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BIOACCESSIBILITY AND HEALTH RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS (PTES) IN CONTAMINATED SOILS

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Abstract
The reliance on total concentrations of potentially toxic elements (PTEs) for human health risk assessment often leads to overestimation of exposure, as it does not account for the bioaccessible fraction available for absorption in the human gastrointestinal system. This study evaluated the oral bioaccessibility and associated health risks of As, Cd, Fe, Mn, Pb, and Zn in contaminated soils from crude oil–impacted sites in Warri, Delta State, and Pb mining areas in Ebonyi State, Nigeria. Surface soil samples were collected using a stratified composite sampling approach, air-dried, homogenized, and sieved to <250 µm prior to analysis. Pseudo-total concentrations were determined using atomic absorption spectrophotometry (AAS), while oral bioaccessibility was assessed using the Unified BARGE Method (UBM) simulating gastric and gastrointestinal phases. Pseudo-total concentrations (mg/kg) varied widely: As (25.0–55.7), Cd (7.4–18.4), Fe (32,740.7–48,666.7), Pb (76.7–7,451.0), Mn (400.1–4,938.3), and Zn (109.1–2,220.0), indicating substantial spatial variability and contamination intensity. Most elements were bioaccessible in both phases, with generally higher values in the gastric phase. Gastric bioaccessibility (%) ranged from As (3.1–37.5) and Cd (0.4–36.0), while Fe, Pb, Mn, and Zn showed variable bioaccessibility depending on site conditions. Cd showed negligible intestinal bioaccessibility across all matrices, while Pb exhibited limited gastrointestinal bioaccessibility in crude oil–impacted soils. Arsenic consistently showed lower bioaccessibility than other elements. Variations were linked to soil physicochemical properties, pH-dependent solubility (gastric: ~1.5–2.5; intestinal: ~6.5–7.5), and metal speciation influenced by crude oil contamination. Daily intake (DI, µg/kg BW/d) of As exceeded TDIoral (0.3) at mine sites (0.31), while Pb exceeded TDIoral (1.9) at auto-mechanic (2.23) and mine sites (41.9). HQ and HI values >1 for Pb and As, especially in children, indicated significant non-carcinogenic risks, while CR values suggested possible long-term carcinogenic concerns.
Keywords: Crude oil–contaminated soils; Niger Delta; Oral bioaccessibility (UBM); Potentially toxic elements (PTEs).

INTRODUCTION

The contamination of soils by potentially toxic elements (PTEs) has become a critical global environmental concern due to its far-reaching implications for ecosystem sustainability, agricultural productivity, and human health (Petropoulos et al., 2023; Sokol et al., 2022). PTEs including cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), Iron (Fe) and Manganese (Mn) occur naturally in the Earth's crust; however, their concentrations in soils have been significantly elevated by anthropogenic activities such as crude oil exploration, refining, transportation, and spill incidents, in addition to mining and industrial emissions (Cao et al., 2020; Li *et al.*, 2021). In crude oil–impacted environments, these elements are often introduced through drilling muds, produced water, pipeline leaks, and oil spills, leading to persistent contamination of soils and sediments (Osuji and Onojake, 2004; Adebayo *et al.*, 2022). Elevated PTE concentrations can alter soil physicochemical properties, disrupt microbial communities, and facilitate bioaccumulation along food chains, thereby posing both acute and chronic health risks to exposed populations (Jin-jin *et al.,* 2021; Qiao *et al.*, 2021). Children are particularly vulnerable due to their higher soil ingestion rates, frequent hand-to-mouth activities, and underdeveloped detoxification systems (Moya *et al.*, 2020). Crude oil mining regions, especially in the Niger Delta of Nigeria, are highly susceptible to PTE contamination due to decades of intensive petroleum exploitation and recurrent oil spills.

Unlike conventional metal mining, crude oil operations introduce a complex mixture of hydrocarbons and trace metals that interact with soil matrices, influencing the mobility, speciation, and persistence of contaminants (Anejionu *et al.*, 2015; Benson *et al.*, 2021).Oil-contaminated soils often exhibit altered pH, increased organic matter, and the presence of complexing agents, all of which can modify the environmental behavior of PTEs. For instance, acidic conditions and hydrocarbon degradation processes can enhance metal solubility, while organic matter may either immobilize or mobilize metals depending on prevailing geochemical conditions (Wu *et al.*, 2023). Consequently, the total concentration of PTEs in crude oil–impacted soils does not necessarily reflect their actual environmental risk. In Nigeria, particularly within the Niger Delta region, numerous studies have reported elevated levels of Ni, Pb, Cd, and Zn in soils affected by oil exploration and spill events, often exceeding permissible limits set by international guidelines (Benson *et al.*, 2021; *Adebayo et al.*, 2022). Communities residing in these areas are chronically exposed through multiple pathways, including ingestion of contaminated soils, inhalation of resuspended particulates, and consumption of polluted crops and water. The situation is exacerbated by socio-economic factors such as dependence on subsistence agriculture, limited environmental awareness, and inadequate remediation efforts, thereby increasing the potential for adverse human health outcomes.

Traditionally, environmental risk assessments have relied on total concentrations of PTEs to evaluate contamination levels and associated health risks. However, this approach has significant limitations, as it does not account for the fraction of contaminants that is actually available for absorption in the human body (Bradham *et al.*, 2021; Ng *et al.*, 2019). The bioavailability of PTEs is strongly influenced by their chemical speciation, binding phases, and interactions with soil constituents. For example, metals bound to sulfides or residual mineral fractions may remain largely inert, whereas those associated with exchangeable or carbonate fractions are more readily mobilized under physiological conditions (Hursthouse, 2001; Luo *et al.*, 2018). To address these limitations, contemporary studies increasingly incorporate the concept of bioaccessibility, defined as the fraction of a contaminant that is solubilized in the gastrointestinal tract and becomes available for absorption (Ruby *et al.*, 1999; Juhasz *et al.*, 2017). In vitro bioaccessibility (IVBA) methods, such as the Unified BARGE Method (UBM), simulate human digestive conditions using synthetic gastric and intestinal fluids, providing a more realistic estimate of human exposure compared to total concentration-based assessments (Denys *et al.*, 2012; Chen et al., 2022). The variability in bioaccessible fractions is influenced by factors such as soil composition, pH differences between gastric (≈1.5–2.5) and intestinal (≈6.5–7.5) environments, metal speciation, and the presence of competing ions, all of which govern the dissolution and mobility of PTEs in the human digestive system.

Incorporating bioaccessibility into human health risk assessment enhances the accuracy of exposure estimates and supports more informed decision-making. Risk indices such as the Hazard Quotient (HQ), Hazard Index (HI), and lifetime Cancer Risk (CR) can be recalculated using bioaccessible concentrations, thereby avoiding overestimation or underestimation of risks (Mehta *et al.,* 2020; Billmann *et al.*, 2023). Generally, HI values greater than 1 indicate potential non-carcinogenic health risks, while CR values exceeding 1×10^{-4} are considered unacceptable by regulatory agencies (USEPA, 2011). Such refined assessments are particularly important in crude oil–impacted regions, where complex contaminant interactions can significantly influence exposure dynamics. Despite the increasing global adoption of bioaccessibility-based risk assessment approaches, their application in crude oil–impacted soils in Nigeria remains limited. Most existing studies in the Niger Delta rely on total metal concentrations, with little consideration of bioaccessible fractions, potentially leading to inaccurate risk characterization and inefficient remediation strategies (Nduka and Orisakwe, 2011; Anejionu *et al.*, 2015). Furthermore, there is a paucity of studies that integrate bioaccessibility data with comprehensive human health risk models in petroleum-contaminated environments. Therefore, This study aimed to evaluate the oral bioaccessibility and associated health risks of selected PTEs in crude oil-contaminated soils in the Niger Delta using the Unified BARGE Method (UBM). By integrating *in vitro* bioaccessibility measurements with established risk assessment models, this work seeks to provide a more realistic assessment of human exposure and contribute to improved environmental management and policy development in oil-producing regions.

