2016; Tyagi and Kumar, 2021; Munir et al., 2021). For instance, their toxicities can affect the environmentally friendly soil microbial population that enhances soil fertility and soil health (Jyothi, 2020). In addition, the toxic nature of these metals can upset human health (Mahurpawar, 2015), affect water quality (Zhang et al., 2022), degrade natural food quality (Munir et al., 2021), and destabilize the overall functioning of the ecosystem (Igwe and Nwachukwu, 2016; Adagunodo et al., 2018; Ebong et al., 2020). Consequently, it is always recommended that contaminated soils be remediated for environmental sustainability (Maturi et al., 2008; Kaparwan et al., 2020). Such soils should first be analyzed to ascertain the concentrations and forms of heavy metals before designing remedial strategies.

For effective determination of levels of heavy metals within contaminated soils, suitable chemical extractants should be employed (Lee and Kao 2004; Santoro et al. 2017; Li 2024), as most extractants differ in their extraction abilities and affinity for heavy metals. The extractant type, therefore, significantly impacts result reliability and accuracy (Hlavay et al., 2004). Incorrect extractant choices could result in partial dissolution of the soil sample, resulting in reduced concentrations of the metal within the soil sample.

Five different classes of extractants: acids, nonionic, chelating agents, surfactants, and cosolvents, were identified by Maturi et al. (2008). Strong single acids, e.g., ultra-pure HNO_3 or double acids, e.g., aqua regia (HCl and HNO_3), have been used to determine pseudo-total concentrations of metallic elements (Ivezić et al., 2013). Aqua regia is widely used for the determination of total forms of Pb, Cr, Cd, Ni, and Zn due to its simple and adaptable nature.

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Aqua regia can oxidize organic matter and metal oxide, just like hydrogen peroxide (Akannam and Kakulu, 2022). On the other hand, synthetic acids (chelating agents), e.g., ethylenediaminetetraacetic acid (EDTA), have been used to determine reactive metal concentrations, while water has been used to extract concentrations of the metals in soil solution (Ivezić et al. 2013).

Owing to different properties of each element in the soil, no particular digestion method may be efficient for all metals (Idera et al., 2014). Factors influencing the choice of extractant employed for analytical processes include the nature of the targeted heavy metal, the chemical form of the metal within the matrix, and the choice of analytical method (Manouchehri & Bermond, 2009). All extractant types do not have the same affinities for heavy metals; if the incorrect extractant type is employed, the accuracy of the results will be adversely affected. Extractants vary in action; for example, H_2SO_4 has been found inappropriate for digesting samples containing Barium (Ba), and HCl has been found unsuitable for digesting samples containing silver (Ag) and lead (Pb) (Abegunde et al., 2018). Similarly, arsenic (As) compounds have been found unsuitable as solvents for alkaline earth metals as they react with volatile compounds with HCl and H_2SO_4 to form insoluble sulphate salts (Twyman, 2005).

To improve metal extraction efficiencies, mixtures of acids have been advocated (Wilson et al. 2005; Szakova et al. 2010). Combining acids like HF-HNO_3-$HClO_4$-H_2SO_4 can enhance the total analysis of Cu, Cd, Ni, and Zn in soils (Idera et al., 2014). This combination can be modified by substituting H_2SO_4 for HCl since Pb can be precipitated with H_2SO_4 in solution. Although these combinations cannot totally dissolve silicates, they have been found capable of extracting heavy metals from the soil matrix. Aqua regia (concentrated HCl and HNO_3 in 4:1 or 3:1 v/v), for example, has been found effective in extracting trace metals in soils (Baker and Amacher, 1982; Tukura et al., 2013; Idera et al., 2014; Rocky et al, 2024).

This study, therefore, aimed to evaluate the heavy metals extracting capacities of different chemical extractants from soils impacted by three different sources of wastes: automechanic, paint-processing, and abattoir dumpsites in Akwa Ibom State, Nigeria. It was hypothesized that different extractant types would significantly influence the concentrations of heavy metals extracted from the soils. Three chemical extractants: aqua regia (HCl and HNO_3 in *a* 3:1 ratio), nitric-perchloric acids, and EDTA were used to assess the concentrations of five heavy metals (lead, cadmium, chromium, nickel, and vanadium) within the waste-impacted soils. The

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employment of multiple digestion methods for analysis of heavy metal concentrations within these different waste types will help ascertain the best heavy metal digestion method with the highest accuracy and analytical efficiency.

