

Heavy Metal Speciation in Contaminated Soils of an Abandoned Hydrocarbon Exploration Field Camp and Workshop Site in Part of The Niger Delta, Nigeria

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ABSTRACT

The chemical mobility of heavy metals is fundamental to the understanding of their environmental accessibility, toxicity and geochemical behaviour. In this paper seven elements were investigated (Cr, Cu, Fe, Mn, Ni, Pb, and Zn), the EDXRF was used to analyse the total content of the metals. The Community Bureau of References extraction scheme was employed (three-step sequential extraction scheme) to determine the bioavailability and mobile chemical forms of the metals in soil contaminated with waste from a field camp mechanical workshop set up for oil exploration at Yenegoa in Bayelsa State of Nigeria, using Flame Atomic Absorption Spectrometry (FAAS) for the chemical analysis. The physical observation of the site shows a serious environmental degradation caused by waste oils, chemicals and metal work from the operations of the oil exploration camp workshop. The results of the total contents of the metals in the area show that the concentration values of the metals were reasonably higher in the test samples than the controlled samples, therefore, calls for intervention. However, the results of the extraction schemes show relatively low bioavailability and mobility potential of the metals with more proportions retained in the residual fractions (inert state), as such, poses little or no danger to the environment and human in the short term, but the area need to be evaluated time-to-time to monitor the release of such occluded element in the crystal lattice of the soil particles in the long term due to change in climatic and environmental conditions.

KEY WORDS: Heavy-metal pollution, bioavailability, mobility, Environmental Degradation, Sequential extraction.

INTRODUCTION

The evaluation of heavy metals contamination of soils as a means of monitoring the status of the environment for the good of the ecosystem is crucial because of the increasing domestic and industrial activities of man. It is possible that significant contamination could be caused by substances which have not previously been measured in site investigations, or which have not traditionally been associated with particular industrial uses, or which are not identified in the industry profile. Previously it was assumed that the elemental composition of soils could only be explained on the basis of local geology. It became clear more recently that the surface layer of soils can be significantly affected by airborne supply of elements from natural as well as anthropogenic sources [1]. It is also estimated that the contributions of metals from anthropogenic sources in soil is higher than the contribution from natural ones, hence, the repeated evaluation of the contamination status of soils [2, 3]. In the area of study, it was observed that the field camp set up during the period of the exploration activities generated a lot of waste such as wood treated with preservatives, metal pipes, spilled engine oil and diesel, refuse, chemical waste and other liquid wastes. These wastes so generated serve as nuisances and contaminants in the area of operation. After the operations when the camp was abandoned, an unusual effect was observed on plants and the surrounding. Previous evaluation reports show that the surface runoff from the site became a problem where it contaminated the surroundings few meters away and was showing up contamination, which was destroying the vegetation and killing trees that were planted around the site; hence, the study to ascertain the bioavailability and the environmental accessibility of these contaminants in the environment.

The evaluation of metal contamination of soils was of vital importance in redevelopment of the contaminated sites. The bioavailable and mobile metal contents in soil exerts a decisive impact on soil quality and its use for food production and development. The bioavailability, mobility and toxicity of heavy metals in the environment depend strongly on their

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content and specific chemical forms. Sequential extraction techniques are commonly used to fractionate solid-phase forms of metals in soils; this is underpinned by the fact that mobility, availability and toxicity of metals are mostly dependent on their chemical forms [4, 5]. Metals from anthropogenic sources tend to be more mobile than lithogenic ones. Fractionation of heavy metals by sequential extraction is operationally defined and can help assess how strongly they are retained in soil and how easily they may be released, and different sequential extraction schemes had been applied to evaluate both actual and potential mobility of metals in the environment [6, 7, and 5].

In this study, the Community Bureau of References three-stage sequential extraction procedure is employed, which operationally classifies metals into four fractions based on their metal-soil interaction: The determination of the chemical forms though difficult in soils, is based on the use of leaching or extraction procedures 'Operationally defined'. [8, 5, 6]. Contamination by heavy metals is one of the less obvious impacts that can have very severe long term consequence. The presence of heavy metals like Copper(Cu), Chromium(Cr), lead(Pb), Zinc(Zn) and a few others is known to be very toxic to plants, animals and human bio-system even when exposed to very low concentrations of these elements [9].