Study Area

The study was conducted in oil–impacted environments within Warri South-West Local Government Area of Delta State, located in the Niger Delta region of southern Nigeria (approximately 5°30′–5°45′N and 5°30′–5°45′E). The Niger Delta is one of the world's largest wetland ecosystems and a major center of petroleum exploration and production, hosting extensive networks of creeks, mangrove forests, and estuarine systems. The area is characterized by a low-lying coastal plain with elevations typically below 20 m above sea level, making it highly susceptible to flooding, tidal influence, and contaminant redistribution. Warri South-West is predominantly occupied by riverine communities, including Gbaramatu and adjoining settlements, where livelihoods are largely dependent on fishing, subsistence agriculture, and small-scale trading. Over several decades, the region has experienced significant environmental degradation due to crude oil exploration, transportation, and processing activities. Frequent oil spills, pipeline leakages, gas flaring, and artisanal refining operations have contributed to the accumulation of petroleum hydrocarbons and associated potentially toxic elements (PTEs) in soils and sediments. The study area exhibits a tropical humid climate with two distinct seasons: a wet season (April–October) and a dry season (November–March). Annual rainfall ranges between 2,000 and 3,000 mm, with average temperatures of 25–32°C and high relative humidity (>80%). The hydrological dynamics of the area, influenced by tidal flux and seasonal flooding, play a critical role in the transport, redistribution, and fate of contaminants within the soil environment.

Sample Sites

Three (3) soil samples were taken from different crude oil polluted sites located in Delta, Nigeria. Contaminated soil samples were taken from spill sites in Warri, Delta State. Mechanic wastes contaminated samples were taken from three different sites; metals scrape site at warri (MSO), auto-battery Workshop site at Ughelli (AAS) and auto-mechanic engine service site at Sapele (CSS), Delta State. The Pb mine wastes contaminated soils were collected from three different locations; mine site (MS), home of local dealer (HLD) and roadside that is about 200m from the mine site (RCM), all in Ishiagu in Ebonyi State, Nigeria

Sample Collection

Composite surface soil samples were taken from 0-15cm depth (Poggio *et al.,* 2009) due to possible contact to soil metals pollution common with the surface soil (Okoye and Okwute, 2014). For each composite sample three samples were taken from

every location and transferred into labeled polyethylene sacs and transported to the research laboratory, where the samples were homogenized.

Sample Preparation

The samples were spread on an uncontaminated plastic sheet placed on table in an open air in the laboratory for some days. The air dried samples were later sieved through a <250um stainless steel mesh screen. The size of <250um was using because this particles size was suggested to be relevant for ingested or inhalable soil fraction Oomen *et al.,* (2003).

Soil pH

10.00 g of every sample were weighed and transferred into a bottle with screw cap and 25 ml of de-ionized water was added and the cap put in place. The resulting suspension was mixed by shaking for about 15 min period. The resulting suspension was stirred and the pH measurement taken with the insertion of the electrode probe. The whole process was also repeated with $CaCl_2$ solution.

Heavy Metals Digestion (Aqua Regia)

About 0.5g samples were weighed and transferred into burning test tubes and 20 ml aqua regia (hydrochloric acid and Nitric Acid, ratio 3:1) solution was added. The resulting mixtures were digested for about 1 hour at 100^{o}C on a hot plate. The resulting digests were allowed to cool and then filtered into a 100ml flask and made to mark with de-ionized water, and submitted to AAS for analysis.

Atomic Absorption Spectrophotometer (AAS)

The filtrates were analysed with Atomic Absorption Spectrophotometer (AAS Raleigh WF X 320) after calibrating the equipment with different standard concentrations. The concentrations of six elements Zn, As, Pb, Cd, Fe and Mn were determined. The selected metals concentrations in soil were calculated in mg/kg.

Oral Bioaccessibility Assessment (Unified BARGE Method, UBM)

Oral bioaccessibility of potentially toxic elements (PTEs) was determined using the Unified BARGE Method (UBM), a widely accepted in vitro procedure that simulates human gastrointestinal conditions (Wragg *et al*., 2009). The method comprises two sequential extraction phases: the gastric phase and the gastrointestinal (intestinal) phase, designed to mimic the physicochemical environment of the human digestive system. All analyses were conducted on the <250 µm soil fraction, which represents the most relevant particle size for human exposure due to its high adhesion to skin and increased likelihood of ingestion via hand-to-mouth activity, particularly in children. Each sample was analyzed in triplicate to ensure reproducibility and analytical reliability.

Gastric Phase Extraction

For the gastric phase, 0.6 g of the <250 µm soil fraction was accurately weighed into acid-washed polycarbonate centrifuge tubes (50 mL). A volume of 9.0 mL of simulated saliva fluid was added and manually mixed for approximately 10 seconds to ensure initial dispersion. Subsequently, 13.5 mL of simulated gastric fluid was introduced to the mixture.

The pH of the suspension was adjusted to 1.2 ± 0.05 using dropwise addition of either concentrated hydrochloric acid (37% HCl) or 1 M sodium hydroxide (NaOH), to replicate human gastric conditions. The samples were then incubated at 37°C in an end-over-end rotator (≈30 rpm) for 1 hour.

Following incubation, the suspensions were centrifuged at 4,500 × g for 10 minutes. The supernatant was carefully decanted, and aliquots were acidified with 0.1 mL of concentrated nitric acid (HNO_3) to stabilize dissolved metals. Extracts were stored at <4°C prior to elemental analysis.

Gastrointestinal Phase Extraction

The gastrointestinal phase extraction was performed sequentially using the same sample residues from the gastric phase. After the initial 1-hour gastric extraction, 27 mL of simulated duodenal fluid and 9.0 mL of simulated bile fluid were added to each tube to simulate intestinal conditions.

The pH of the mixture was measured and adjusted, where necessary, to approximately 6.3–6.8 to reflect the near-neutral conditions of the small intestine. The samples were then incubated at 37°C on an end-over-end rotator for an additional 4 hours.

At the end of the incubation period, the suspensions were centrifuged at 4,500 × g for 10 minutes. The supernatant was collected, acidified with 0.1 mL of concentrated HNO_3, and stored at <8°C until analysis.

Quality Assurance

All reagents used for the preparation of simulated fluids were of analytical grade, and deionized water was used throughout. Procedural blanks and replicates were included to ensure data quality and method reliability.

Analysis and Determination of PTEs Bioaccessible fractions

Bioaccessible concentrations of Cd, Cr, Cu, Pb, Ni, and Zn were determined using a GBC XplorAA flame atomic absorption spectrophotometer (FAAS) following extraction by the Unified BARGE Method (UBM). Results were expressed as mg/kg of the <125 µm soil fraction.

The percentage bioaccessible fraction (%BAF) was calculated as:

$$\text{Bioaccessible fraction (BAF)}(\%) = \frac{Cbioaccessibility}{Ctotal\ content} \times 100 \qquad (1.1)$$

Where, $C_{Bioaccessibility}$ = Concentration of PTE released from125 µm fraction soil (mg/kg) obtained viaBARGE stage I (gastric) or stage II (gastric + intestinal); $C_{total\ content}$ = total concentration of PTE in 125 µm fraction soil (mg/kg).

Estimation of Daily Oral Intake (DI) of PTEs from soil samples

The estimated daily intake (EDI) (mg $kg^{-1}day^{-1}$) of potentially toxic elements through the incidental ingestion of 125 µm fraction of soil sample with the highest concentration was calculated with the equation below:

$$EDI_{ingestion} = \left(\frac{Csoil\ X\ IngRsoil\ X\ EF\ X\ ED\ X\ CF}{BW\ X\ AT}\right) \quad (1.6)$$

where C_{soil} is the PTE concentration (mg/kg), IngR is the ingestion rate (100 mg/day for adults; 200 mg/day for children), EF is exposure frequency (days/year), ED is exposure duration (years), BW is body weight (kg), AT is averaging time (years), and CF is the conversion factor (10^{-6} kg/mg).

To improve risk estimation, EDI was adjusted using bioaccessibility:

$$EDI_{Adjusted} = EDI \times B \quad (1.3)$$

Where B is the bioaccessible fraction derived from UBM extraction.

