

Rapid estimation of heavy metals in crude oil contaminated soils by X-ray fluorescence (XRF) spectroscopy

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ABSTRACT: Crude oil exploration and exploitation activities in the Niger Delta, Nigeria have caused the contamination of numerous land sites. A total of 45 sub-surface soil samples were collected from three genuinely crude-oil spill sites and their heavy metal concentrations were measured using X-Ray fluorescence spectroscopy. The range of measured heavy metal concentrations (mg/kg) in the three study sites are as follows: chromium (Cr) 54-75, copper (Cu) 5.4-16.6, iron (Fe) 14841-23404, lead (Pb) 13.5-21.4, manganese (Mn) 158-555, zinc (Zn) 32.6-47.2 in Site 1; Cr (35-66), Cu (5-16.1), Fe (10166-20967), Pb (12-17.8), Mn (209-440), Zn (17.6-33.6) in Site 2; and in Site 3: Cr (32-115), Cu (6.5-20.8), Fe (7538-22800), Pb (12-135), Mn (98-338), Zn (19.9-177). The trend of heavy metals contamination in the three sites are as follows: Fe > Mn > Cr > Zn > Pb > Cu. Their mean concentrations were relatively higher than background concentrations of heavy metals in soils previously reported in same region. Using the contamination factor (CF), the intensity of heavy metal (Mn, Cr, Zn, Pb, and Cu) contamination in soils from the three oil spill sites were evaluated and compared. The index showed Cr > Mn across the three sites, which was highest in site 1 and least in site 2. The trend of CF varies for the other metals. The high values of CF for Mn and Cr show that Mn and Cr have extreme level of contamination while Cu, Pb, and Zn lie within the range of moderate level contamination. Furthermore, statistical analyses shows significant ($p < 0.05$) correlation between the concentrations of the metals, which indicates the link between the metals. Thus, crude-oil spill may be the common denominator for the heavy metal pollution in the study locations. Based on the contamination indicator parameter, the soils of the studied sites are threatened by contamination of Cr and Mn.

Keywords: Contamination factor, heavy metal, soil contamination, X-Ray fluorescence.

INTRODUCTION

Soil is a great reservoir for contaminants as well as a natural buffer for transportation of chemical materials and elements in the environment. There has been an increasing concern in many nations about the levels of potentially toxic elements (PTE) including heavy metals in soils and the resultant risks to both the ecosystems and human life. Soil contamination by oil spill is a severe environmental issue of global concern. The Niger Delta region is the heart of the oil and gas industry in Nigeria and has contributed enormously to the growth and development of the country. However, since the beginning of the establishment of the oil and gas industries in the

region, several oil spill incidents have been reported; and, to date, it has been estimated that 13 million tons of hydrocarbons have been spilled in the region due to pipeline fatigue, well blowout, pipeline vandalism, and sabotage (Ambituuni et al., 2014; Nwilo and Badejo, 2006). Similarly, Ite et al. (2013) reported that the number of contaminated sites in the Niger Delta region is in excess of 2,000. Furthermore, the United Nation Environment Programme (UNEP) reported in 2011 that in Ogoniland alone (a small part of the Niger Delta), over 69 sites were heavily contaminated with crude oil (concentration > 139,000 mg/kg affecting soil, air and water quality criteria

and posing a serious human health threat. This, in turn, impacts on the quality of water resources: directly affecting the health of local communities, which are drinking contaminated water (Davies and Abolude, 2016; Nganje et al., 2017; UNEP, 2011).

Crude oil contains metals including cobalt (Co), copper (Cu), lead (Pb), iron (Fe), magnesium (Mg), manganese (Mn), zinc (Zn), cadmium (Cd), chromium (Cr), nickel (Ni), arsenic (As), titanium (Ti), silver (Ag) amongst others. Heavy metals contamination in soil has attracted significant ecological concern because of their toxicity and bioaccumulation. Unlike most pollutants (e.g. petroleum hydrocarbons), heavy metals cannot be degraded and have long-lasting effects in soil as a result of strong adsorption of many metals on humic and clay colloids in soils (Iwegbue et al., 2009). Heavy metals have physiological effects on living organisms as they are not degradable (Esmailzadeh et al., 2018). Thus, research involving the evaluation of heavy metals in petroleum release sites in the Niger Delta would be valuable to appropriately guide the direction of mitigation and remediation actions.