Soils are sinks of heavy metals, and the heavy metals are strongly retained and highly persistent in soils for a very long period of time without been degraded biologically or chemically. The soil of the area of study is clayey, which favours the adsorption of metals to the fine particles of the clay minerals. When metals enter the environment and find their way to the soil, metal-soil interaction takes place during which different chemical forms are bonded to different phases that determine their degree of bioavailability and mobility, hence their toxicity [10]. When these metals are released into groundwater or surface water by leaching or erosion respectively, they may be absorbed by aquatic organisms and taken up by plants from soil water thereby enter the food chain creating more risk to man [11, 12]. Heavy metals are known to be toxic, carcinogenic, mutagenic and/or teratogenic, irritating. Especially Cr is carcinogenic, Pb poisoning causes neurotoxic effects and anaemia because of its toxic effects on the red blood cells [13]. Other health effects of heavy metals on human are: sensory disturbance, hyporeflexia, tremor, gingivitis, night blindness, damage of the immune system, skin cancer, alteration of body metabolism etc. These toxic effects of heavy metals on target organs in human differ from metal-to-metal because of the differences in their interaction with enzymes and proteins [10, 13, 14]. Therefore, their presence in the environment becomes a great concern to all, but they are only a risk if they are bioavailable and mobile, and there is an available pathway for them to be taken up by the human body [15, 9].

In this present work, the actual degree of pollution and the potential impact on the environment was determined by identify and quantify the distribution of the different species and forms of metals, and their association with binding phases of particulate materials (soil).

MATERIALS AND METHODS

Description of the area and soil sampling

The abandoned oil exploration field camp mechanical workshop site at Yenegoa of Bayelsa state of Nigeria covers an area of about one square kilometer and rigorous metal and chemical works were carried out there during the period of operation. The site is located in the coastal area of the transitional environment of the recent Niger Delta, which is characterized by its beaches, mangroves, swamps, and barrier bars. The area lies between longitude 7°.30' East and 8°.05' West, and latitude 4°15' South. The area has a tropical climate, with an average annual temperature of 28°C. It is also known for its incessant rain fall, and flooding as such its soil is characterized by the presence of detrital-alluvial sediments. The site was abandoned some years ago (about 5 years) before this study was carried out on the site, implying that elements deposited on the topsoil has not been depleted by erosion or leaching, and the elements are still well adsorbed to the soil matrix.

Soil sampling was done in February, 2009. This stage in environmental study and monitoring is very important because any error or fault created cannot be rectified even by a perfect analytical procedure and technique [16, 17]. Soil sampling technique was chosen after considering the depth, the soil characteristics, and the nature of the analyses of interest. Surface sampling was chosen because the contamination was recent, and analyses of interest were not volatile. Only topsoil samples were collected from the site using a shovel and a sample scoop; sample locations were chosen in a square grid at 16m centers for representative sample collection. Six samples though not many were carefully collected at random from the study site. The sample numbers were reduced to minimize analytical cost since about seven elements are investigated.

In the rapid and accurate determination of heavy metals in an environmental matrix such as soils, several analytical techniques could be applied to obtain reliable chemical information in a very short period of time. However, the choice of a suitable analytical instrumentation with appropriate sensitivity as regards the target elements or compounds is of paramount importance in all soil analysis; base on this assertion the Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry especially the SPECTRO X-LAB 2000 model spectrometer shown in Figure 1 was used as an excellent multi-elemental analysis tool for the determination of the total heavy metal contents of the bulk soil samples. For the analysis of the extracted analytes, the Flame atomic absorption spectrometer (FAAS) was used specifically the (Perkin

Elmer-Analyst 100 model) as shown in Figure 2, which is very reliable equipment as it monitors one metal at a time without interference, easy to operate and less expensive.