RESULTS AND DISCUSSION

Table 1: Soil pH in di-ionise water and $CaCl_2$

SAMPLES	pH (H_2O)	pH ($CaCl_2$)
MSO	7.60	7.45
AAS	6.85	6.70
CSS	7.65	7.62
HLD	7.55	7.50
RCM	5.18	4.45
MS	5.88	5.25
OSS	2.97	2.95
MSS	1.90	1.88
ES	4.60	4.55

Table 2 Total, gastric and gastrointestinal concentrations, and gastric and gastrointestinal bioaccessibilities for As

Sample	Total As (mg/kg)	G-phase (mg/kg)	GI-phase (mg/kg)	% G-phase	% GI-phase
MSO	39.22 ± 5.3	2.713	6.212	6.9	15.8
AAS	18.67 ± 2.9	1.529	5.606	8.2	30.0
CSS	17.00 ± 5.0	1.897	5.000	11.2	29.4
HLD	62.19 ± 8.1	2.925	6.357	4.7	10.22
RCM	51.59 ± 3.1	0.983	3.345	1.9	6.5
MS	53.35 ± 3.1	2.184	4.216	4.1	7.9
OSS	28.67 ± 7.6	4.843	5.060	16.9	17.7
MSS	49.82 ± 5.3	4.674	5.317	9.4	10.7
ES	35.05 ± 3,7	2.364	9.450	6.7	27.0

Soil pH and Its Implications for PTE Bioaccessibility and Health Risk

Soil pH is a critical geochemical parameter controlling the mobility, speciation, and bioaccessibility of potentially toxic elements (PTEs) in contaminated environments. The measured pH values (Table 1) revealed a wide variation across the study sites, ranging from strongly acidic to slightly alkaline conditions. Specifically, pH (H_2O) values ranged from 1.90 (MSS) to 7.65 (CSS) (Table 1), while pH ($CaCl_2$) values ranged from 1.88 to 7.62, indicating consistent trends across both measurement media. The soils can be broadly categorized into three groups: (i) near-neutral to slightly alkaline soils (MSO, CSS, HLD; pH 7.55–7.65), (ii) moderately acidic soils (AAS, RCM, MS, ES; pH 4.60–6.85), and (iii) strongly acidic soils (OSS and MSS; pH 1.90–2.97). The extremely low pH observed in OSS and MSS suggests severe acidification, likely resulting from prolonged crude oil contamination, oxidation of sulfur-containing compounds, and the formation of acidic by-products during artisanal refining processes. Similar acidification patterns have been reported in hydrocarbon-impacted soils in the Niger Delta, where oil spills and refining residues significantly alter soil chemistry. From a bioaccessibility perspective, soil acidity plays a fundamental role in enhancing the solubility and mobilization of PTEs. Under strongly acidic conditions (pH < 4), metals such as Cd, Pb, Zn, and Mn are more readily desorbed from soil particles and mineral phases, increasing their dissolution into pore water and simulated gastric fluids. Consequently, the highly acidic soils (OSS and MSS) are expected to exhibit elevated gastric bioaccessibility, as the low pH mimics or even exceeds the acidity -of the human stomach (pH ~1.5–2.5). This can lead to increased oral exposure and higher estimated daily intake, particularly in vulnerable populations such as children. In contrast, near-neutral to slightly alkaline soils (MSO, CSS, HLD) tend to reduce metal solubility through processes such as adsorption onto mineral surfaces, precipitation as hydroxides or carbonates, and stronger binding to soil organic matter.

These conditions generally result in lower bioaccessible fractions of PTEs, thereby potentially reducing immediate human exposure risk despite high total concentrations. The moderate pH range observed in AAS, RCM, MS, and ES suggests intermediate behavior, where metal mobility and bioaccessibility may vary depending on other controlling factors such as organic matter content, redox conditions, and metal speciation. Notably, the consistently lower pH values measured in $CaCl_2$ compared to deionized water indicate the presence of exchangeable acidity and highlight the potential for greater metal mobility under natural soil solution conditions. From a human health risk perspective, the presence of highly acidic soils is particularly concerning. Increased metal solubility under such conditions enhances the likelihood of oral bioavailability, which directly influences non-carcinogenic risk indicators such as hazard quotient (HQ) and hazard index (HI). Therefore, sites with low pH (especially OSS and MSS) are likely to contribute disproportionately to health risks due to enhanced PTE bioaccessibility, even if total concentrations are comparable to other locations.

Concentration of PTEs in the Soil Matrices

The concentrations of Arsenic in auto-mechanic workshop sites, mine waste sites and crude oil contaminated sites were 17.0 - 39.22, 51.59 -62.19and 28.67 -49.82 respectively (Table 2). The concentrations of As were found to be more in mine waste site compared to values recorded in crude oil and auto-mechanic contaminated sites respectively. The range of As concentrations reported in auto-mechanic workshop by Imasuen and Omorogieva (2013) (18.59-22.41 mg/kg) were close to the range generated in this study. However, the concentration range observed (Femi Oloye *et al*., 2014) with concentration values of (2.45 - 2.53 mg/kg) were lower compare to the data observed in this study (17.0 - 39.22 mg/kg). The concentration range for As in mine sites from this work is related to those previously recorded (Ikenaka *et al*., 2010) with concentrations range of 3-52 mg/kg and (Barkouch *et al*., 2016) with concentrations range of 46.2-78.5 mg/kg for other mine sites. However, the range observed in this study were above those recorded by (Boisa *et al.,* 2013; Ekwe *et al*., 2012 and Okorie *et al*., 2012), who recorded concentrations ranges of 0.00-8.62 mg/kg, 1.61-21mg/kg and 4.4-8.6 mg/kg respectively for other mine sites. The higher concentrations range from this study may be due to the fact that the sites might have been exposed to much activities for some time. Other research (Jose et *al*., 2010; Shamsoddini *et al*., 2014; Liao G. *et al*., 2007 and Filimon *et al*., 2016) recorded concentrations range of 338-994 mg/kg, 311-20150 mg/kg, 18.9-207.0 mg/kg and 13.723-858.59mg/kg respectively. The ranges of Jose et *al*., (2010), Shamsoddini *et al*., (2014), Liao *et al*., (2008) and Filimon *et al*., (2016) are above concentrations observed in this study. The variations in arsenic concentrations observed in this study and previously reported ones cited in this study may be due variations in arsenic mineralogy at the different study sites or period of exposure. The data observed from this study (49.82 - 28.67 mg/kg) for arsenic in crude oil contaminated sites were above those reported by Onojake and Okonkwo (2011) (0.001 mg/kg) and Basumatary *et al*., (2012)(0.005-0.055 mg/kg) for similar soils matrix. The higher range from this study may be due to fact that the sites in this study may be rich in geogenic content of arsenic.

The concentrations range of cadmium in auto-mechanic workshop sites, mine waste sites and crude oil contaminated sites were5.8 -8.7 mg/kg, 15.5 - 22.2 mg/kg and 6.8 - 8.7 mg/kg respectively (Table 3). Higher level of cadmium concentrations were recorded at the mine waste contaminated sites compared to the two other sites (auto-mechanic workshop and crude oil contaminated site). The concentrations recorded for auto-mechanic workshop contaminated soils sand crude oil contaminated soils are similar. The concentrations range, 5.8 -8.7 mg/kg for cadmium in auto-mechanic workshop sites from this study is similar to those (5.0-5.93 mg/kg) previously recorded by Odoh *et al*., (2011) for related matrix. The arsenic concentrations in auto-mechanic waste contaminated soils are above NESREA/FEPA limit values of 3-6 mg/kg for soil. The concentrations ranges observed by Luter *et al*., (2011) and Akpoveta *et al*., (2010) were 0.5-4.4 mg/kg and 1.50-1.52 mg/kg respectively. Their concentrations were lower compare to the data recorded in this study (5.8- 8.7 mg/kg). The results of cadmium concentrations from this work were however, above those reported by Nwanchwukwu *et al*.,(2010); Akporido et al.,(2015); Ololade *et al*., (2015); Pam Aloysius *et al*.,(2013); Imasuen and Omorogieva (2013) and Akporido *et al.,(*2015) who reported 8.00-23.00 mg/kg, 22.6-43.2 mg/kg, 37.5-67.4 mg/kg, 11.74-21.83 mg/kg, 12.17-37.40 mg/kg and 20.1 - 442.7 mg/kg, respectively in similar studies. The levels of cadmium observed from auto-mechanic workshop contaminated soils may be due to the activities of motor repairs which include body work, soldering, painting, engine oils and corrosion of metals. The concentrations range 15.5 - 22.2 mg/kg for cadmium in mine waste contaminated soils from this work are similar to1.36-18.65 mg/kg recorded by Yoshinori *et al*., (2010) in similar study. The cadmium concentrations observed from this study were however, more than those previously recorded in soils around mine waste sites by Pan & Li, (2016), Lioa *et al*.,(2008), Abbas *et al*., (2015), Chukwu, (2011) and Ekwue et al., (2012), who reported 0.0002-0.426 mg/kg, 1.6-11.5 mg/kg, 0.3-11.20mg/kg,0.05-10.00mg/kg and 0.42-0.7 mg/kg, respectively. Higher concentrations of cadmium in this study show that the sites must have been seriously affected by mining activities for long time. The concentrations ranges observed by Boisa *et al*., (2013) and Shamsoddini *et al*.,(2014) from mine waste contaminated soils were 69.4-72.0 mg/kg and 4.0-64.4 mg/kg, respectively were however, higher than those recorded in this study15.5 - 22.2 mg/kg.