LOCATION AND GEOLOGY OF THE STUDY SITES

This study was undertaken in Akwa Ibom State, located within Southern Nigeria. The State has a humid tropical climate and is situated between latitudes 4°32′ and 5°33′ N and longitudes 7°25′ and 8°25′ E. It is bordered by Cross River State to the east, Rivers State to the west, Abia State to the north, and the Atlantic Ocean to the south. About 70 % soils of Akwa Ibom State are from the Benin Formation (coastal plain sands) (Udoh et al. 2008; Ekanem and Udosen, 2023a, b; Udosen et al. 2024a, b). Other parent materials include sandstones, beach ridge sands, shales, and alluvial deposits (Udoh and Ibia, 2022; Udosen and George, 2024). A typical soil originating from coastal plain sands is dominantly coarse-textured, making the soils generally well-drained (Udo et al. 2009a, b; Akpan-Idiok 2012).

Three local government areas (LGAs): Uyo, Ikot Ekpene, and Etinan were chosen for the study (Figure 1). Uyo is the State's capital city, and as such, the center of all developmental projects in the State with its attendant polluting tendencies (Opara et al., 2005). The location of Ikot Ekpene along the major federal highway linking the State to the southeastern part of the country has given it an advantage for fast development, characterized by widespread automobile repair workshops and metal works, as well as food processing industries. Etinan had also witnessed some level of heavy metal contamination through heavy metals-laden waste discharges. For example, one of the leading paint processing plants in Nigeria, Peacock Paint Limited, was located in Etinan.

Three dumpsites receiving waste from automechanic (A), paint processing (P), and abattoir (AB) operations were selected in each LGA to represent multiple contamination sources. One control site from each LGA with no known history of waste-disposal or industrial activities was selected while ensuring a similar soil type to the waste-impacted soils. The soils were sampled at depths: 0–20, 20 - 40, and 40-60 cm.

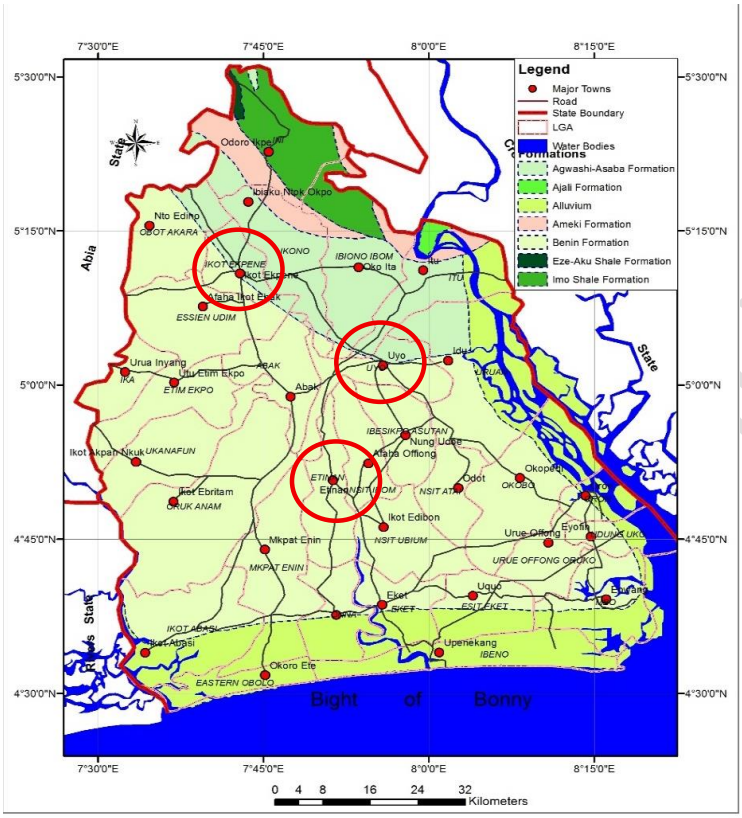

Figure 1: Map indicating locations of study areas.

MATERIALS AND METHODS

Extractions of the heavy metals from the soils

(i) Extraction with aqua regia (concentrated hydrochloric and nitric acids (HCl/HNO_3) in the ratio of 3:1).

This procedure is outlined in Abegunde et al. (2018). 1 g of soil sample was weighed into a digestion flask, and 20 ml of aqua regia was added to the flask. The digestion was carried out using a heating mantle in the fume cupboard. The temperature was gradually increased with occasional agitation of the mixture until the heated content within the flask reduced to approximately 5 ml. The flask was then covered with a watch glass to prevent excessive

evaporation. The remaining solution was filtered, washed with deionized and double-distilled water, before being turned into a 50 ml volumetric flask. Some distilled water was then added up to the mark, and the flask's content was analyzed with an Atomic Absorption Spectrophotometer (AAS), model AA500, manufactured by PG Instruments.