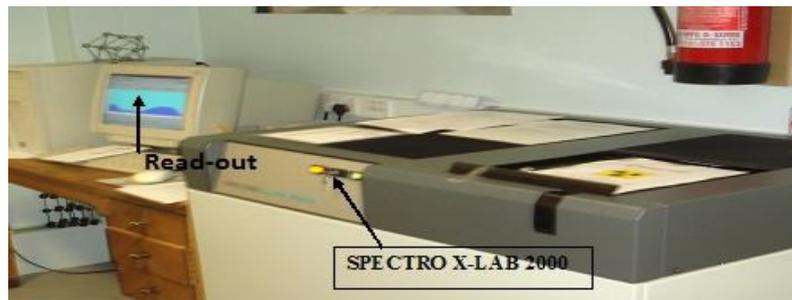


Fig. 1: A photograph of SPECTR X-LAB 2000 and PC- Data processo

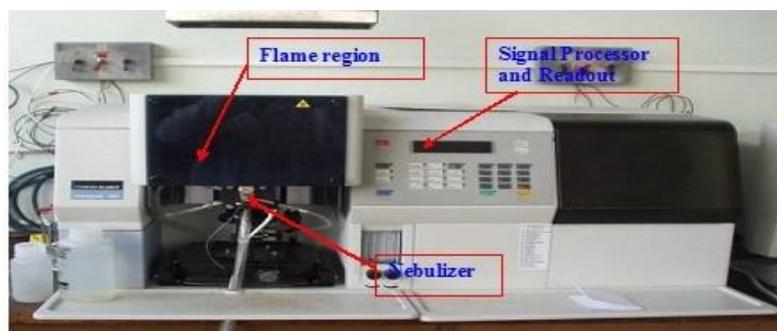


Fig. 2: Flame Atomic Absorption Spectrometer (Perkin Elmer-Analyst 100)

Soil sample analysis

To make the test samples ready for the extraction schemes, the six bulk soil samples were oven dried at a regulated temperature of 50°C for 48 hours, and a sieve of mesh size 600µm was used to separate and remove the large particles to obtain the desired particle sizes [5]. After the sieving stage, the soil samples obtained are then grinded to powdered form using an agate mortar and pestle. This action leaves the particle sizes in the micrometers and/or nanometres range, which ensure the homogenisation of the test samples, and also enhance the sample to be in suspension in the mixture during the extraction process for optimum extractability [18].

The total metal content of the soil samples were determined using the energy dispersive X-ray fluorescence (EDXRF) technique. Approximately 4.0g of grinded soil sample was weighed into disposable plastic sample tubes and 0.6g of Hoechstwax HWC binder (supplied by Spectro Analytical Ltd.) was also added to each tube. Each tube containing the soil sample and binder was fitted to a Retsch shaker, and shaken at high speed to properly mix the contents. A 32mm pellet was made from these thorough mixtures using a Graseby Space Press operated at a pressure of 10 tonnes for each sample. The prepared pellets from each sample are then placed in the sample chamber of the EDXRF spectrometer (Spectro X-Lab 2000) for analysis with an integration time of 150sec. This instrument scans the samples at five different levels to ascertain accurate analysis.

The Community Bureau of References three-stages sequential extraction procedure was used, which operationally classifies metals into four fractions based on their metal-soil interaction: (1) acetic acid-(exchangeable and specifically adsorbed fractions); (2) reducing agent-Hydroxylamine hydrochloride (fractions bound to Fe/Mn oxides); (3) oxidising agent-H₂O₂/ammonium acetate (fractions bound to soil organic matter); (4) residual fractions occluded in mineral structures [7, 5].

The three-stage chemical extraction procedure [0.11mol HOAc, 0.1mol NH₂OH – HCl), 8.8mol H₂O₂/1mol NH₄OAc]. 1g of soil sample was used in all the extraction stages and 25ml of reactant, the mixtures were shaken for 6 hours using a mechanical shaker at room temperature (20 ± 2°C) and centrifuged at 3000 rpm for 10 minutes, and the supernatant (clear sample solution) taken for immediate analysis or store at 4°C prior to analysis, and at least two replicates were carried out for each sample. For this work, the air-acetylene flame was used to properly analyse the elements. All glass and plastic wares used were cleaned by immersion in (10%v/v) nitric acid overnight and rinsed with large volume of deionised water to prevent contamination that will arise from apparatus, and analytical-grade chemicals were used for the extraction schemes.