The concentrations range, 6.8 - 8.7 mg/kg for cadmium in crude oil contaminated sites from this study were more than1.86-4.80 mg/kg,0.01-0.07 mg/kg, 0.6-3.0 mg/kg and 0.98-2.03 mg/kg, previously reported by Adesina and Adelasoye (2014), Ideriah *et al.*,(2010), Chukwujindu (2011), and Agbogidi (2013), respectively. The cadmium concentrations observed from this work were however, lesser than those reported by Iwegbue *et al.,* (2009) as 37.3-37.5 mg/kg.

Table 1: Total, gastric and gastrointestinal concentrations, and gastric and gastrointestinal bioaccessibilities for Cd

Sample	Total Cd (mg/kg)	G phase (mg/kg)	GI phase (mg/kg)	%G-phase	%GI-phase
MSO	5.8 ± 0	1.67	< detection	28.8	NC
AAS	7.7 ± 1.7	0.15	< detection	2.0	NC
CSS	8.7 ± 0	0.90	< detection	10.3	NC
HLD	15.5 ± 1.7	0.34	< detection	2.2	NC
RCM	22.2 ± 1.7	< detection	< detection	NC	NC
MS	17.4 ± 0	0.37	< detection	1.7	NC
OSS	6.8 ± 1.7	< detection	< detection	NC	NC
MSS	8.7 ± 0	< detection	< detection	NC	NC
ES	6.8 ± 1.7	< detection	< detection	NC	NC

Table 2: Total, gastric and gastrointestinal concentrations, and gastric and gastrointestinal bioaccessibilities for Fe

Samples	Total Fe (mg/kg)	G-phase (mg/kg)	GI phase (mg/kg)	%G-phase	%GI-phase
MSO	5400 ± 1155	676	448	1.3	0.8
ASS	17333 ± 1155	204	219	1.2	1.3
CSS	26889 ± 385	556	364	2.1	1.4
HLD	45556 ± 1540	205	399	0.5	0.9
RCM	32667 ± 661	201	40	0.6	0.1
MS	67778 ± 5670	133	222	0.2	0.3
OSS	45333 ± 2309	959	337	2.1	0.7
MSS	39111 ± 2143	1478	307	3.8	0.8
ES	38666 ± 0	1338	743	3.5	1.9

The concentrations range of iron in auto-mechanic workshop contaminated sites, mine waste sites and crude oil contaminated sites were 5400-26889mg/kg, 32667-67778mg/kg and 4533 – 38666 mg/kg, respectively (Table 4). Higher level of iron concentrations were recorded at the mine waste contaminated sites compared to the two other sites (auto-mechanic workshop and crude oil contaminated site). Higher levels of iron concentrations recorded in all the three soil matrices shows that most soils from study are have appreciable quantities of iron. The concentrations range, 5400-26889 mg/kg for iron in auto-mechanic workshop sites from this study is similar to those 10100-23620 mg/kg previously recorded by Sam *et al.*, (2013) for related matrix. Nwanchwukwu *et al.*,(2010), recorded concentrations of 748-70606 mg/kg for similar matrix. Their concentrations were lower compare to the data recorded in this study 5400-26889 mg/kg. The concentrations range32667-67778 mg/kg for iron in mine waste contaminated soils from this work were more than the one previously reported in soils around mine waste sites by Jesús *et al.*, (2010) who recorded 23813 – 47875 mg/kg. Higher concentrations of iron in this work may be as a result of difference iron mineralogy of the two study sites. The concentrations ranges 4533 – 38666 mg/kg for iron in crude oil contaminated sites from this work were more than those previously recorded by Basumatary *et al.*, (2012), Agbogidi, (2013), Okoye and Okwute (2014), and Egai and Imaseun (2015), who reported1.5 – 1.9mg/kg,0.03 – 3.57 mg/kg, 80.25 – 90.45m/kg and 14.53 – 20.35mg/kg, respectively in related studies. The large variance in concentration at our work site and those previously reported by others is difficult to explain.

The concentrations range of manganese in auto-mechanic workshop sites, mine waste sites and crude oil contaminated sites were 276-574.1mg/kg, 2130-9167 mg/kg and 332-493mg/kg, respectively (Table 5). Higher level of manganese concentrations were observed in mine waste site compared to the two other sites (auto-mechanic workshop and crude oil contaminated site). The higher levels observed at the mine site may be due to the possible presence of Mn-based minerals at the sites. The concentrations range 276-574.1 mg/kg for manganese in auto-mechanic workshop sites from this work are similar to,402 – 486.67 mg/kg and 186 – 600 mg/kg recorded by Nwanchukwu et al., (2010) and Odoh *et al.*,(2011), respectively for similar matrix. The manganese concentrations observed from this work were however, more than the one previously recorded in soil around auto-mechanic workshop by Oladeji *et al.,* (2016) who reported 203.9 – 293.8mg/kg, for a similar study. The

concentrations observed by Nwanchukwu *et al.,* (2010), for auto-mechanic workshop contaminated The concentrations range,2130 – 9164mg/kg for manganese in mine waste sites from this study were higher than 300 – 2375mg/kg and549.6 – 1411.7mg/kg previously recorded by Jesús *et al.*,(2010) and Addo *et al.*, (2011), respectively. The higher range from this work may be due to fact that the sites in this study may be rich in $(Mn^{4+}, Mn^{2+})_8O_{16}$ coronadite content of manganese from Pb-bearing minerals. The concentrations range 332mg/kg – 493 soils, 864 mg/kg, was however, higher than those recorded in this study.

mg/kg for manganese in crude oil contaminated soils from this work is similar to65.6-509.4 mg/kg recorded by Chukwujindu (2011) in related studies. The manganese concentration range obtained from this study is however, higher than the one previously recorded in soils around crude oil contaminated sites by Ideriah *et al.*, (2013),17.7-77.4mg/ kg, in similar study.

Table 3 Total, gastric and gastrointestinal concentrations, and gastric and gastrointestinal bioaccessibilities for Mn

mple	Total Mn (mg/kg)	G-phase (mg/kg)	GI–phase (mg/kg)	%G-phase	%GI-phase
MSO	574.1 ± 6	100	36	17.4	6.3
AAS	353 ± 16.7	49	21	13.9	6.0
CSS	276 ± 47.9	56	17	20.3	6.2
HLD	3519 ± 802	249	79	7.1	2.3
RCM	2130 ± 321	198	44	9.3	2.1
MS	9167 ± 833	660	296	7.2	3.2
OSS	493 ±29.7	186	37	37.8	7.5
MSS	332 ± 126	102	19	30.7	4.8
ES	387 ± 23.3	170	49	43.9	12.6

Table 4 Total, gastric and gastrointestinal concentrations, and gastric and gastrointestinal bioaccessibilities for Pb

Sample	Total Pb (mg/kg)	G-phase (mg/kg)	GI-phase (mg/kg)	% G-phase	% GI-phase
MSO	506.7 ± 04	174	63	34.3	12.4
ASS	473.3 ± 26.6	109	47	23.0	9.9
CSS	213.3 ± 41.6	116	31	54.4	14.5
HLD	10333.3 ± 577.4	2484	793	24.0	7.7
RCM	1686.7 ± 127.4	191	< detection	11.3	NC
MS	10333.0 ± 127.4	802	111	7.8	1.1
OSS	60 ± 10	9	< detection	15.0	NC
MSS	86.7 ± 15.3	10	< detection	11.5	NC
ES	83.3 ± 20.8	14	< detection	16.8	NC