(ii) Digestion with nitric and perchloric acids (HNO_3/$HClO_4$)

The soil sample (1 g) was measured into a 250 ml digestion flask, and 10 ml of concentrated HNO_3 was added. The mixture was gently boiled for about 40 minutes to get rid of all oxidizable materials. It was allowed to cool, and 5 ml of perchloric acid (70% w/w) was added. This mixture was boiled again until whitish fumes appeared. It was then allowed to cool again, and then 20 ml of distilled water was added. It was boiled again to eliminate fumes, cooled, and filtered with Whatman filter paper No 42 and < 0.451 Millipore filter paper before being transferred into a 50 ml volumetric flask. Distilled water was then added to the mark in preparation for analysis with AAS.

(iii) Digestion with ethylenediamine tetraacetic (EDTA):

Extraction was undertaken using the method of Lindsay and Norvell (1978) as described by Omaka et al. (2015). 1 g of the soil sample was weighed into extraction bottles to which 50 ml of 1M EDTA (pH 7.0) was added and agitated for 60 minutes on a rotary shaker. The resulting suspension was then filtered with Whatman filter paper No 42, and concentrations of heavy metals in the extract were determined using AAS.

Statistical analyses

Data obtained from the analyses were subjected to analysis of variance (ANOVA). Where a significant difference was noticed among means, they were separated using the least significant difference (LSD) at 95% confidence interval.

RESULTS AND DISCUSSION

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Extracting capacities of the extractants

The extracting capacities of the three extractants for heavy metals are presented in Table 1.

Table 1: Mean concentrations of the heavy metals extracted with different extractants

Extractant	Lead	Cadmium	Chromium	Nickel	Vanadium
	← mg/kg →				
Aqua regia	1534.0	82.9	294.8	158.0	142.3
Nitric-perchloric acids	1419.0	56.9	254.5	116.8	105.0
EDTA	1192.0	31.7	197.9	75.4	63.5
LSD	**31.0**	**3.3**	**3.8**	**5.1**	**4.9**

Table 1 shows that the mean concentration of aqua regia extracted Pb was 1534.0 mg/kg, that of nitric-perchloric acids (NP) was 1419.0 mg/kg, and that of Ethylenediamine tetraacetic acid (EDTA) was 1192.0 mg/kg. These values were higher than the regulatory limit of 300 mg/kg for Pb in residential zones (Table 2) by 411, 373, and 267%, respectively. Pb values from the three extractants were significantly different from each other and followed the sequence: AR>NP>EDTA, with the ratios 1.29: 1.19: 1.0, respectively.

Table 2: Regulatory guideline values of heavy metals compared with those obtained with different extractants. Keys: NC = natural concentration in soils, TV = threshold value, L = lower guideline value, H = higher guideline value, a = MEF, (2007), D = field data, AR = aqua regia, NP = nitric-perchloric acids, EDTA = ethylenediamine tetraacetic acid, e = ecological risk, t = health risk

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Heavy metal	NC (a) (mg/kg)	TV (mg/kg) (a)	L (a)	H (a)	AR		NP		EDTA	
					D (mg/kg)	AR - H (%)	D (mg/kg)	NP - H (%)	D (mg/kg)	EDTA - H (%)
Lead	1-5	60.0	200(t)	750.0 (e)	1534.0	667	1419.0	609.5	1192.0	496
Cadmium	0.01-0.15	1.0	10	10.0 (e)	82.9	729	56.9	469	31.7	217
Chromium	6-120	100.0	200	300.0 (e)	294.8	47.4	254.5	27.27	197.9	-1.05
Nickel	3-100	50	100	250 (e)	158.0	216	116.8	16.8	75.4	-24.6
Vanadium	10-115	10	150	150 (e)	142.3	-5.13	105.0.	-30	63.5	-57.67

The values extracted by AR and NP were pseudo-total trace metal concentrations, while those extracted by EDTA were exchangeable metal concentrations (Ivezić et al. 2013). AR values reflected total recoverable metals, including those bound in silicate and oxides of metals,

providing a conservative estimate for assessing overall contamination. These results agree with previous research (Abegunde et al. 2018) that indicated that aqua regia extracted the highest concentration of Pb from dumpsite soils of Ado-Ekiti, Nigeria, in comparison to $HNO_3/HClO_4$ and HNO_3. These results also corroborated previous research that indicated that EDTA-extracted forms of Pb were linked to the exchangeable and carbonate fractions of the metal, while reduced solubility with EDTA was obtained in organic, oxides, and residual forms (Elless and Blaylock, 2000).