Studies assessing the environmental quality of soils in the Niger Delta region of Nigeria are very scarce, especially involving heavy metals in crude oil-contaminated land sites. Most studies focused on waste dump sites (Ololade, 2014; Ossai, 2014; Iwegbue et al., 2006a), while Iwegbue et al. (2009) and (2006b) assessed the level of heavy contamination in oil fields and crude oil impacted soils. Therefore, further studies are needed to assess the extent of heavy metal contamination in the numerous crude oil-contaminated sites in the Niger Delta, Nigeria. In the area of analytical methods applied for metal determination, all the above studies used labour-intensive and costly laboratory analytical methods: atomic absorption spectrometry (AAS) or inductively coupled plasma-mass spectrometry (ICP-MS) which requires sample extraction or digestion. These methods are relatively difficult and expensive. None has used proximal soil sensors (PSS) such as X-ray fluorescence (XRF) spectroscopy which has significant advantages including little or no sample preparation, nondestructive, cost-effective, rapid; and offers simultaneous multi-elemental analysis in soil (Weindorf et al., 2014; Ulmanu et al., 2011). In this context, the aim of this research is to determine heavy metal concentrations in genuinely crude oil-contaminated soils (field-moist soils) in the Niger Delta region by a portable X-ray fluorescence (XRF) Analyser. The study objectives were to: (1) assess the potential of XRF as a rapid measurement tool for heavy metal contamination in soils contaminated with crude oil, and (2) evaluate the source of heavy metals in soils using contamination factor (CF) to determine the potentially responsible party causing soil heavy metal pollution, which would enable regulators make more accurate decisions. To our knowledge, this study represents the first research on the concentrations of heavy metals in genuinely crude

oil-contaminated soils in the Niger Delta, Nigeria by XRF Analyser.

MATERIALS AND METHODS

Study area and sample collection

The study area located in Bayelsa and Rivers State, Niger Delta, Southern Nigeria has a tropical rain forest climate characterised by two seasons: the rainy season lasts for about 7 months between April and October with an overriding dry period in August (known as August break); and the dry season lasts for about 5 months, between November and March. The temperature varies between 25 and 35°C. The regional geology of the Niger Delta is relatively simple, consisting of Benin, Agbada (the kitchen of kerogen) and Akata formations, overlain by various types of quaternary deposits (Kogbe, 1989; Wright et al., 1985). Soils of the area studied were classified according to the United State Department of Agriculture (USDA) (Soil Survey Staff, 1999) soil taxonomy into two orders, i.e. Inceptisols and Entisols, which include four subgroups of Typic Dystrudepts, Aeric Endoaquepts, Typic Udipsammerts and Typic Psammaquents (Udoh et al., 2013). A total of 45 representative spot sample points were collected from three oil contaminated sites (Site 1= Ikarama: 15 samples; Site 2= Kalabar: 15 samples; and Site 3= Joinkrama: 15 samples) in August 2015. The three sites were selected for sampling due to their similar exploration activities and oil spill history. The soil samples (approx. 5 kg) were collected from visible 'hot-spots' in the top 15-cm soil layer using a shovel. Figure 1 shows the sampling location maps. Soil samples were kept in air-tight centrifuge tubes and stored at 4°C using ice block to avoid hydrocarbon volatilisation and preserve field-moist status until shipment to Cranfield University. The samples were then stored in a freezer at -20°C prior to heavy metal analysis by XRF spectroscopy.

