Variation of Selected Metal Pollutants with Depth and Seasons in Petroleum Contaminated Soils

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Abstract

Human activities have led to increased metal contamination in the environment, among these is petroleum spillage. Conventional methods of analysis are concerned with determination of metal levels along soil surfaces and in water. To assess complete toxicological effects, it is important to determine the variation of metal levels with depth and seasons. This study sought to investigate the effect of petroleum spillage on the Fe, Pb, Ni, Zn, Cd and Cu levels extracted from petroleum-contaminated soils. A total of 40 samples were collected from four sites (S_1*-* S_4) *in both wet and dry seasons. Soils were sampled at 15 cm depth intervals from 0 - 75 cm and kept in clean polythene bags. Stones and plant fragments in the samples were immediately removed by passing the samples through a < 0.2 mm sieve and then crushed to fine powder using mortar and pestle. The concentration of heavy metals was analyzed using atomic absorption spectrophotometer. For* S_1 *at shallower depth (0-30 cm), the levels were 3.95 ppm, 0.51 ppm, 0.05 ppm, 0.20 ppm and 0.08 ppm for Fe, Zn, Ni, Pb and Cu, respectively. At deeper depth (45-75 cm), the corresponding values were 3.31 ppm, 0.55 ppm, 0.55 ppm, 0.27 ppm and 0.10 ppm for Fe, Zn, Ni, Pb and Cu. As for* S_2 *at shallower depth, the values were 4.83 ppm, 0.72 ppm, 0.99 ppm, 0.47 ppm and 0.10 ppm for Fe, Zn, Ni, Pb and Cu, apiece. At deeper depth, the respective values were 3.20 ppm, 0.82 ppm, 0.42 ppm, 0.00 ppm and 0.12 ppm for Fe, Zn, Ni, Pb and Cu. Site 3 at shallower depth had respective values 4.67 ppm, 0.69 ppm, 0.57 ppm, 0.44 ppm and 0.14 ppm for Fe, Zn, Ni, Pb and Cu, whereas at deeper depth, the corresponding values were 3.48 ppm, 0.67 ppm, 0.70 ppm, 0.11 ppm and 0.13 ppm. For* S_4 *at shallower depth, the levels were 4.72 ppm, 0.70 ppm, 0.54 ppm, 0.47 ppm and 0.11 ppm for Fe, Zn, Ni, Pb and Cu, respectively. At deeper depth, the levels were 4.00 ppm, 0.78 ppm, 0.64 ppm, 0.45 ppm and 0.14 ppm for Fe, Zn, Ni, Pb and Cu, sequentially. There were insignificant statistical differences between the four sites with* $p> 0.05$*. Levels of Fe and Pb decreased with depth, whereas Zn and Ni levels increased with depth. Copper had little vertical movements. Variation of Ni with depth was statistically significant* ($p = 0.01098$, $F = 3.83$) *unlike Zn, Pb, Cu, Fe and Cd and this could threaten ground water. Wet season had higher mean levels than the dry season and this was significant for Ni, Zn and Cu with* $p < 0.05$*. A significant correlation* ($p < 0.05$, $r > 0.5$) *existed between mean metal levels and petroleum spillage signifying spillage of petroleum elevate metal levels in soil. Mean Pb levels were above the crude oil quality group (COQG) permissible limits at sites* S_2, S_3 *and* S_4 *unlike the other elements. Regular* *assessment of Pb from petroleum should provide a framework for its control in the environment. Heavy metal permissible levels should be included in assessment of petroleum quality by the Kenya Bureau of Standards (KEBS) Organic matter should be added to soil to reduce movement of Ni to deeper depths.*

Key Words: Metal Pollutants, Petroleum Spillage, Seasons and Soil Depth

INTRODUCTION

Soils receive potentially toxic elements from both natural and a wide range of anthropogenic sources, including the weathering of primary minerals, mining, fossil fuel combustion, the metallurgical, electronic and chemical industries and waste disposal. The application of domestic and industrial sludge to soils for agricultural and disposal purposes is often the most environmentally acceptable and economical method (Tokalioglu *et al*., 2001).