Cd obtained with AR, NP, and EDTA were 82.3, 56.9, and 31.7 mg/kg, respectively, and these were higher than FAO's regulatory limit (5 mg/kg) for residential zones (Table 2) by 1546%, 1038%, and 534%. Cd concentrations from the 3 extractants were significantly different from each other, with the ratio: 3.6: 1.8: 1.0 for AR: NP: EDTA, respectively. EDTA, though having the least values, represented the reactive fractions of total metal concentration (Ivezić et al. 2013). This is important in environmental management as it informs the most chemically active and bioavailable part of the total metal concentration within the soils.

Cr obtained with AR, NP, and EDTA were 294.8, 254.5, and 197.9 mg/kg, respectively. These values were less than FAO's regulatory limit (300 mg/kg) for residential zones by 1.73, 15.17, and 34.03 %, respectively. Cr concentrations from the 3 extractants were significantly different from each other, with the ratio: 1.48: 1.29: 1 for AR: NP: EDTA, respectively. These results validated previous research that reported higher values of aqua regia-extracted Cr than EDTA (Tukura et al., 2013).

Ni obtained with AR, NP, and EDTA were 158.0, 116.8, and 75.4 mg/kg, respectively. These values were higher than FAO's regulatory limit (150 mg/kg) by 5.87, 22.13, and 49.73%, respectively. Cr concentrations from the 3 extractants were significantly different from each other with the ratio: 2.11: 1.55: 1 for AR: NP: EDTA, respectively. These results confirmed results from previous research that reported higher values of aqua regia-extracted Ni than EDTA (Tukura et al., 2013; Akannam & Kakulu, 2022).

Values of V obtained with AR, NP, and EDTA were 142.3, 105.0, and 53.5 mg/kg, respectively. These were less than FAO's regulatory limit (300 mg/kg) by 52.57, 65, and 82.17%, respectively. V concentrations from the 3 extractants were significantly different from each other and in the ratio: 2.66: 1.96: 1 for AR: NP: EDTA, respectively. EDTA is a good complexing agent that can form mixed solutions with dilute acids and inorganic salts to improve the

extractability of metal from the soil, but it may not produce the same result for all the metals (Yang et al. 2022). Complexation between EDTA and metals like Zn, Pb, Cd, Cu, and Ni is more stable than that formed with V, resulting in lower EDTA-extracted results compared to those of other aforementioned metals.

The results, therefore, showed that the three chemical extractants (AR, NP, and EDTA) have different metal extraction capacities. Concentrations of the extracted metals were generally significantly different from each other and followed the order: AR>NP>EDTA. Aqua regia and nitric-perchloric acids performed better than EDTA (Abegunde et al. 2018) due to the combination of two strong acids present in these two reagents. Previous work (Bozym 2017), however, found that 0.05 M EDTA could extract up to 37.7 mg/kg of Pb from foundry sand waste, and this was the highest concentration compared to other concentrations extracted by H_2O, HCl, $MgCl_2$, CH_3COOH, and NaCOOH. Another research (Maturi et al. 2008) used different concentrations of EDTA (0.01, 0.05, 0.1, and 0.2 M); the results indicated that the amount of zinc extracted from soils was directly proportional to the concentration of the extractant.

In our study, a concentration of 1.0 M of EDTA was used against 0.01, 0.05, 0.1, and 0.2 M used by Maturi et al. (2008). Despite the high concentrations employed in our study, EDTA could only extract the lowest concentrations of these metals (Pb, Cd, Cr, Ni, and V) when compared to those of aqua regia and nitric-perchloric acids. This has highlighted the low strength of EDTA in extracting some metals from soil (Tukura et al, 2013). Similar results (Maturi et al. 2008) reported that two chelating agents used in their study (EDTA and DPTA) performed poorly in extracting Zn and Pb from the soil. This was due to the presence of other metals, which affected the stability of zinc-chelate and lead chelate complexes. Another reason was that the chelating agents formed complexes with other non-target metals.

In other research (Elless and Blaylock 2000; Lee & Kao 2004), EDTA was found more suitable for extracting the exchangeable forms of Pb than immobile fractions, i.e., those attached to Fe-Mn oxides and soil matrix (residual form). The soils in our study area have been reported to have high Fe contents (Udo et al., 2008; Udoh et al. 2008; Ebong et al. 2020), probably contributing to high concentrations of Fe-Mn oxides bound to Pb, making Pb less available for EDTA extraction.