RESULTS AND DISCUSSION

Total heavy metal analysis

The results of the total metal contents analysis performed on the six bulk soil samples are given in Table 3. All the test soil samples were found to have reasonably higher concentration of the elements than the values of the controlled soil sample collected some distance away from the site, with the concentrations of the elements within the target values. The metal concentration of the test soil samples at some sample points were above the target values or limits defined by the European Union [19] for soils of public, private and residential areas. Table 1 shows the metals, their wavelength to ensure their respective absorbance, their detection limits that indicate the sensitivity of the instrument to the metals and the permissive level. The Fe and Mn permissive levels were not included in Table 1 because their threshold values were not available; as they rarely pose serious problem to the environment and human.

Table 1: Metals, wavelength values, detection limits, and permissive level in the soil

Metal	Wavelength (nm)	Detection limit (mg/l)	Permissive level in the soil ($\mu\text{g/g}$)
Chromium (Cr)	357.0	0.078	100-130
Copper (Cu)	324.8	0.077	30-40
Iron (Fe)	248.3	0.100	
Lead (Pb)	217.0	0.190	85-450
Manganese (Mn)	285.2	0.052	
Nickel (Ni)	232.0	0.140	30-75
Zinc (Zn)	213.9	0.018	135-150

In Table 3, total contents of Fe, Cu, Ni, and Zn were significantly correlated, suggesting common origin of these elements in the soils (anthropogenic). It was also observed that Fe concentration values were particularly very high; ranging from about 25000 -177600 $\mu\text{g/g}$; this was attributed to the fact that most soils are Fe- rich in nature. Also, the contents of Cu and Pb were reasonably higher than the target values.

Table 2: Calibration Standard Solutions

Conc. (ppm)	Absorbance Values						
	Cr	Cu	Fe	Mn	Ni	Pb	Zn
0	0.000	0.000	0.000	0.000	0.0000	0.0000	0.000
2	0.056	0.090	0.031	0.075	0.0385	0.0010	0.200
4	0.118	0.178	0.058	0.155	0.0720	0.0022	0.462
6	0.172	0.270	0.087	0.228	0.1040	0.0030	0.632
8	0.235	0.345	0.117	0.300	0.1350	0.0046	0.785
10	0.280	0.430	0.141	0.371	0.1660	0.0055	1.054

Table 3: Total Concentration of Metals.

Conc. (ppm)	Concentration Values ($\mu\text{g/g}$)						
	Cr	Cu	Fe	Mn	Ni	Pb	Zn
SS 1	89.9 \pm 1.6	81.5 \pm 2.8	177600 \pm 200	85.1 \pm 1.5	39.9 \pm 3.4	388.6 \pm 4.6	83 \pm 2.3
SS 2	60.7 \pm 1.2	18.9 \pm 1.1	53080 \pm 80	27.3 \pm 0.9	17.1 \pm 1.4	988.7 \pm 4.3	19.0 \pm 0.8
SS 3	95.7 \pm 4.0	46.0 \pm 1.7	49410 \pm 90	141.3 \pm 3.4	24.1 \pm 1.9	383.4 \pm 3.2	38.1 \pm 1.2
SS 4	126.7 \pm 1.6	73.2 \pm 1.4	25730 \pm 50	243.9 \pm 1.9	59.0 \pm 1.7	93.9 \pm 1.4	172.3 \pm 1.7
SS 5	87.7 \pm 1.5	19.6 \pm 1.1	64510 \pm 100	26.0 \pm 1.1	23.4 \pm 1.6	345.8 \pm 2.7	20.6 \pm 0.8
SS 6	72.3 \pm 1.3	22.0 \pm 1.1	60770 \pm 90	86.4 \pm 1.2	24.1 \pm 1.6	305.8 \pm 2.5	38.8 \pm 1.0

Heavy metal sequential extractions

Calibration solutions of 2, 4, 6, 8, and 10ppm for each element was prepared from the stock solution of the elements. These calibration solutions were analysed using FAAS to obtain the absorbance values for the various concentrations of the calibration solutions. A plot of the concentrations and the absorbance values for each element was done to producing the calibration curves that show linearity of about 99% from which the unknown concentrations of the

test soil samples were deduced and determined. The absorbance values and the corresponding concentration of the calibration solutions are shown by Table 2.