There is concern that heavy metals and other contaminants in sludge accumulate in the soil, reducing its quality for agriculture *inter alia*. Indeed, many potential contaminants are necessary for agricultural production but become hazardous when they occur in excess in the soil. The ash contained in heavy fuel oil contains the (inorganic) metallic content, other non-combustibles and solid contaminants. The ash content after combustion of a fuel oil derived from solid foreign material (sand, dust, catalyst particles), dispersed and dissolved inorganic materials, such as V, Ni, Fe, Na, K or Ca (American Bureau of Shipping, 2001).

Heavy fuel oils with high trace metal (oil soluble) concentrations of V, Ni and Pb can cause accelerated fouling and tenacious deposits, performance reductions and corrosion. To compensate for the effects of these trace metals on exhaust valves and turbo charger blading, a chemical inhibitor can be mixed with the heavy fuel oil to modify the chemical and physical properties of the resulting ash, which is the source of previously mentioned deposits and fouling (American Bureau of Shipping, 2001).

The Crude Oil Quality Group (COQG) is dedicated to the belief that maintaining the integrity and consistency of the refining characteristics of petroleum products promotes petroleum quality and environmental safety. According to COQG, the commonly used industry standards of gravity and sulphur do not adequately assess petroleum quality and should be expanded to include other characteristics like the allowable metal levels. It is opposed to concealed modification of petroleum properties through alteration and blending of different petroleum streams that have different properties, which traditionally has been done by pipeline companies without informing shippers. Among these, blending petroleum oil with gasoline, butanes and chlorinated hydrocarbons have led to contamination of petroleum. Chlorinated hydrocarbons are capable of decomposing into HCl which causes corrosion, forming pits in the heat exchangers. Pipeline companies can control contamination of its oil by minimizing blending and alterations. Alteration is normally through addition of salt water and augmentation of production chemicals which contain heavy metals like Pb, Zn, Fe, Ni, Mn and Cu (COQG, 2004).

A comprehensive knowledge of the interactions between the trace elements and the soil matrix is required in order to judge their environmental impact. The depth profile studies of heavy metal concentration in soils provide information on mobility and sorption of the selected cations in soil. Since the behaviour of the elements in a soil-water-plant system depends on their forms, the determination of trace metals in soils is often performed by single or sequential extraction (Tokalioglu *et al*., 2001).

Petroleum products have been continuously released to the environment through accidents, as managed releases, or as unintended by-products of industrial, commercial or private actions. Indiscriminate disposal of industrial, petrochemical, agrochemical and mining wastes along road highways has led to accumulation of toxic elements. Through weathering processes and water run-offs, these elements have found their way into arable lands leading to extensive contamination of lands (TPHCWG, 1997).

In water, oil forms an insoluble layer that *anoxiates* aquatic organisms. Although microbial degradation breaks down petrochemicals into simple inert products, the presence of toxic heavy metals in soils appears to hinder petroleum biodegradation through impacting both the physiology and ecology of organic degrading microorganisms. This passivates microbial degradation processes (Sandrin & Maier, 2003). There are reported cases of plants wilting in areas of oil spillage, death of animals and even events of rapid fires. Thus petrochemicals need to be broken down into simple environmentally innocuous products by these microorganisms.

In a study by Onojake and Okonkwo (2011) on metal pollution through oil spillage, soil samples were collected from crude oil polluted sites in Bodo city in Niger Delta. An uncontaminated sample collected 50 metres away from the spill site but within the same geographical area was used as control sample. Trace elementsAs, Cu, Cr, Cd, Fe, Pb, Ba, Ni, V, Hg and cation exchange capacity constituents of the oil contaminated and non-contaminated soils were determined with AAS. The values of these trace elements were relatively higher at the epicenter of the spill and enhanced more at the surface soils signifying input from oil pollution.

A study was conducted to evaluate soil pollution in the downstream area of a landfill, North of Iran, in relation to changes in soil chemical characteristics and heavy metals concentrations. Soil samples were analyzed for Cd, Ni, Pb, Fe and Mn using AAS. It was observed that the selected metal levels in soil varied with depth. Iron and Manganese levels in shallower depths were higher than in deeper depth. Lead, Cadmium and Nickel showed fluctuations in all the three sites. The main factor for these variations was due to the kind of organic compounds whose composition varied with depth. These compounds had the ability to stabilize these elements in soil (Shirdast*et al*., 2010).