Comparison of extracted heavy metal concentrations with international threshold values

Table 2 compares the concentrations of the extracted heavy metals with threshold values established by the 2007 Ministry of Environment, Finland (MEF) international guidelines and government decrees on the assessment of soil contamination and remediation needs.

Concentrations of lead at 1534.0, 1419.0, and 1192.0 mg/kg obtained with AR, NP, and EDTA were higher than the 2007 MEF lower guideline value of 60 mg/kg by 667, 609.5, and 496 %, respectively. Cadmium values were also higher than the threshold values. Chromium extracted with AR and NP exceeded the lower guideline value by 47.4% and 27.27%, respectively, while the concentration obtained with EDTA was below the lower guideline value. Similar observations were noted for nickel. For vanadium, the AR, NP, and EDTA extracted values were less than the lower guidelines by 5.13, 30, and 57.67%. These variations were due to the different extracting capacities of the extractants (Idera et al., 2014; Abegunde et al., 2018).

Comparison of heavy metal concentrations from diverse dumpsites when extracted with the three extractants

According to Table 3, the mean values of Pb from abattoir soils (68.2 mg/kg) and control soils (8.2 mg/kg) were statistically the same but different from those of automechanic soils (3877.0 mg/kg) and paint soils (1465.3 mg/kg). The mean values of Pb from automechanic soils were significantly different from those of paint soils. The sequence was: control & abattoir < paint < automechanic. The concentration of lead extracted with aqua regia was 1534.2 mg/kg, the concentration extracted with nitric-perchloric acid was 1341.1 mg/kg, while that extracted with EDTA was 1188.0 mg/kg, giving the sequence: EDTA & NP <AR.

Table 3: Concentrations of lead extracted with the three extractants from the top soil (0-20 cm) of different dumpsite soils. Keys: AR = Aqua regia; EDTA = Ethylenediamine tetraacetic acid; NP = Nitric-perchloric acids; LSD = Least Significant Difference

Extractant	Dumpsites				Mean
	Abattoir	Automechanic	Control	Paint	
	→ mg/kg →				
Aqua regia (AR)	73.0	4310.1	10.2	1745.0	1534.2
EDTA	63.1	3498.3	6.1	1187.3	1188.0
Nitric-perchloric acids (NP)	67.1	3824.2	8.4	1464.1	1341.1
Mean	68.2	3877.0	8.2	1465.3	
LSD	Extractants (336.1); Dumpsite (388.1); Extractants/Dumpsite (672.2)				

The mean concentrations of Cd obtained from the dumpsite soils (abattoir, automechanic, control, and paint) were significantly different from each other (Table 4). The values followed this sequence according to their order of magnitude: automechanic > paint >abattoir > control. The concentration extracted with AR (82.3 mg/kg) was significantly different from that extracted with EDTA (71.7 mg/kg), but was the same as that extracted with NP (78.2 mg/kg). This gave the sequence: EDTA & NP <AR.

Table 4: Concentrations of cadmium extracted with the three extractants from the top soil (0-20 cm) of different dumpsite soils. Keys: AR = Aqua regia; EDTA = Ethylenediamine tetraacetic acid; NP = Nitric-perchloric acids; LSD = Least Significant Difference

Extractant	Dumpsite soils				Mean
	Abattoir	Automechanic	Control	Paint	
	→ mg/kg →				
Aqua regia (AR)	26.5	179.0	0.8	122.9	82.3
EDTA	22.1	158.2	0.5	106.1	71.7
Nitric-perchloric acids (NP)	24.1	171.5	0.7	116.6	78.2
Mean	24.2	169.6	0.7	115.2	
LSD	Extractants (10.51); Dumpsite (12.59); Extractants/Dumpsite (21.81)				

The mean values of chromium (104.6, 430.0, 1.3, and 552.2) mg/kg obtained from the dumpsites (abattoir, automechanic, control, and paint), respectively, were significantly different from each other in the following sequence: automechanic > paint > abattoir > control (Table 5). There were also significant differences among Cr values obtained by different extractants, and the sequence was EDTA < NP < AR.