Sample preparation and XRF analysis of soil heavy metals

The concentrations of the heavy metals in oil-contaminated soils were determined using a portable Olympus Delta Premium 6000 Series XRF Analyser (Olympus, USA). In diffuse reflectance mode, the Delta XRF analyser is three beams configured, where each beam was programmed to scan soil samples for 30 seconds. Prior to soil scanning, the instrument's setting and operational conditions were done in accordance with the manufacturer's specifications; and the analyser was calibrated with alloy 316 stainless steel coupon. Fresh soil samples were thoroughly mixed and scanned using single open-ended and snap-post venting (30.7 mm O.D x 23.1 mm High) sample cups, sealed by Prolene Thin-Film

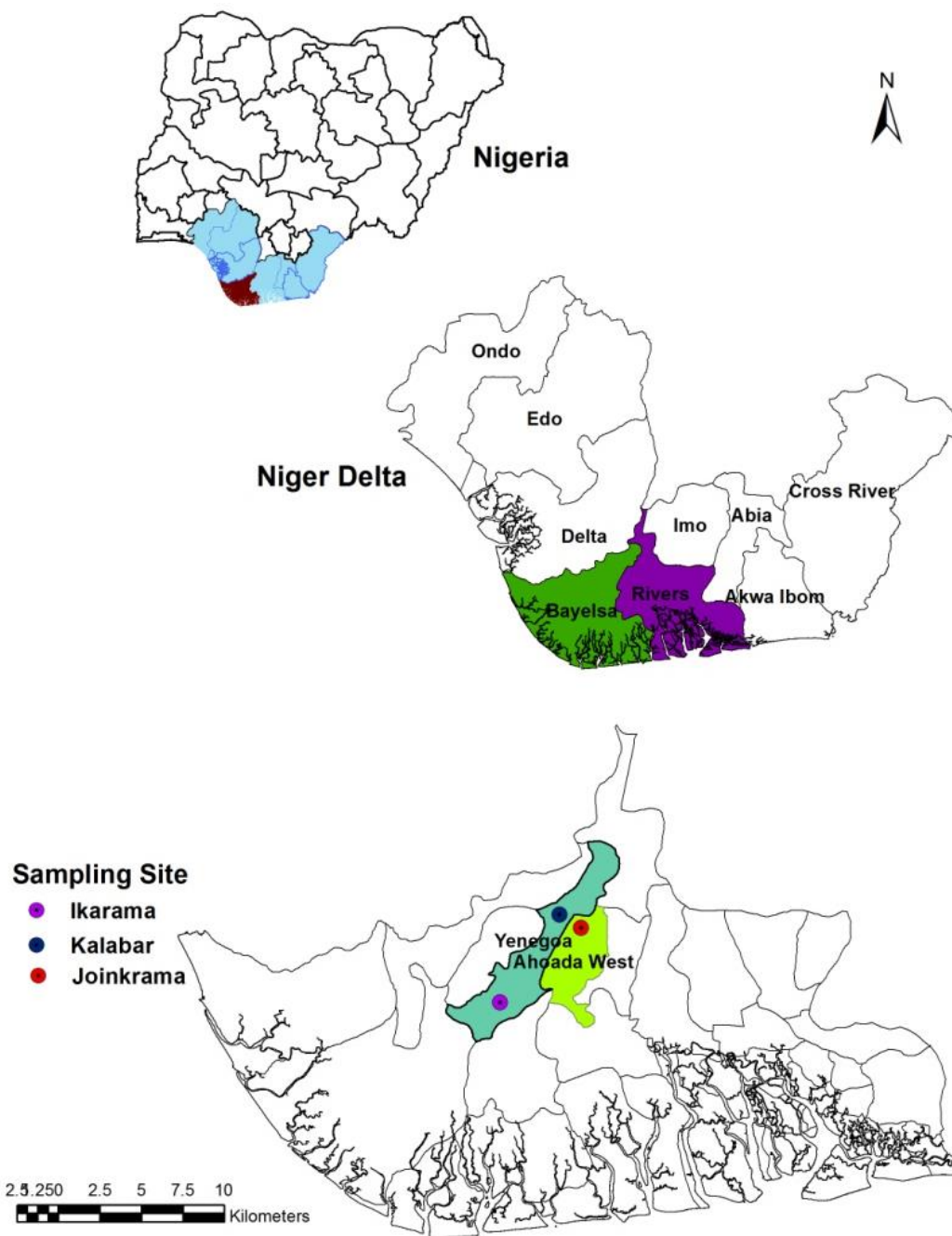


Figure 1. Soil sampling locations for the three oil spill sites in the Niger Delta, Nigeria.