The metal fractions – consisting of (1) soluble, exchangeable and carbonate bound (HOAc-extractable); (2) occluded in easily reducible manganese and iron oxides (reducible); (3) organically bound (oxidizable); and (4) residual fraction mainly present in the mineral lattice structures (inert) [6, 7]. The extracted amount of each metal in each fraction is given in Tables 4a to 4d.

The relative amounts of each metal in each fraction, expressed as a percentage of the cumulative total extracted from the soil samples are presented in Figures 3a-3g.

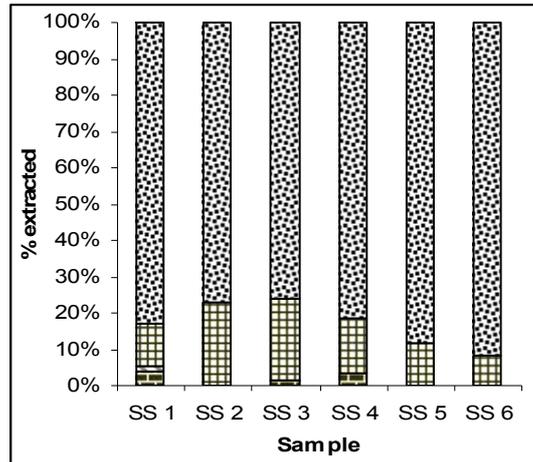
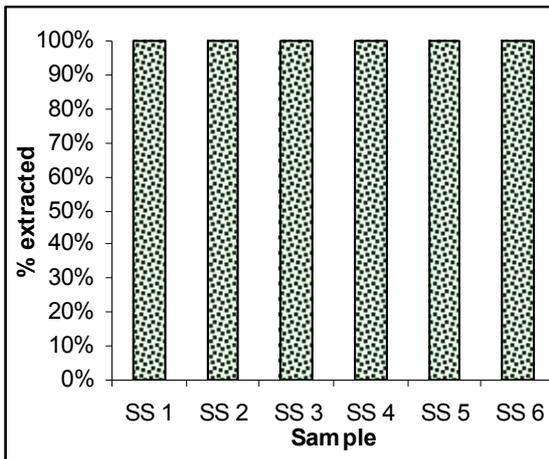


Fig 3a: Cr Extracted by the Three Steps & the Residual Fraction

Fig 3b: Cu Extracted by the Three Steps & the Residual Fraction

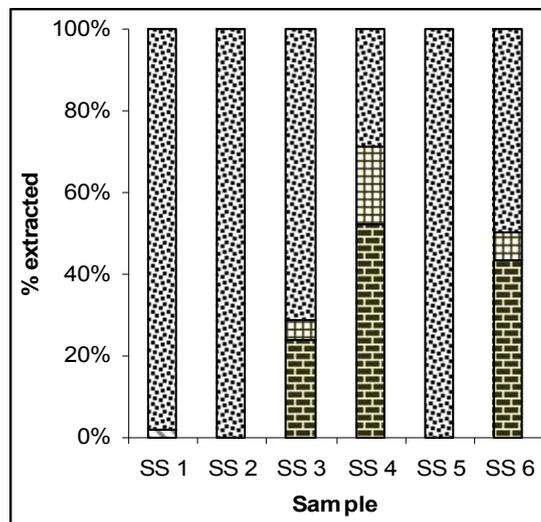
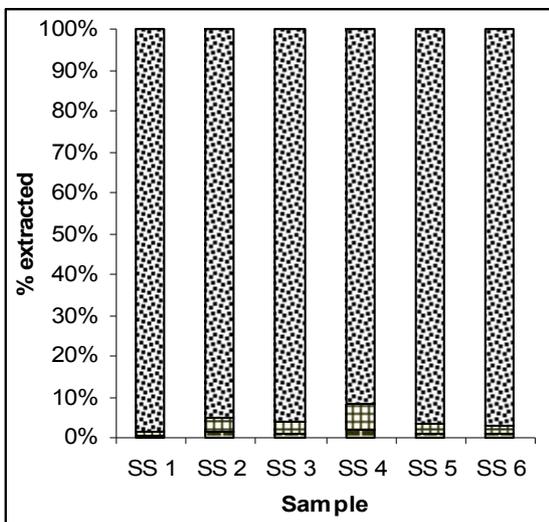