Table 5: Concentrations of chromium extracted with the three extractants from the top soil (0-20 cm) of different dumpsite soils. Keys: AR = Aqua regia; EDTA = Ethylenediamine tetraacetic acid; NP = Nitric-perchloric acids; LSD = Least Significant Difference

Extractant	Dumpsites				Mean
	Abattoir	Automechanic	Control	Paint	
	→ mg/kg →				
Aqua regia (AR)	109.3	467.5	1.5	600.7	**294.8**
EDTA	98.6	387.7	1.1	509.7	**249.3**
Nitric-perchloric acids (NP)	105.9	434.6	1.3	546.2	**272.0**
Mean	**104.6**	**430.0**	**1.3**	**552.2**	
LSD	**Extractants (22.73); Dumpsite (26.48); Extractants/Dumpsite (45.87)**				

Table 6 presents the concentrations of Ni obtained from different dumpsites (abattoir, automechanic, control, and paint). The mean values of nickel obtained from the different

dumpsites were significantly different from one another. Furthermore, Ni concentration extracted with AR (158.0 mg/kg) was greater than that of NP (139.1 mg/kg), which was in turn higher than that of EDTA (119.8 mg/kg), creating the sequence AR > NP > EDTA.

Table 6: Concentrations of nickel extracted with the three extractants from the top soil (0-20 cm) of different dumpsite soils. Keys: AR = Aqua regia; EDTA = Ethylenediamine tetraacetic acid; NP = Nitric-perchloric acids; LSD = Least Significant Difference

Extractant	Dumpsites				Mean
	Abattoir	Automechanic	Control	Paint	
	→ mg/kg →				
Aqua regia (AR)	128.5	302.5	6.3	194.6	**158.0**
EDTA	105.9	240.8	3.5	128.8	**119.8**
Nitric-perchloric acid (NP)	119.9	271.8	5.0	159.6	**139.1**
Mean	118.1	271.7	4.9	161.0	
LSD	**Extractants (30.55); Dumpsite (35.27); Extractants/Dumpsite (61.10)**				

The concentrations (mg/kg) of vanadium obtained from the different dumpsites in the order of increasing magnitude were (1.8, 94.8, 201.4, and 215.7) mg/kg for control, abattoir, paint, and automechanic, respectively (Table 7). Subjecting these values to statistical analyses revealed that the mean value for control soils was significantly different from those of abattoir, automechanic, and paint soils. On the other hand, those of the automechanic and paint waste soils were statistically the same. Mean concentrations of vanadium (142.3 mg/kg) extracted with AR were statistically similar to those extracted with NP, but dissimilar to those obtained from EDTA.

Table 7: Concentrations of vanadium extracted with the three extractants from the top soil (0-20 cm) of different dumpsite soils. AR = Aqua regia; EDTA = Ethylenediamine tetraacetic acid; NP = Nitric-perchloric acids; LSD = Least Significant Difference

Extractant	Dumpsites				Mean
	Abattoir	Automechanic	Control	Paint	
	→ mg/kg →				
Aqua regia (AR)	99.5	227.6	2.2	240.0	**142.3**
EDTA	89.6	178.8	1.3	192.5	**115.5**
Nitric-perchloric acid (NP)	95.2	197.9	1.9	214.6	**127.4**
Mean	**94.8**	**201.4**	**1.8**	**215.7**	
LSD	**Extractants (25.45); Dumpsite (29.39); Extractants/Dumpsite (50.90)**				

Depth-Dependent Distribution of Heavy Metals

The concentration of heavy metals across soil depths (0–20, 20–40, 40–60 cm) indicated a decrease with depth (Figures 2–6).

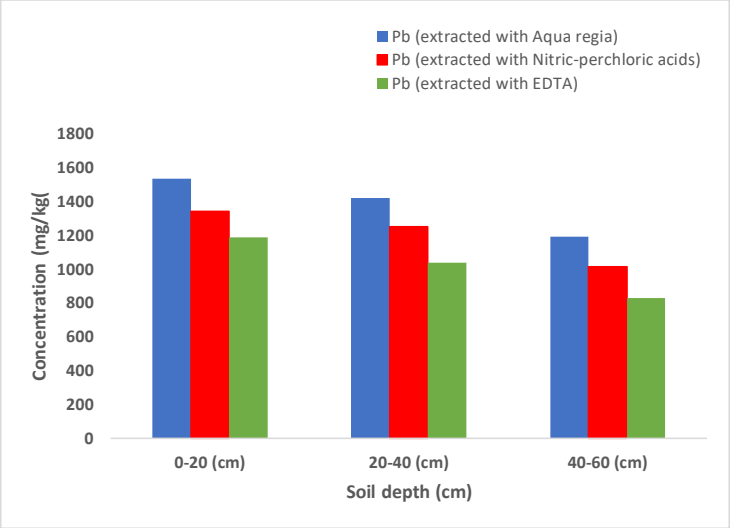

Figure 2: Comparison of lead (Pb) concentrations (mg/kg) in soils at three different depths (0-20cm, 20-40cm, and 40-60cm) using three extraction methods: aqua regia, nitric–perchloric acid digestion, and EDTA extraction.