(Diam. 63.5 mm) (Chemplex, USA). Each soil sample was analysed for Cr, Cu, Fe, Pb, Mn and Zn concentrations.

Statistical analysis

Statistical analysis was performed using the raw data in Table 1. Relationship between metals in the three different sites was determined using Statistica software (version 64).

RESULTS AND DISCUSSION

Heavy metal concentration in soils

Table 1 reports on the heavy metals (Cr, Cu, Fe, Pb, Mn and Zn) concentrations in 45 genuinely crude oil-contaminated soil samples collected from three petroleum release sites in the Niger Delta, Nigeria. Furthermore, analyses were carried out and presented in the preceding sections.

Table 1. Heavy metal concentrations (mg/kg) in 45 soil samples collected from 3 oil spill sites (15 samples from each site) in the Niger Delta, Nigeria. Concentrations were determined using portable Delta Premium 6000 Series X-ray Fluorescence (XRF) Analyser.

Site 1 (number of samples = 15)															
Fe	22368	23040	20393	21392	23344	23073	23404	21912	23251	17951	18201	18555	19146	19495	14841
Mn	312	401	445	463	555	506	517	488	511	210	193	179	158	222	171
Cr	62	66	55	61	66	63	65	59	54	66	72	67	59	59	75
Zn	44.2	32.6	33.9	37.3	45.8	34.4	38.4	32.6	34.1	46.9	47.2	43.3	39.6	44.6	46.6
Pb	18.5	14.9	17.5	21.4	20.9	16.2	16.6	17.3	13.5	18.6	18.5	17.9	15.8	14.3	16.8
Cu	16.6	7.6	11.7	12.4	15.6	11.5	13.3	11.6	12.8	8.6	11.7	8.9	10.4	5.4	8.5
Site 2 (number of samples = 15)															
Fe	11721	15595	10924	13899	10166	14278	20967	14017	12097	13812	10313	16361	13577	19285	13699
Mn	216	358	259	292	209	372	372	343	210	286	278	440	325	415	300
Cr	40	66	36	43	41	48	53	40	39	43	35	49	40	48	38
Zn	21	27.8	19.8	33.6	17.6	22.7	31.3	24.4	30.6	30.6	22.3	30.4	19.4	30.9	28
Pb	15.7	15.9	16.7	15	14.9	17.8	16	12.9	12	15.3	15.8	16.6	16.1	17	14.1
Cu	8.3	11.1	7.3	10.6	6.2	7.8	16.1	7.1	6.8	5	7.8	10.5	nd	9.5	6.6
Site 3 (number of samples = 15)															
Fe	13538	17296	15194	19087	22213	21148	13042	22800	13848	7538	19418	19667	15182	20222	13730
Mn	234	270	146	255	251	284	191	338	209	98	236	263	212	276	205
Cr	37	73	32	65	115	49	34	62	52	47	49	58	61	61	39
Zn	26.9	29.3	41.7	78.4	177	41.1	28.9	60.6	43.3	19.9	61.7	47.7	63.7	68.9	64.9
Pb	16.9	12.7	35.8	80.4	135	14.5	12	29.6	47.2	21.4	24	28.6	34.9	56.5	69.9
Cu	7.6	11.5	13.9	20.1	20.8	12.2	7.6	12.1	6.6	6.5	16.2	14.9	13.4	13.3	9

Fe= iron, Mn= manganese, Cr= chromium, Zn= zinc, Pb= lead, Cu= copper, and nd = not detected.