Fig 3c: Fe Extracted by the Three Steps & the Residual Fraction

Fig 3d: Mn Extracted by the Three Steps & the Residual Fraction

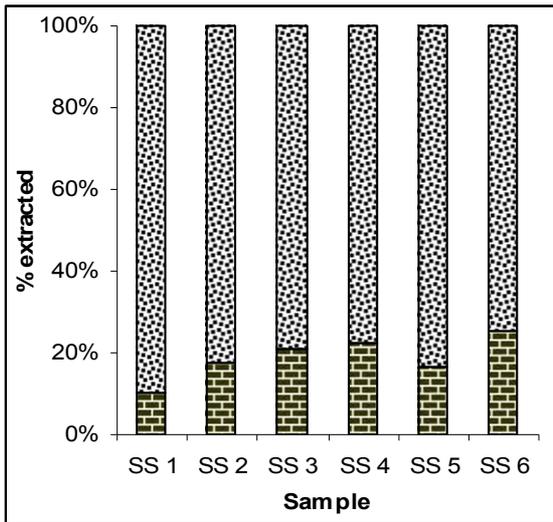


Fig 3e: Ni Extracted by the Three Steps & the Residual Fraction

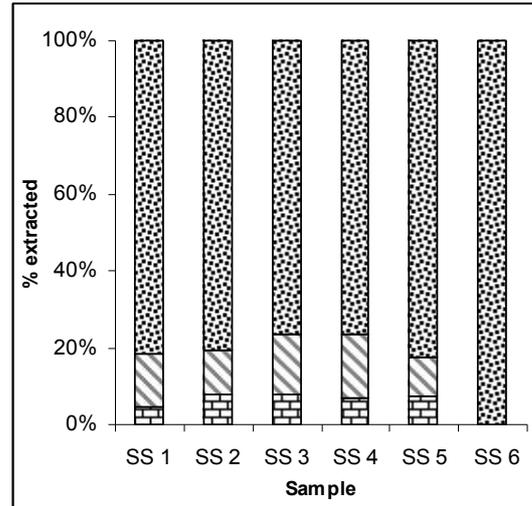


Fig 3f: Pb Extracted by the Three Steps & the Residual Fraction

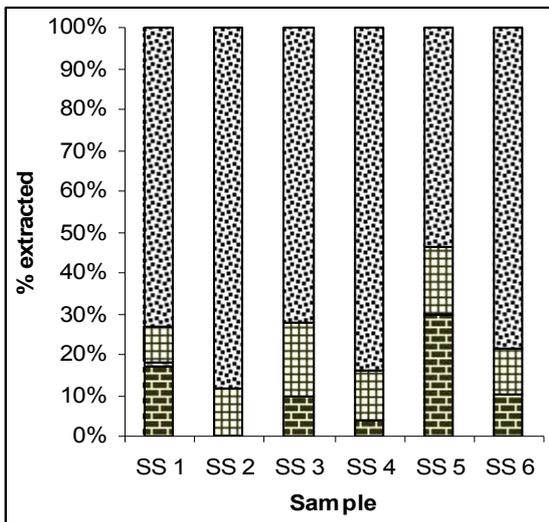
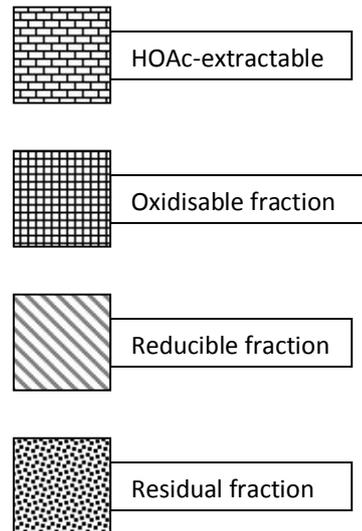


Fig 3g: Zn Extracted by the Three Steps & the Residual Fraction



In all the analysed soil samples, as shown by Tables 3a-3c and Fig 3a Cr was not detected in all the extraction scheme. This is perhaps due to the sensitivity of the analyser, and specifically the strong association of Cr with the residual fractions, which implies that it has a very minimal mobility potential and poses no danger to the environment and human despite its total content in the soil samples.