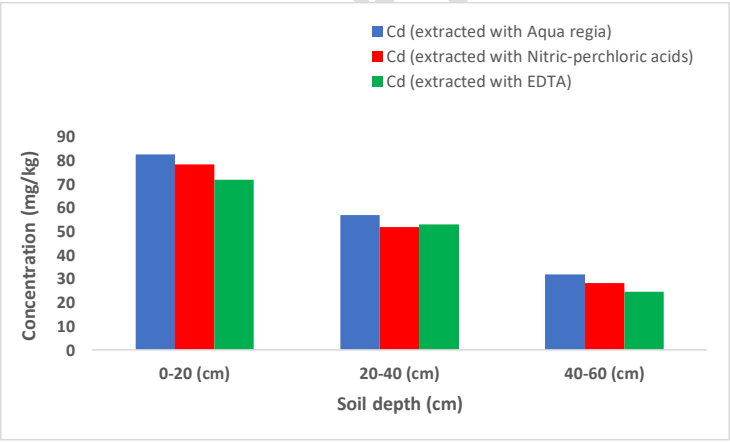

Figure 3: Comparison of cadmium (Cd) concentrations (mg/kg) in soils at three different depths (0-20cm, 20-40cm, and 40-60cm) using three extraction methods: aqua regia, nitric–perchloric acid digestion, and EDTA extraction.

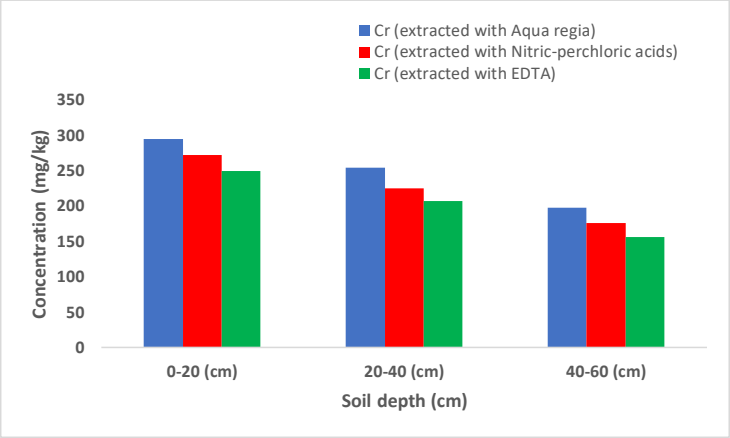

Figure 4: Comparison of chromium (Cr) concentrations (mg/kg) in soils at three different depths (0-20cm, 20-40cm, and 40-60cm) using three extraction methods: aqua regia, nitric–perchloric acid digestion, and EDTA extraction.

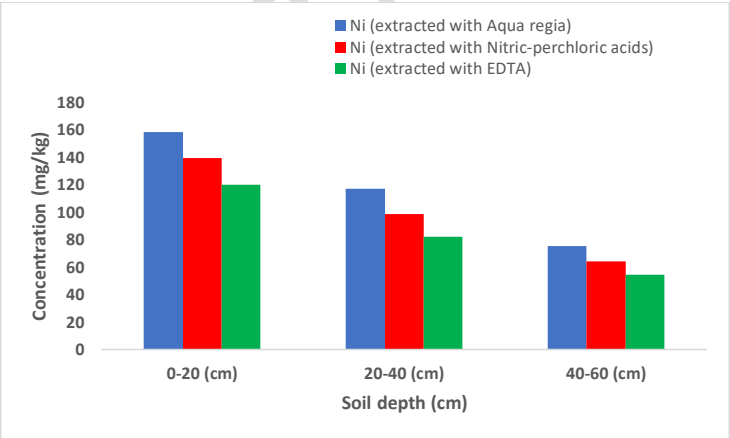

Figure 5: Comparison of nickel (Ni) concentrations (mg/kg) in soils at three different depths (0-20cm, 20-40cm, and 40-60cm) using three extraction methods: aqua regia, nitric–perchloric acid digestion, and EDTA extraction.