The concentrations of lead in auto-mechanic workshop sites, mine waste sites and crude oil contaminated sites were 213.3 -506.7 mg/kg, 1686.7 -10333.3 mg/kg and 60-86.7 mg/kg, respectively (Table 6). The maximum concentrations of lead were found to be more than twenty times higher than those recorded in crude oil and auto-mechanic contaminated sites. The lead concentrations in mine and auto-mechanic workshop contaminated soils are above tolerable limit values of 140 mg/kg for residential area (CCME, 1999). The concentrations range 213.3 -506.7 mg/kg for lead in auto-mechanic workshop sites from this study are within the same range to, 513 – 582 mg/kg recorded by Odoh *et al.*,(2011) in similar studies. The lead concentrations observed from this work were however, more than those previously recorded in soils around auto-mechanic workshop sites by Ipeaiyeda *et al.*, (2007), Ilemobayo and Kolade (2008), who reported 34.5 – 298mg/kg, 70.8 – 192.35mg/kg, respectively. The concentrations ranges observed by Michael et al,(2010), Nwanchuku *et al.,(*2010), Adelekan and Abegunde (2011) and Aloysius *et.al.*,(2013) and were 1162 ± 572mg/kg,99 – 1090 mg/kg, 11.75 – 2882.50 mg/kg and 45.35 – 1265.3 mg/kg respectively. Their concentrations were higher compare to the data recorded in this study (213.3 -506.7 mg/kg). The elevated levels of lead observed from auto-mechanic workshop contaminated soils may be due to the disposal motor batteries indiscriminately. The concentrations range 1686.7 -10333.3 mg/kg for lead in mine waste sites from this work is similar to,0.5 – 13671mg/kg recorded by Chukwu, E. (2011) at the same mining district in Ishiagu, south eastern Nigeria. The similarity between this work and that of Chukwu, E. (2011), validate the level of Pb contamination in soils around Ishiagu mining area. The lead concentrations observed from this work were however, more than those previously recorded in soils around mine waste sites by Jesus *et al.*, (2010), Ekwue *et al.*, (2012), Shamsoddini et al., (2014), Damangir *et al.*, (2015), Pan, and Li, (2016). and Barkouch *et al.*,(2016) who recorded 126 – 3855mg/kg, 8.0 – 15.0mg/kg, 0.04 – 5.0 mg/kg, 20.10 – 152.80 mg/kg, 17.92 – 395.60mg/kg and 61.3 – 255.3 mg/kg, respectively for other mine waste sites.

The reasons for high level of Pb in this study may be due to the release from mine dumps and buried Pb-Zn lodes around the mining area. The concentrations observed by Jose *et al.,* (2010),Yoshinori *et al.*,(2010) and Denys *et al.*, (2012) who reported 3967 – 84130 mg/kg, 880 – 16951 mg/kg and 2141 – 77009 mg/kg, respectively were however, higher compare to the data in this study (1686.7 -10333.3 mg/kg). The variations in lead concentrations observed in this study and previously reported ones cited in this study may be due difference in Pb-minerals at the different sites. The concentrations range 60-86.7 mg/kg for lead in crude oil contaminated site from this work is above those previously recorded in soils around crude oil spill by Osuji and Onojake (2004), Iwegbue et al., (2009), Chukwujindu and Iwegbue (2011), Ideriah et. al.,(2012) and Egai and Imaseun (2015) who recorded 0.32 – 0.80mg/kg, 1.59 – 14.0 mg/kg, 14.2 – 38.0mg/kg,0.98 – 2.38mg/kg and 12.8 – 12.9 mg/kg, respectively.

The concentrations of zinc in auto-mechanic workshop sites, mine waste sites and crude oil contaminated sites are 250-5277.8 mg/kg, 548.9-3333.3 mg/kg and 98.9-126.7 mg/kg respectively (Table 7). The concentrations of zinc were found to be higher in auto-mechanic workshop sites compared to the two other sites (mine waste sites and crude oil contaminated sites). The higher concentrations of zinc observed in auto-mechanic workshop sites may be attributed to various automobile bodyworks conducted at auto-mechanic sites. The zinc concentrations in mine and auto-mechanic workshop contaminated soils are above tolerable limit values of 200 mg/kg for residential area (CCME, 1999). The concentrations range 250-5277.8mg/kg for zinc in auto-mechanic workshop sites from this work is similar to, 1503.8-3424.5 mg/kg recorded by Ololade, (2015) in related studies. The zinc concentrations observed from this work were however, higher than those previously recorded in soils around auto-mechanic workshop sites by Akpoveta et al., (2010) Odoh et al., (2011), Abidemi, (2011), Pam, *et al.,* (2013), and Akporido *et al.,* (2015) who reported 74.26-91.21 mg/kg,115.33-138.33mg/kg, 105.80-125.20 mg/kg, 214.9-381.6mg/kg and 67.69-599.45 mg/kg, respectively. The concentrations range 548.9-3333.30 mg/kg for zinc at mine waste sites from this work were more than those previously reported in soils around mine waste sites by Liao et al., (2007), Ekwue *et al.*, (2012), Ladwani *et al.*, (2012) and Boisa *et al.*, (2013) who reported 52.1-976.0mg/kg, 34-49 mg/kg,61.1-175.8 mg/kg and 1063-1088mg/kg, respectively. The concentrations observed by Ikenaka *et al.*, (2010) and Filemon *et al.*, (2016) who reported 2180-40534mg/kg and 87.82-7190mg/kg, respectively were however, higher compared to the data in this study (548.9-3333.30 mg/kg). The variations in zinc concentrations observed in this study and previously reported ones may be due to varying Zn-minerals at the different locations. The concentrations range, 98.9-126.7 mg/kg for zinc in crude oil contaminated sites from this study is similar to the one 1.27-128 mg/kg previously reported by Iwegbue *et al.,* (2009) for related matrix. The concentrations range observed in this study were however, higher than those 4.47- 46.0 mg/kg and 6.34-19.1 mg/kg previously reported by Chukwujindu (2011) and Ideriah *et al.*, (2012), respectively in related studies. The results of zinc concentrations from this study were however, lower than those recorded by Liao *et al.,* (2007), Abbas *et al.*, (2015), Filimon *et al.*, (2016) and Barkouch *et al.,* (2016) as 52.1-976.0 mg/kg, 20.70-513.30 mg/kg, 87.82-7190 mg/kg and 223.0-890.5 mg/kg, respectively in similar studies.

Table 5 Total, gastric and gastrointestinal concentrations, and gastric and gastrointestinal bioaccessibilities for Zn

Sample	**Total Zn (mg/kg)**	**G-phase (mg/kg)**	**GI-phase (mg/kg)**	**%G-phase**	**%GI-phase**
MSO	5277.8 ± 96.2	211	345	4.0	6.5
ASS	250 ± 7.5	80	23	32.0	9.2
CSS	422.8 ± 20.6	108	25	25.5	5.9
HLD	3333.3 ± 166.7	86	19	2.6	0.6
RCM	2777.8 ± 166.7	13	< detection	0.5	NC
MS	548.9 ± 15.4	16	< detection	2.9	NC
OSS	101.7 ± 3.3	14	< detection	13.8	NC
MSS	98.9 ± 6.7	25	< detection	25.3	NC
ES	126.7 ± 2.9	22	25	17.7	19.7

Table 6 Results of Stastical Analysis of Total Concentrations (mg/kg) and pH in Auto-Mechanic Workshop Soil, Mine Soil and Crude Oil Waste Soil. n = 3

Sample	pH (H_2O)	pH ($CaCl_2$)	As	Cd	Fe	Pb	Mn	Zn
Mean	7.37	7.26	24.96	7.40	32740.70	397.80	400.90	1983.50
Minimum	6.85	6.70	17.00	5.808.	17333.3054	213.30	275.905	250.00
Maximum	7.65	7.26	39.22	70.00	000.00	506.70	74.10	5277.8
			Mine					
Mean	6.20	5.73	55.71	18.40	48666.70	7451.00	4938.30	2220.00
Minimum	5.18	4.45	51.59	15.52	32666.70	1686.00	2129.69	548.90
Maximum	7.55	7.50	62.19	2.20	7777.80	10333.30	166.70	3333.30
			Crude					
Mean	3.12	3.13	37.85	7.43	41036.80	76.70	403.90	109.10
Minimum	1.90	1.88	28.67	6.80	38660.00	60.00	332.204	98.90
Maximum	4.60	4.55	49.82	70.00	45333.30	86.70	92.60	126.70

Bioaccessible concentrations and Correlation between bioaccessible concentrations and total concentrations