Statistical analysis

Summary statistics of the 6 heavy metal concentrations are presented in Table 2. Cr ranged from 54-75, Cu (5.4-16.6), Fe (14841-23404), Pb (13.5-21.4), Mn (158-555), Zn (32.6-47.2) in Site 1; Cr (35-66), Cu (5-16.1), Fe (10166-20967), Pb (12-17.8), Mn (209-440), Zn (17.6-33.6) in Site 2; in Site 3, Cr (32-115), Cu (6.5-20.8), Fe (7538-22800), Pb (12-135), Mn (98-338), Zn (19.9-177). As it can be seen, trend of heavy metal contamination in the three sites are in the order: Fe > Mn > Cr > Zn > Pb > Cu. Fe contamination level

was found to be highest in site 1. Results (mean values) were compared with other studies (Iwegbue et al., 2009, 2006b) conducted in the Niger Delta, Nigeria, the case study area of the current research. Except Fe which had no records at the moment to be compared with; most of the metal values were higher than those reported by Iwegbue et al. (2009) and (2006b). Also, the mean concentrations of Mn, Cr, Cu, Zn, and Pb were observed to be higher than the background concentrations reported by Agip (2000). This is an indication that crude oil spill is the source of heavy metal pollution in the study sites.

Correlation matrix

The results of matrices of correlation coefficient between the 6 heavy metal concentrations in 45 crude oil-contaminated soils were determined using the raw data presented in Table 1. This approach was applied to reduce possible bias that might result from the mean concentration values. Results (highlighted bold) show significant ($p < 0.05$) correlation (Table 3). The observed significant correlation between the concentrations of the different metals reveal links between them, which may be attributed to their common source-crude oil.

Table 2. Descriptive statistics of heavy metal concentrations (mg/kg) in 15 oil contaminated soil samples each collected from 3 of oil spill sites (n=45) in the Niger Delta region of Nigeria. Heavy metal concentrations were determined using a portable Olympus Delta Premium 6000 Series XRF Analyser. These results were compared with results of previous studies (A, B, C) in the same region.

Metal	Site 1			Site 2			Site 3			A	B	C
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max			
Fe	20691.07	14841	23404	14047.40	10166	20967	16928.20	7538	22800	NB	61625	NB
Mn	355.4	158	555	311.67	209	440	231.20	98	338	26.1	199.6	201.8
Cr	63.27	54	75	43.93	35	66	55.60	32	115	2	17.78	28.75
Zn	40.1	32.6	47.2	26.03	17.6	33.6	56.93	19.9	177	23	38.13	29.3
Pb	17.25	13.5	21.4	15.45	12	17.8	41.29	12	135	11	7.44	25.02
Cu	11.11	5.4	16.6	8.05	5	16.1	12.38	6.5	20.8	4	7.78	11.21

A= background level of metal in soil samples collected from the Niger Delta, Nigeria (Agip, 2000); B= mean concentration of heavy metals in soils collected from an oil field in the Niger Delta, Nigeria (Iwegbue et al., 2006b); C= mean concentration of heavy metals in soils impacted with crude oil in the Niger Delta, Nigeria (Iwegbue et al., 2009); and NB= no background concentration.

Table 3. Correlation matrix between six (n=6) heavy metals concentrations in 45 soils collected from three crude oil-contaminated sites in the Niger Delta, Nigeria. The analysis was performed using Statistica software (version 64). Marked bold correlations are significant at $p < 0.05$.