Heavy metal transfer in soil profiles is a major environmental concern because even slow transport through the soil may eventually lead to deterioration of groundwater quality. In a study to determine variation of levels of Cd and Cu with depth, soil samples in sludge and wastewater irrigation were collected in the soil profiles from the surface to 100 cm. Cadmium accumulated in soil surface layers and had low vertical movement with much of Cd being found in topsoil that was 0-20 cm depth with a concentration of 4.5 mg/kg. Concentration of Cd, however, decreased after 20 cm. Most Cu was obtained in top soil

27.76 mg/kg and similarly decreased with depth. Heavy metals remained in topsoil layer which is a result of chemical reaction between heavy metals and organic matter and firm bounds with these components (Behbahaninia *et al*., 2008).

From a study done by Bada and Olarinre (2012) to characterize soils and determine metal content in oil - spilled sites in Nigeria; it was reported that soil pH increased with distance from the epicenter of spillage, higher heavy metal levels were obtained in the soil very close to the source of pollution and this decreased with soil depth. The higher metal content was likely to be due to proximity to the source of pollution and reduced leaching due to increased alkalinity.

From a study done to examine seasonal variations in heavy metal status of the Calabar River in Nigeria, Ewa *et al.* (2013) reported that the wet season had higher levels than the dry season, attributing the increase to mineral weathering and runoff from oil industries, agricultural inputs and residential land-uses. The sequence of metal levels was Mn>Pb> Cu > Zn > Fe during both seasons probably because Mn was more soluble in the river water. Furthermore, in a study conducted to investigate the impact of mining and agriculture on heavy metal levels in environmental samples in Nigeria, soil samples from the dry and rainy seasons were analyzed for Cd, Cu, Pb and Zn. The levels of these metals were higher during the rainy season compared to the dry season due to factors like rainfall distribution, erosion, soil drainage, redox potential, texture and organic matter and clay content of soil. The rainy season having higher metal levels could be due to topography of the farm, differences in the individual metal solubility, non-equilibrium distribution of water and microbial mediated processes (Omono & Kakulu, 2012).

Delbari and Kulkarni (2011) investigated the effects of seasonal variations on concentrations of heavy metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in agricultural soil in Iran during the rainy and dry seasons. From their study, Zn, Cr, Pb, Cu and Ni had higher levels during the rainy season while Mn and Fe had higher levels during the dry season. The differences in levels of Fe between the two seasons were insignificant. The levels of Cd remained unchanged during both seasons. Metals bind differently to various soil types and the binding ability could be enhanced or depressed or be unaffected during the wet season. This explains why the levels of some metals were higher during the rainy season, some were higher during the dry season while some remained constant.Olubunmi and Olanipekun (2010) evaluated the status of heavy metal pollution of soil and plants around the Bitumen deposit area in Nigeria during the rainy and dry seasons. They reported that the wet season had higher metal levels than the dry season. Runoff water is capable of removing and mobilizing metals from soil hence the higher metal levels during the rainy season than the dry season. The decreasing order of metal levels was Fe > Zn > Ni > Cu > Cd. Iron binds less firmly to soil compared to Zn, Ni, Cu and Cd justifying why run-off water mobilized Fe more than other elements from the Bitumen deposit area.

Achudume and Olawale (2009) investigated the variations in Fe, Pb, Cd, Cr and Cu concentrations in plants and soil from a waste dumping site in Nigeria during the dry and wet seasons. Generally, higher values were noted in the wet season than in dry season. There were significant variations in the concentrations of various metals at different sites, perhaps due to differences in land gradient. The order of metal levels was Fe > Cd > Cr

>Pb> Cu during both seasons. The slope of land could enhance faster erosion of metals down from the waste dumping site.

A study was done to assess the effect of seasonal variations on the concentration of heavy metals Pb, Cd, Zn, Ni, Cr, Cu, Co, V and Hg along two main roads in Saudi Arabia. From their findings, the wet season had higher levels than the dry season. This could be due to increase in pH and organic matter content in the rainy season compared to the dry season. The pH value of soil samples was alkaline and the organic matter content was higher in the rainy relative to the dry season. The elevated pH values were probably due to hydrolysis reaction between water and calcium carbonate derived from the upper cretaceous rocks. Hydrolysis yields hydroxyl ions (OH^-) leading to pH increase hence increasing the ability of soil to adsorb and fix these elements. The order of concentration was Zn > Cr > Ni > V >Pb> Cd> Co > Cu > Hg (Odat & Alshammari, 2011).