Table 4a: Results of Step 1 of Sequential Extraction (HOAc-extractable).

Sample names	Concentration Values ($\mu\text{g} / \text{g}$)						
	Cr	Cu	Fe	Mn	Ni	Pb	Zn
SS 1	ND	2.98 ± 0.00	129.71±4.99	3.25 ± 0.32	3.75 ± 0.00	18.58 ± 3.39	4.07 ± 0.34
SS 2	ND	ND	47.75 ± 1.25	3.92 ± 0.00	3.75 ± 0.20	77.63 ± 5.64	1.21 ± 0.00
SS 3	ND	1.82 ± 0.00	29.24 ± 0.00	66.42 ± 3.24	8.30 ± 0.60	27.81 ± 3.18	14.82±0.00
SS 4	ND	13.16 ± 1.23	843.49±34.90	112.12±6.47	14.37 ± 1.10	7.51 ± 0.41	25.38±1.03
SS 5	ND	ND	49.51 ± 3.73	1.91 ± 0.00	3.75 ± 0.20	24.11± 1.66	1.21 ± 0.00
SS 6	ND	ND	120.89 ± 7.48	50.67 ± 0.00	6.78±0.20	ND	7.68 ± 0.34

Table 4b: Results of Step 2 of Sequential Extraction (Reducible fraction).

Sample names	Concentration Values ($\mu\text{g} / \text{g}$)						
	Cr	Cu	Fe	Mn	Ni	Pb	Zn
SS 1	ND	2.70 ± 0.24	633.76±13.06	ND	ND	57.33 ± 3.14	14.81 ± 0.34
SS 2	ND	ND	575.60± 4.17	ND	ND	112.70±10.20	ND
SS 3	ND	0.68 ± 0.00	372.92± 8.51	13.33 ± 1.12	ND	54.49 ± 0.00	3.12 ± 0.35
SS 4	ND	2.70 ± 0.24	596.75± 5.60	74.49 ± 3.24	ND	18.58 ± 1.20	6.46 ± 0.17
SS 5	ND	ND	528.01± 8.67	ND	ND	31.50 ± 0.00	7.67 ± 0.17
SS 6	ND	ND	531.54±10.62	16.69 ± 1.12	ND	ND	3.61 ± 0.69

Table 4c: Results of Step 3 of Sequential Extraction (Oxidizable fraction).

Sample names	Concentration Values ($\mu\text{g} / \text{g}$)						
	Cr	Cu	Fe	Mn	Ni	Pb	Zn
SS 1	ND	8.66 ± 0.57	1750.86±40.12	ND	ND	ND	7.31 ± 0.72
SS 2	ND	3.37 ± 0.00	1274.65± 6.13	ND	ND	ND	1.69 ± 0.00
SS 3	ND	8.66 ± 0.57	1242.57±22.61	2.67 ± 0.00	ND	ND	5.70 ± 0.17
SS 4	ND	12.32 ± 0.00	1807.62±40.12	27.18±1.12	ND	ND	20.07 ± 0.24
SS 5	ND	1.74 ± 0.00	1521.39±13.20	ND	ND	ND	4.36 ± 0.48
SS 6	ND	1.33 ± 0.28	1351.14± 9.40	2.67 ± 0.21	ND	ND	4.04 ± 0.23