The bioaccessible concentrations of potentially toxic elements (PTEs) varied across matrices and digestive phases, with most elements exhibiting higher bioaccessibility in the gastric phase than in the gastrointestinal phase, except arsenic (As). For As, gastric phase concentrations (mean; range, mg/kg) were 2.05 (1.53–2.71) in auto-mechanic soils, 2.03 (0.98–2.93) in mine waste soils, and 3.96 (2.36–4.84) in crude oil–contaminated soils, whereas gastrointestinal phase concentrations were higher at 5.61 (5.00–6.21), 4.64 (3.35–6.36), and 6.61 (5.06–9.45) mg/kg, respectively, all below UK (32 mg/kg) and Dutch (55 mg/kg) guideline values. Cadmium (Cd) was bioaccessible only in the gastric phase, with mean values of 0.91 (0.15–1.67) mg/kg in auto-mechanic soils and 0.36 (0.34–0.37) mg/kg in mine waste soils, while gastrointestinal concentrations were below detection limits; these values were below international and local soil quality guidelines (1.4–12 mg/kg). Iron (Fe) displayed mean gastric concentrations of 478.7 (204–676) mg/kg, 179.7 (133–205) mg/kg, and 1258.3 (959–1478) mg/kg for auto-mechanic, mine waste, and crude oil soils, respectively, with gastrointestinal values of 343.7 (219–448), 220.3 (40–399), and 462.3 (307–743) mg/kg; bioaccessibility was higher in the gastric phase for auto-mechanic and crude oil soils but higher in the gastrointestinal phase for mine soils. Lead (Pb) was highly bioaccessible in the gastric phase, with mean values of 133 (109–174), 1159 (191–2484), and 11 (9–14) mg/kg in auto-mechanic, mine waste, and crude oil soils, respectively; gastrointestinal concentrations were 47 (31–63) mg/kg for auto-mechanic and 452 (111–793) mg/kg for mine soils, with mine waste exceeding UK (450 mg/kg) and Dutch (530 mg/kg) residential guideline values. Manganese (Mn) exhibited gastric concentrations of 68.3 (49–100), 369 (198–660), and 152.7 (102–186) mg/kg for auto-mechanic, mine waste, and crude oil soils, and gastrointestinal values of 24.7 (17–36), 139.7 (44–296), and 35 (19–49) mg/kg, respectively, with mine soils showing the highest bioaccessibility in both phases. Zinc (Zn) also demonstrated higher gastric bioaccessibility across all matrices, with mean values of 133 (80–211), 38.3 (13–86), and 20.3 (12–25) mg/kg, and gastrointestinal values of 131 (23–345) mg/kg for auto-mechanic soils, 19 mg/kg (n=1) for mine soils, and 25 mg/kg (n=1) for crude oil soils, all below Dutch (720 mg/kg), Italian (150 mg/kg), and NESREA (300–600 mg/kg) intervention values. Correlation analysis revealed strong positive associations between total and bioaccessible concentrations for most elements: As showed gastric correlations of 0.93 and 0.88 in auto-mechanic and mine soils and gastrointestinal correlations of 0.90 and 0.97, while crude oil soils exhibited a negative correlation (−0.62). Cd in auto-mechanic soils was negatively correlated (−0.65). Fe showed positive gastric correlations in auto-mechanic soils (0.86) but negative correlations in mine (−0.91) and crude oil (−0.95) soils, with gastrointestinal correlations of 0.91, 0.09, and −0.61, respectively. Pb exhibited gastric correlations of 0.51, 0.71, and 0.56 and a strong gastrointestinal correlation of 0.91 in auto-mechanic soils. Mn demonstrated strong positive correlations in both phases, with gastric correlations of 0.93, 0.99, and 0.87, and gastrointestinal correlations of 0.99, 0.99, and 0.17 in auto-mechanic, mine, and crude oil soils, respectively. Zn showed strong positive correlations in auto-mechanic soils (gastric 0.98, gastrointestinal 0.99) and moderate correlations in mine soils (gastric 0.63). These results indicate that bioaccessibility is element-specific and phase-dependent, influenced by both contamination source and soil properties, with particularly elevated gastric bioaccessibility for Pb and Mn in mine and crude oil–impacted soils, suggesting increased human exposure risk despite total concentrations. This study provides novel data on the bioaccessibility of PTEs in auto-mechanic and crude oil–contaminated soils, contributing to improved human health risk assessment models in contaminated environments.

Table 7 Results of Stastical Analysis of Percentage Bioaccessibility Values Determined in Auto-Mechanic Workshop Soil, Mine Soil and Crude Oil Waste Soil.

	As		Cd		Fe		Pb		Mn		Zn	
	G	**GI**	**G**	**GI**	**G**	**GI**	**G**	**GI**	**G**	**GI**	**G**	**GI**
						Auto-mechanic soil						
Mean	8.77		13.70	NC	1.50	1.20	37.2	12.3	17.2		20.50	7.20
	25.06								6.20			
Minimum	8.20	15.80	2.00	NC	1.20	0.80	23.00	9.90	17.40		4.00	5.90
Maximum	11.20		28.80	NC	2.10	1.40	54.40		6.00		32.00	9.20
	30.00						14.50		20.30			
									6.30			
						Mining soil						
Mean	3.53		2.00	NC	0.40	0.40	14.40	4.40	7.90		2.00	
	8.20								2.50		0.60	
Minimum	1.90		1.70	NC	0.20	0.10	7.80		7.10		0.50	
Maximum	6.48		2.20	NC	0.60	0.90	1.10		2.10		0.60	
	4.70						24.00		9.30		2.90	NC
	10.22						7.70		3.20			
						Crude oil soil						
Mean	11.00		NC	NC	3.10	1.10	14.40	NC	37.50	8.30	18.80	
	18.47										19.70	
Minimum	9.40		NC	NC	2.10	0.70	11.50	NC	30.70		13.80	
Maximum	10.70		NC	NC	3.80	1.90	16.80	NC	4.80		19.70	
	16.90								43.90		25.30	NC
	27.00								12.60			

Table 10a Description Statistics of the Bioaccessible Concentrations of As and Cd

Heavy Metal	N	Phase	Soil Matrix	Mean (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
As	3	Gastric	Mechanic	2.05	1.53	2.71
	3		Mine	2.03	0.98	2.93
	3		Crude oil	3.96	2.36	4.84
	3	Gastro-intestinal	Mechanic	5.61	5.00	6.21
	3		Mine	4.64	3.35	6.36
	3		Crude oil	6.61	5.06	9.45
Cd	0	Gastric	Mechanic	0.91	0.15	1.67
	0		Mine	0.36	0.34	0.37
	0		Crude oil	BD	BD	BD
	3	Gastrointestinal	Mechanic	BD	BD	BD
	3		Mine	BD	BD	BD
	3		Crude oil	BD	BD	BD

Table 10b: Description Statistics of the Bioaccessible Concentrations of Fe and Pb

Heavy Metal	N	Phase	Soil Matrix	Mean (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
Fe	3	Gastric	Mechanic	478.7	204	676
	3		Mine soil	179.7	133	205
	3		Crude oil	1258.3	959	1478
	3	Gastro-intestinal	Mechanic	343.7	219	448
	3		Mine soil	220.3	40	399
	3		Crude oil	462.3	307	743
Pb	3	Gastric	Mechanic	133	109	174
	3		Mine	1159	191	2484
	3		Crude oil	11	9	14
	3	Gastroin-testinal	Mechanic	47	31	63
	2		Mine soil	452	111	793
	0		Crude oil	BD	BD	BD

Table 10c: Description Statistics of the Bioaccessible Concentrations of Mn and Zn

Heavy Metal	N	Phase	Soil Matrix	Mean (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
Mn	3	Gastric	Mechanic	68.3	49	100
	3		Mine soil	369	198	660
	3		Crude oil	152.7	102	186
	3	Gastroin-testinal	Mechanic	24.7	17	36
	3		Mine soil	139.7	44	296
	3		Crude oil	35	19	49
Zn	3	Gastric	Mechanic	133	80	211
	3		Mine soil	38.3	13	86
	3		Crude oil	20.3	12	25
	3	Gastro-intestinal	Mechanic	131	23	345
	1		Mine soil	19	BD	19
	1		Crude oil	25	BD	25

Table 11 Correlation coefficient between bioaccessible and total metal concentrations