MATERIALS AND METHODS

Sample Area and Sampling

This study was done near the Kenya Pipeline Company, Eldoret. Eldoret town is located in Uasin Gishu County in the Western region of Kenya and borders Kakamega and Trans Nzoia counties to the west, Nandi County to the south and ElgeyoMarakwet and Nakuru counties to the east. It experiences two rainy seasons, namely long and short rains. Long rains start from March to May. The short rains start in August and end in October. The dry spell starts from December to February. Figure 1 presents a map of Uasin Gishu County in Kenya where the study was done, whereas Fig. 1.2 represents the location of the four (4) sampling sites. The control point, site one (S_1) was 50 metres from experimental sites 2, 3 and 4. The experimental sites S_2, S_3 and S_4 were 20 metres apart.

Research Design

The study used an experimental approach which involved determination of levels of Pb, Ni, Cd, Cu, Fe and Zn in both petroleum contaminated and uncontaminated sites by comparing the effect of spillage on metal levels, effect of depth variation on metal concentrations and the effect of seasonal variation on the levels of these selected elements.

Sample Preparation and Wet Digestion

Soil samples were collected from four (4) different sites 1, 2, 3 and 4 within the same geographical area. A total of forty samples were collected in polyethylene bags. Soils from all the four sites were sampled at 15 cm depth intervals 0-15, 15-30, 30-45, 45-60 and finally 60 - 75 cm using a soil auger. Sampling was carried out during the dry and wet season. Twenty (20) samples were collected during the dry season while another twenty were collected during the wet season. Because of no petroleum contamination, site one (S_1) was taken as the control site.

The Okalebo *et al*. (2002) digestion procedure was used for total metal determination in soils. Stones and plant fragments in the soil samples were removed by passing the samples through a < 0.2 mm sieve. Soils were crushed to fine powder using mortar and pestle. Afterwards, the soil sampleswere then oven dried at 70 ˚C overnight. A 0.3 g of dried samples was transferred into a clean, dry digestion tubes. A 2.5 mL of fresh digestion mixture (3.2 g salicylic acid in 100 ml of Se powder/ H_2SO_4 mixture) was added to each tube and also reagent blanks for each sample. Digestion was then done at 110 ˚C for 1 hour. The digest was then removed, cooled and three successive portions of 1 mL H_2O_2 added. The temperature was raised to 330 ˚C with continued heating. The contents were allowed to cool and 25 mL distilled water added. The contents were thoroughly mixed and finally made to 50 mL with de- ionized water. Determination of Cd, Zn, Fe, Cu, Ni and Pb in the extracts was performed by FAAS at the Kenya Government Chemist in Nairobi. The linear range of FAAS was between 0 - 5 ppm.

RESULTS AND DISCUSSIONS

Table 1. Heavy metal levels in four sites during the dry and wet season

Site	Season	Depth (cm)	Pb (ppm)	Ni (ppm)	Zn (ppm)	Cu (ppm)	Cd (ppm)	Fe (ppm)
1	Dry	0-15	.0000	.2293	.3079	.0818	.0000	.5731
		15-30	.0000	.0491	.2808	.0514	.0000	.0882
		30-45	.1956	.3222	.3460	.0076	.0000	.0000
		45-60	.0450	.0000	.3007	.1046	.0992	.0294
		60-75	.2713	.5461	.4782	.0590	.0108	.0735
1	Wet	0-15	.1956	.1529	.4492	.0456	.0000	1.9693
		15-30	.0000	.2348	.5072	.0380	.0090	1.5945
		30-45	.1202	.4150	.4782	.0932	.0000	3.9532
		45-60	.0901	.2130	.5489	.0152	.0000	2.2926
		60-75	.0000	.0874	.3478	.0628	.0000	3.3140
2	Dry	0-15	.4234	.1474	.2500	.0590	.0000	.2719
		15-30	.3624	.0000	.4637	.0913	.0000	.3894
		30-45	.0000	.0000	.2953	.0228	.0000	.0000
		45-60	.0000	.0000	.5271	.0609	.0000	.1396
		60-75	.0000	.2348	.2753	.1141	.0000	.4556
2	Wet	0-15	.6533	.3659	.7191	.1176	.0000	.0000
		15-30	.4692	.5515	.3804	.1008	.0000	3.6373
		30-45	.0000	.9884	.5634	.1217	.0000	4.8277
		45-60	.0000	.2621	.3424	.0780	.0072	2.9319
		60-75	.0000	.4150	.8188	.1160	.0992	3.1970
3	Dry	0-15	.3320	.4205	.3442	.0285	.0000	.0000
		15-30	.0000	.0218	.3333	.0533	.0000	.3747
		30-45	.0000	.3386	.4402	.0742	.0000	.1249
		45-60	.0000	.0273	.7988	.0742	.0000	.1690
		60-75	.3624	.0382	.4673	.0304	.0000	.1029
3	Wet	0-15	.0000	.3877	.6757	.1408	.0307	3.5638
		15-30	.4386	.0000	.6865	.0856	.0000	3.2846
		30-45	.0150	.5679	.5833	.0856	.0000	4.6733
		45-60	.4539	.2020	.6738	.1617	.0000	3.4095
		60-75	.1051	.6990	.6213	.1293	.0000	3.4756
4	Dry	0-15	.0000	.0928	.2101	.0247	.0000	.1837
		15-30	.1654	.0000	.3188	.0057	.0000	.3968
		30-45	.4386	.5351	.1830	.1065	.0000	.3380