Table 4d: Concentration of Metals in the Residual Fraction of the Samples

Sample names	Concentration Values ($\mu\text{g} / \text{g}$)						
	Cr	Cu	Fe	Mn	Ni	Pb	Zn
SS 1	60.8 ± 1.70	59.8 ± 2.8	150400±200	49.9 ± 1.90	32.9 ± 3.40	339.6 ± 4.40	63.5 ± 2.20
SS 2	43.60 ± 0.80	11.3 ± 1.0	37400±70	15.1 ± 0.70	17.6 ± 1.50	793.5 ± 7.60	12.8 ± 0.80
SS 3	110.6 ± 6.90	29.8 ± 2.9	38240±110	39.9 ± 5.30	31.0 ± 3.70	265.5 ± 2.40	22.9 ± 2.70
SS 4	79.0 ± 1.20	66.1 ± 1.7	27400±60	41.10 ± 1.10	49.8 ± 2.00	84.4 ± 1.80	140.5 ± 0.90
SS 5	55.7 ± 1.10	13.0 ± 1.2	57030±100	15.30 ± 1.00	19.0 ± 1.90	261.7 ± 2.80	13.8 ± 0.90
SS 6	47.0 ± 1.10	15.1 ± 1.2	60700±110	19.0 ± 1.00	19.8 ± 1.90	288.1 ± 3.20	27.7 ± 1.10

Fe was prevalently held in the residual fraction (92%), with the oxidizable form making up for much less than 10%. Ni was held in the HOAc-extractable (exchangeable) and the residual fractions. Residual fraction (78%), HOAc-extractable fraction (22%). Cu was also more occluded in the residual fraction (75%), Oxidizable fraction (20%) because of its affinity to organic matters, with very small amount held in the HOAc-extractable fraction (5%). In all the analysed soil samples, the proportion of the total Pb found in the reducible fraction was significant, though, higher proportion was held in the residual fraction; residual fraction (77%), reducible fraction (15%), and HOAc-extractable fraction (8%). Mn was mainly distributed between exchangeable fraction (35%), and the residual fraction (55%), with the oxidizable fraction assuming about 10%. Zn was distributed among the exchangeable fraction, the oxidizable fraction, and the residual fraction, with the residual fraction being the dominant fraction. Exchangeable fraction (15%), oxidizable fraction (13%), and residual fraction (70%).

In the tropical soil where the content of organic materials is significant, and the metals are mostly introduced by human activities rather than lithogenic, HOAc, and the H₂O₂/ NH₄OAc may represent simple effective reagents to extract heavy metals bound to these exchangeable and organic phases, providing indications about the actual and potential mobility of contaminant in the test soils [5, 9]. The amounts of metals released by this reagent were very low when compared with their respective total contents. The results further showed that Cu, Ni, Pb, and Zn were the main metallic contaminants of the studied soils from the abandoned oil exploration field camp mechanical workshop. Therefore, containment and recycling of the wastes; sequestration of the site, and remediation of site after use can go a long way to reduce the access of these metals to the ecosystem.

CONCLUSION:

In the contaminated soils of the abandoned oil exploration field camp mechanical workshop, Cu and Pb were found to occur above regulatory levels. The utilization of exploration and drilling chemicals, cable works, and metal works are the main sources and contributors of these metals in the studied soils. The variation in the degree of mobility of metals in the multiple step extractions in the soil samples explained the differences in soil organic matter content and how they influence the release of the metals adsorbed to them, the influence of the soil properties on metal-soil interaction and the strength of the reagents to desorb and release the metals from their binding sites [7, 5]. The high total concentration of

metals does not match their mobility and bioavailability as such; total contents of metals cannot be fully used to quantify the degree of danger posed by such elements to human and the ecosystem. Despite the observed immediate impact of the workshop activities on the environment; the death of plants and trees at the site may be due to suffocation caused by the presence of the pollutant and not necessarily their toxicity, as such cannot be used to predict and/or conclude for a dangerous scenario on the environment. The bulk contents of the metals were moreover observed held in the residual fractions making them inert and pose little or no danger to the ecosystem. Nevertheless, regular evaluation is very necessary, because these metals can under favourable conditions be re-mobilised from their inert state to active state by weathering or other agents thereby increase their potential risk of contamination and danger to the ecosystem. The study demonstrates the need of a multidisciplinary approach for contamination site characterization and the use of more sophisticated multi-element analytical equipment (ICP-MS) to be able to detect metals of very low detection limit for proper analysis of the bulk soil matrix.

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