Variables	As	Cd	Fe	Pb	Mn	Zn	Reference
	0.89	0.99		0.95	0.32	0.95	Biosa *et al.*,(2013) (Mine)
	0.10	0.99		0.94	0.90	0.99	Biosa *et al.*,(2013) (Tailings)
		0.16		0.93		0.95	Gbefa *et al.,* (2011) (mine)
Gastric phase concentrations				0.90			Sialelli *et al.,* (2010) (Mine)
				0.65		0.53	Poggio *et al.,* (2009) (Mine)
				0.92			Fcarmer *et al.*, (2011) (Urban)
VS				0.98		0.91	Sialelli *et al.,* (2011) (Urban)
Total Concentrations	0.70						Sarker *et al.*, (2007) (Mine)
	0.93	-0.65	0.86	0.51	0.93	0.98	This study (mechanic)
	0.88		-0.91	0.71	0.99	0.63	This study (mine)
	0.16		-0.95	0.56	0.87	0.16	This study (crude oil)
Bioaccessible concentrations in gastrointestinal Phase	0.88	0.28		0.83	0.48	0.60	Biosa *et al.*,(2013) (Mine)
	0.11	0.65		0.88	0.27	0.98	Biosa *et al.*,(2013) (Tailing)
	0.99	0.95		0.89		0.95	Okorie *et al.*,(2011) (Urban)
		0.08		0.93		0.96	Gbefa *et al.*, (2011) (mine)
VS				0.84		0.82	Poggio *et al.*, (2009) (Mine)
Total metal Concentrations		0.82				0.37	Pelfteren *et al.*,(2011) (Mine)
				0.85			Farmer *et al.*, (2011) (Urban)
	0.76						Sarker *et al.,* (2007) (Mine)
	0.90		0.91	0.91	0.99	0.99	This study (mechanic)
	0.97		0.09		0.99		This study (mine)
	₋0.62		₋0.61		0.17		This study (crude oil)

Oral bioaccessibility of the PTEs

The mean gastric % bioaccessibility in this study for As, Cd, Fe, Pb, Mn and Zn were 8.8% (6.9 – 11.2%), 13.7% (2 – 28.8%), 1.5% (1.2 – 2.1%), 37.2% (23.0 – 34.3%), 17.2% (13.9 – 20.3%) and 20.5% (4.0 – 32.0%), respectively. Mean and range bioaccessibility for As, Fe, Pb, Mn and Zn in gastrointestinal phase were1.2% (25.1% (15.8 – 30.0%), 0.8 – 1.4%), 12.3% (9.9 – 14.5%), 6.2% (6.0 – 6.3%) and 7.2% (5.9 – 9.2%), respectively. The trend of mean % bioaccessibilty of auto-mechanic workshop sites in the gastric phase is Pb>Zn>Mn>Cd>As>Fe and the gastrointestinal phase is As>Pb>Zn>Mn>Fe. The trend of mean % bioaccessibility in the gastric phase from mine soil is Pb>Mn>As>Zn>Cd and the gastrointestinal phase is As >Pb>Mn>Zn>Fe. The gastric phase mean and range % bioacessibility from mine waste sites in this study shows that As, Cd, Fe, Pb, Mn and Zn are 3.6 % (1.9-4.2 %), 2% (1.7-2.2%), 0.4% (0.2-0.6%), 14.4 (7.8-2.4%), 7.9% (7.1-9.3%) and 2.0% (0.5-2.9%) respectively. The gastrointestinal phase mean and range bioaccessibility for As ,Fe, Pb, Mn, and Zn 8.3% (6.5-10.2%), 0.4% (0.1-0.9%), 4.4% (1.1-7.7%), 2.9% (2.1-3.2%) and 0.6% (n=1) respectively.

The trend of mean % bioaccessibility in the gastric phase from crude oil contaminated soil is Mn> Zn >Pb> As > Fe and As > Zn >Mn> Fe in order of mean % bioaccessibility in gastro intestinal phase. The result from this study show that mean and range % bioacessibility in gastric phase for As, Fe, Pb, Mn and Zn are 11% (6.7-16.9%), 3.1% (2.1-3.8%), 14.4% (11.5-16.8%),37.5% (30.7-43.9%) and 18.8% (13.8-25.3%), respectively, The gastrointestinal phase mean and range % bioaccessibily for As ,Fe, Mn, and Zn are 18.5% (10.7-27.0%), 1.1% (0.7-1.9%), 8.2% (4.8-12.4%) and 19.7% (n=1) respectively . The percentage oral bioaccesibility of Cd, Fe, Pb, Mn and

Zn in all the three matrices are consistently greater in the gastric phase than gastrointestinal phase except As The auto-mechanic data from this study indicated the highest mean bioaccessibility in both phases for most of heavy metal analyzed .While mine soil sample indicated lowest bioaccessibility in both phases for all the heavy metal investigated. The mean % bioaccessibility order in gastric phase for Cd, Pb, and Zn is auto-mechanic >crude oil >mine. For As, Fe, and that is greater in the gastrointestinal phase than gastric phase.

Pb in gastro-intestinal phase the order of mean % bioaccessibility is auto-mechanic>crude oil >mine. The order of mean % bioaccessibility in gastric phase for As, Fe, and Mnis crude oil>auto-mechanic mine while that for gastrointestinal phase for Mn and Zn crude oil>auto-mechanic>mine.

Table 12 Mean and range bioaccessibility of heavy metals in soil matrices.

	Heavy Metal	Gastric Bioaccessibility (%)			Gastrointestinal Bioaccessibility(%)		
		Auto-mechanic	Mine Soil	Crude Oil	Auto-mechanic	Mine Soil	Crude Oil
	Mean	8.8	3.6	11.0	25.1	8.3	18.5
As	Minimum	6.9	1.9	6.7	15.8	6.5	10.7
	Maximum	11.20	4.7	16.9	30.0	10.2	27.0
	Mean	13.7	2.0				
Cd	Minimum	2.0	1.7				
	Maximum	28.8	2.2				
	Mean	1.5	0.4	3.1	1.2	0.4	1.1
Fe	Minimum	1.2	0.2	2.1	0.8	0.1	0.7
	Maximum	2.1	0.6	3.8	1.4	0.9	1.9
	Mean	37.2	14.4	14.4	12.3	4.4	
Pb	Minimum	23.0	7.8	11.5	9.9	1.1	
	Maximum	34.3	24.0	16.8	14.5	7.7	
	Mean	17.2	7.9	37.5	6.2	2.9	8.2
Mn	Minimum	13.9	7.1	30.7	6.0	2.1	4.8
	Maximum	20.3	9.3	43.9	6.3	3.2	12.4
	Mean	20.5	2.0	18.8	7.2	0.6	19.7
Zn	Minimum	4.0	0.5	13.8	5.9		
	Maximum	32.0	2.9	25.3	9.2		

For As the mean and range percentage bioaccessibility indicated in gastric phase were 8.8% (6.9 – 11.2%), 3.6% (1.9-4.2 %) and 11% (6.7-16.9%) for auto-mechanic, mine waste and crude oil contaminated soils, respectively (Table 12). The mean and range percentage bioaccessibility indicated in gastrointestinal phase were 25.1% (15.8 – 30.0%), 8.3% (6.5-10.2%), and 18.5% (10.7-27.0%) for auto-mechanic, mine waste and crude oil soil samples respectively. The % range bioaccessibility of arsenic from mine waste (1.9-4.2 %) in this study is lower than the range, 5-39% reported for arsenic by Boisa *et al*., (2013). The As range percentage bioaccessibility from mine waste in gastrointestinal phase (6.5-10.2%) in this study is similar to (1.80-8.30%) reported by Wragg *et al*., (2011) for related matrix. Only the gastric phase Cd of auto-mechanic and mine soil samples were detected during the analysis (Table 12). The mean and range % bioaccessibility, 13.7% (2-28.8%) for auto-mechanic samples is higher than the values, 2.0% (1.7-2.2) for mine waste samples. The maximum gastric bioaccessibility, 2.2% we obtained in this study obtained for mine waste contaminated soils is very low compared to 86%, 63 %, 111% and 15% previously reported by Navarro *et al*., (2006), Morrison and Gulson (2007), Pelferene *et al.,* (2011) and Boisa *et al*., (2013), respectively. The mean and range bioaccessibility indicated in gastric phase were 1.5% (1.2-2.1%), 0.4% (0.2-0.6%) and 3.1% (2.1-3.8%) for auto-mechanic, mine waste and crude oil respectively. In the gastrointestinal phase /mean and range of bioaccessibility were 1.2% (0.8-1.4%), 0.4% (0.1-0.9%) and 1.1% (0.7-1.9%) for auto-mechanic, mine and crude oil soil samples respectively. Crude oil has more bioaccessibility in gastric phase than auto-mechanic and mine soil samples. The percentages bioaccessibility of Fe were very low in all the three soil matrices investigated in both gastric and gastrointestinal phases. Fe indicated the lowest bioaccessibility of all the metals investigated in spite of the fact that in the three soil matrices Fe had the highest total concentration.