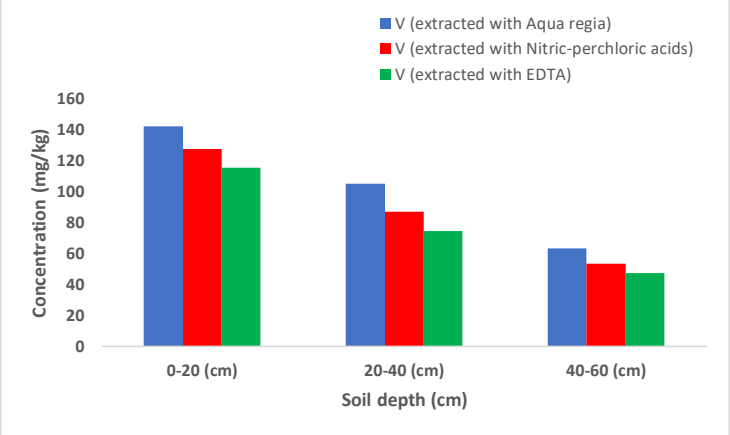

Figure 6: Comparison of vanadium (V) concentrations (mg/kg) in soils at three different depths (0-20cm, 20-40cm, and 40-60cm) using three extraction methods: aqua regia, nitric–perchloric acid digestion, and EDTA extraction.

These results (Figures 2 -6) indicated that surface soils were more heavily contaminated than subsurface soils. Lead (Pb) concentrations extracted with aqua Regia (AR) decreased from 1534 mg/kg at 0–20 cm to 1192 mg/kg at 40–60 cm, while cadmium (Cd) decreased from 82.3 at 0–20 cm to 31.7 mg/kg at 40–60 cm. Chromium (Cr), nickel (Ni), and vanadium (V) exhibited similar downward trends, suggesting limited vertical migration, except for Cd, which maintained relatively high concentrations even at 40–60 cm; this is consistent with its high mobility and solubility in water. The surface enrichment of these metals highlighted the risk of exposure to plants, humans, and soil organisms, as the topsoil is the most interactive layer for biological and agricultural processes. This is particularly concerning Pb and Cd, which showed significant concentrations even in the bioavailable fraction (EDTA-extractable), indicating high potential for bioaccumulation.

In summary, this study indicated that aqua regia (AR) was the most effective extractant, suggesting that the mixture of nitric and hydrochloric acids was particularly efficient. High AR extracted values were due to the component acids' ability to dissolve and mobilize the metals from their soil matrices. HNO_3 worked as a strong oxidizer to convert metals into their oxidized state, and HCl donated chlorine ions to stabilize the metallic ions in the solution via the formation of metal-chlorine complexes. These two mechanisms enabled aqua regia to dissolve metals effectively.

The mixture of nitric acid (HNO_3) and perchloric acid ($HClO_4$) was also effective; however, it was not as aggressive as aqua regia. The HNO/ $HClO_4$ was a "wet digestion" method that extracted metals by breaking down complex organic matter and dissolving mineral components. The mechanism relied on a two-stage process where HNO_3 acted as the initial, less aggressive oxidizer. This was followed by $HClO_4$, which acted as a powerful, high-temperature oxidizer to finalize the decomposition.

EDTA, which worked by chelating metals, extracted the lowest values, though its effectiveness might be further reduced in soils with tightly-bound metals or less available metal forms. EDTA was effective as a chelating agent because of its metallic ions exchange capacity and redox reactions (Manouchehri & Bermond, 2009). It has a hexadentate ligand structure with four carboxyl and two amine groups; all these combined to enhance its ability to form chelates with different metallic ions. It therefore serves as a good reagent for remediation because of its high solubility with metallic elements in solutions and its ability to mobilize metal ions.

CONCLUSION

This study demonstrates that the metal extraction efficiencies of aqua regia (AR), nitric-perchloric acids (NP), and ethylenediamine tetraacetic acid (EDTA) vary significantly. The combination of two acids in the cases of AR and NP gave them more strength to attack and destroy any soil component to release heavy metal which was tightly held. EDTA, on the other hand, had weaker strength and could not remove metals highly bound to the soil matrix. However, sole reliance on strong acid digestion procedures may overestimate the associated health and ecological risks, while dependence on mild extractants may underestimate contamination levels and the associated risks. This emphasizes the necessity of employing multiple extractant approaches for realistic contamination assessment.

It is recommended that environmental policymakers and managers adopt integrated assessment arrangements that take into consideration the total and exchangeable (mobile and bioavailable) concentrations of metals when setting up remediation strategies and land-use planning. Environmental monitoring and regulations programs should demand an explicit specification of extraction procedures and guides for data interpretation to ensure accuracy and consistency. Stricter waste management protocols and regular environmental monitoring arrangements should be enforced to safeguard public health, especially in urban and peri-urban environments.

DATA AVAILABILITY

All relevant data are included in the paper or its Supplementary Information.

COMPETING INTERESTS STATEMENTS

The authors have no competing interests to declare that are relevant to the content of this article.

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