Fe	Mn	Cr	Zn	Pb	Cu
1.000	0.609	0.608	0.381	0.148	0.634
0.609	1.000	0.151	-0.128	-0.188	0.251
0.608	0.151	1.000	0.702	0.500	0.554
0.381	-0.128	0.702	1.000	0.902	0.641
0.148	-0.188	0.500	0.902	1.000	0.541
0.634	0.251	0.554	0.641	0.541	1.000

Index of pollution

In order to assess heavy metal contamination in soils collected from crude oil spill sites, contamination factor (CF) approach was applied. CF was calculated using soil heavy metal background data in the Niger Delta region of Nigeria published by (Agip, 2000). This was achieved by applying equation 1. Results are displayed in Table 4. The CF values were all greater than 1 in all the metals across the three sites. The high values of the CF (> 1) in all the

heavy metals can be attributed to the influence of crude oil spill; as it contains metals including Fe, Mn, Cr, Zn, Pb, Cu. As it can be seen in Table 4 below, the CF values exist in the order: $Cr > Mn > Cu > Zn > Pb$ in site 1; site 2 ($Cr > Mn > Cu > Pb > Zn$) and in site 3 ($Cr > Mn > Pb > Cu > Zn$). The trend of CF of metals varies in all the three sites, except those of Cr and Mn ($Cr > Mn$). CF values in this study (Table 4) are lower than maximum allowable toxic metal concentration (mg/kg) limits [Cu = 30, Cr = 100, Pb = 100, and Zn = 300] in soil (WHO, 1996). Nevertheless, since heavy metal

pollution in the area is attributed to continuous exploration and exploitation activities; the regulators and the regulated should form a synergy to embark on remediation of such contaminated sites to reduce the associated risks to the environment and the possible effects on human health.

$$\text{Contamination factor (CF)} = C_{\text{sample}}/C_{\text{background}} \quad (1)$$

Where, C_{sample} = mean metal content in polluted soil; $C_{\text{background}}$ = mean natural background value of that metal; n = number of metals = 5.

Table 4. Heavy metal contamination factor (CF) of soils collected from three crude oil spill sites in the Niger Delta, Nigeria.

Metal	Background values (mg/kg) (AGIP, 2000)	Site 1		Site 2		Site 3	
		Mean values (mg/kg) (Current study)	CF	Mean values (mg/kg) (Current study)	CF	Mean values (mg/kg) (Current study)	CF
Mn	26.1	355.4	13.62	311.67	11.94	231.20	8.86
Cr	2	63.27	31.64	43.93	21.97	55.60	27.80
Zn	23	40.1	1.74	26.03	1.13	56.93	2.48
Pb	11	17.25	1.57	15.45	1.40	41.29	3.75
Cu	4	11.11	2.78	8.05	2.01	12.38	3.10

Conclusions

Portable XRF analyser was found to be a rapid tool for the assessment of heavy metals (Fe, Mn, Cr, Zn, Pb, and Cu) contamination in genuinely crude oil-contaminated soils collected from three crude oil spill sites in the Niger Delta, Nigeria. This reckons the first study on the use of a proximal soil sensor such as XRF for soil heavy metal pollution assessment associated with crude oil in the region. The concentration of heavy metals across the 3 sites was Fe > Mn > Cr > Zn > Pb > Cu. While the mean values of some metals obtained in this study (sites 1 and 2) ranked higher than those reported in previous studies; mean metal values in site 3 was higher than all the previously published results in the region. Matrices of correlation coefficient between the heavy metal concentrations showed significant ($p > 0.05$) correlation, which confirms the source of contamination to be crude oil spill. Furthermore, contamination factor (CF) approach was applied to investigate the source of heavy metal pollution. The high values of the CFs (> 1) in all the sites also confirm crude oil spill to be the source of heavy metal contamination. Consequently, it can be concluded that crude oil spills on land sites contributed to the higher concentrations of the metals relative to the natural background values. Since heavy metals are not degradable (bioaccumulants), they may pose a threat to environment and human wellbeing. Therefore, it is recommended that the Nigerian Government should set up appropriate bodies and/or measures to screen the site-specific risks of heavy metals in the Niger Delta, Nigeria based on the numerous petroleum release sites. This would help to assess the environmental risk of heavy metals contamination in both the areas where soils are potentially polluted, and sites that have recorded series of oil spill incidents.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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