Table 13 Mean and range (in parentheses) of HM daily intake (HM DI) orally ingested from topsoil from auto-mechanic workshop, mine waste and crude oil contaminated sites and tolerable daily intake (TDIoral).

Heavy Metal	TDI_{oral} (µg/kg BW/d)	HM DI (µg/kg BW/d) based on 100mg/d ingestion Auto-mechanic site	Mine site	Crude oil site
As	0.3[a]	0.14 (0.011-0.22)	0.31 (0.29-0.35)	0.2 (0.16-0.28)
Cd	0.36[b]	0.04 (0.03-0.05)	0.1 (0.09-0.12)	0.04 (0.04-0.05)
Fe	700	183.9 (97.4-303.4)	273.4 (183.5-380.8)	230.5 (217.2-254.7)
Pb	1.9[c]	2.23 (1.20-2.85)	41.9 (9.5-58.1)	0.43 (0.34-0.49)
Mn	140[d]	2.25 (1.55-3.22)	27.7 (12.0-51.5)	2.27 (1.89-2.77)
Zn	600[e]	11.1 (1.40-29.7)	12.5 (3.08-18.7)	0.61 (0.56-0.71)

a: Environmental Agency (2009a), b: Environmental Agency (2009b), c: JECFA (2012), d: USEPA (2011), e: Nathanail et al., (2009)

The Pb bioaccessibility mean and range for auto-mechanic soils were 37.2% (23.0-34.3%) in gastric phase and 12.3% (9.9-14.5%) in gastrointestinal phase. The mean and range bioaccessibility for mine waste soils were 14.4% (7.8-24.0%) in gastric phase and 4.4% (1.1-7.7%) in gastrointestinal phase. For the crude oil contaminated soils, mean and range bioaccessibility is 14.4% (11.5-16.8%) in gastric phase. The Pb bioaccessibility range in gastric phase (7.8-24.0%) obtained for mine waste soil samples in this study is similar with the ranges,(8-16%), (5-15%) and (3-15%) recorded by Ruby et al., (1996), Boisa *et al.,* (2013), and Ruby *et al.,* (1993) respectively. The mean and range percentage bioaccessibility in gastrointestinal phase were 12.3% (9.9-14.5%) and 4.4% (1.1-7.7%) for auto-mechanic waste and mine waste contaminated soils, respectively. The mean and range bioaccessibility of 4.4% (1.1-7.7%) obtained in this study is consistent with the mean and range of 4.21% (1.48-6.93%) by Boisa *et al*., (2013) for mine tailings soil. The percentage bioaccessibility of lead in all the three matrices are more in gastric phase than gastrointestinal phase. Although, the higher percentage bioaccessbility of Pb were recorded in gastric phase of auto-mechanic soil samples while crude oil and mine soil samples indicate the same mean value percentage bioaccessibility in gastric phase (14.4%).

The means and ranges bioaccessibility observed in all three matrices in the gastric phase were 17.2% (13.9 – 20.3%), 7.9 % (7.1 – 9.3%) and 37.5(30.7 – 25.3%) for auto-mechanic, mine and crude oil samples, respectively. The Mn means and ranges recorded in this study in the gastrointestinal phase were 6.2% (6.0 – 6.3%), 2.9% (2.1 – 3.2%) and 8.2% (4.8 – 12.4) for auto-mechanic, mine waste and crude oil samples, respectively. For mine waste soils from this study the range for gastric, 7.9 % (7.1 – 9.3%) and gastrointestinal 2.9% (2.1 – 3.2%) phases were lower than those previously reported by Karadas and Kare (2011). (33.6 – 75.5%) and (3.3 – 65.9%) for Mn-Pb-Zn mines waste contaminated soils. The lower bioaccessibility observed in gastrointestinal phase is expected since the extraction was conducted at higher pH values.

The mean and range bioaccessiblity observed in the gastric phase were 20.5% (4.0 – 32.0%), 2.0% (0.5 – 2.9%) and 18.8 %(13.8 – 25.3%) for auto-mechanic, mine waste and crude oil soils respectively. The Zn mean and ranges recorded in the gastrointestinal phase were 7.2% (5.9 – 9.2%), 0.6% (n=1) and 19.7% (n=1) for auto-mechanic, mine and crude oil impacted soil respectivelvy. Zn percentage bioaccessibility order in gastric phase is auto-mechanic>crude oil>mine, whilst in the gastrointestinal order crude oil>auto-mechanic>mine. The few data from the literature for mine waste contaminated soils were higher than the one generated in this study. Boisa *et al*., (2013), Pelfrene *et al.,* (2011) and Roussel *et al.,* (2010) reported higher percentage bioaccessibility in both gastric and gastrointestinal phases from top soil using the BARGE protocol.

Soil ingestion exposure assessment in crude oil, auto-mechanic and mine soil

The soil samples analyzed in this study were from residential areas. Calculations of topsoil samples were made using total concentrations with the mean and range data (Table 13). Recommended tolerable daily intake (TDI) for As, Cd, Fe, Pb, Mn and Zn were also given in (Table 13).Based on total PHE concentrations mine waste site indicated daily chronic intake concentrations above TDI for arsenic and lead (Table 13). The auto-mechanic soil samples also indicated daily chronic intake above TDI for Pb (Table 1.13). The crude oil spill soil samples daily intake concentrations were below TDI_{oral} for all the metals analyzed (Table 1.13). For As, data obtained showed that the health risk is less compare to Pb, however, mine site had a DI 41.9 ug/kg BW/d (9.5-58.1 ug/kg BW/d) in excess of the recommended value of 1.9 ug/kg BW/d (Table 1.13). For As in soil samples the calculated daily intake mean and range were 0.2 ug/kg BW/d (0.16-0.28 ug/kg BW/d), 0.14 ug/kg BW/d (0.01-0.22 ug/kg BW/d), and 0.31 ug/kg BW/d (0.29-0.35 ug/kg BW/d) for crude oil spill, auto-mechanic workshop and mine waste soil samples, respectively. A similar range of

arsenic DI had been reported for aqua regia in mine soil 0.38 ug/kg BW/d (0.03-1.02 ug/kg BW/d) by Boisa et al., (2013). Cd, Fe Mn and Zn daily intake estimated were below the TDI_{oral} for all the three soil matrices investigated (Table 13). The data indicated significant possibility of harm through exposure to topsoil ingestion in the mine site as well as in auto-mechanic workshop.

CONCLUSION

The soils exhibited a pH trend of auto-mechanic contaminated soils > mine waste soils > crude oil–contaminated soils. Mean total concentrations (mg/kg) of As, Cd, Fe, Pb, Mn, and Zn were 25.0, 7.4, 32,740.7, 397.8, 400.1, and 1,983.5 in auto-mechanic soils; 55.7, 18.4, 48,666.7, 7,451.0, 4,938.3, and 2,220.0 in mine waste soils; and 37.9, 7.4, 41,036.8, 76.7, 403.9, and 109.1 in crude oil–contaminated soils, with mine waste soils showing the highest concentrations across all metals. All PTEs were bioaccessible in both gastric and gastrointestinal phases, except Cd in crude oil soils (gastric phase), Pb in crude oil (gastrointestinal phase), and Cd in all matrices (gastrointestinal phase). Except for As, bioaccessibility was higher in the gastric phase. Strong positive correlations between total and bioaccessible concentrations were observed for As, Mn, and Zn in auto-mechanic soils, while Fe showed strong negative correlations in mine waste and crude oil soils (gastric phase). Gastrointestinal phase correlations were positive for Fe and Pb in auto-mechanic soils and As and Mn in mine waste soils. Mean gastric bioaccessibility (%) in auto-mechanic soils was: As 8.8, Cd 13.7, Fe 1.5, Pb 37.2, Mn 17.2, Zn 20.5; gastrointestinal bioaccessibility: As 25.1, Fe 1.2, Pb 12.3, Mn 6.2, Zn 18.8. In mine waste soils, gastric bioaccessibility was: As 3.6, Cd 0.2, Fe 0.4, Pb 14.4, Mn 7.9, Zn 2.0; gastrointestinal: As 8.3, Fe 0.4, Pb 4.4, Mn 2.9. In crude oil soils, gastric bioaccessibility was: As 11.0, Fe 3.1, Pb 14.5, Mn 37.5, Zn 18.8; gastrointestinal: As 18.5, Fe 1.1, Mn 8.2. Notably, auto-mechanic and mine waste soils exhibited daily chronic intake concentrations exceeding tolerable daily intake values for As and Pb, indicating potential human health risks, particularly through incidental soil ingestion.

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