		45-60	.3624	.0382	.2319	.0000	.0000	.0073
		60-75	.4539	.6389	.3351	.1350	.0000	.0514
4	Wet	0-15	.0300	.0000	.6539	.1084	.0000	4.7248
		15-30	.4692	.1038	.6793	.1122	.0000	4.5580
		30-45	.3929	.0328	.4257	.0514	.0956	2.2191
		45-60	.0000	.1474	.4710	.0970	.0613	2.1971
		60-75	.1353	.3495	.7753	.0266	.0000	3.9973

Fig.1 depicts the metal levels in site 1 during the dry season ranging from 0 - 75 cm depth. The most abundant metal was Fe while Cd was the least abundant.

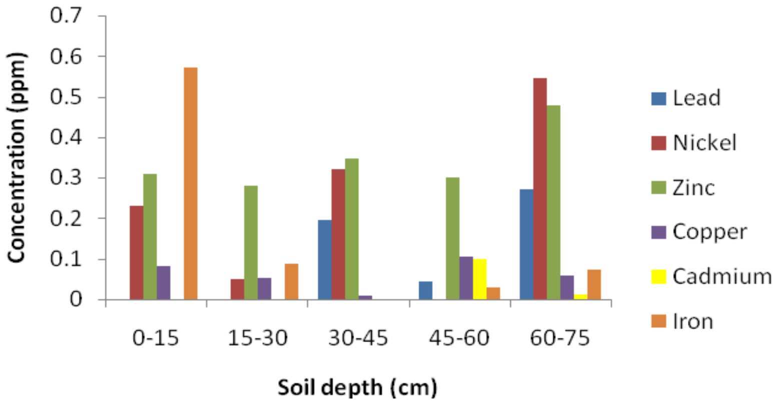

Fig 1. Actual metal levels in site 1 during dry season

Fig 2 presents metal levels in site 1 during the wet season in the range of 0 - 75 cm depth. From the Figure, Fe had highest levels whereas Cd had the least levels.

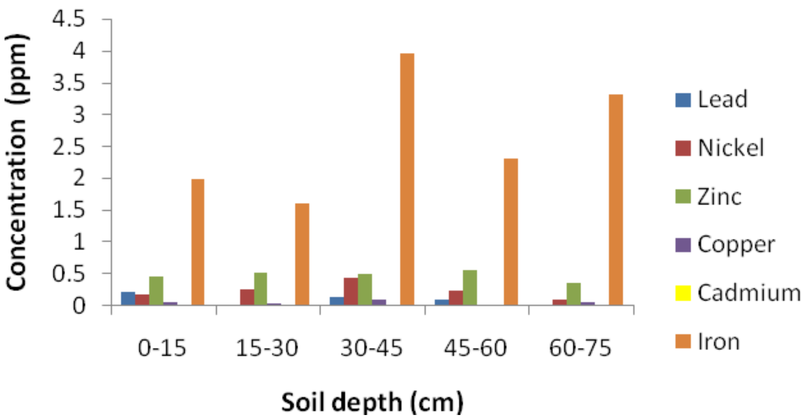

Fig 2. The actual metal levels in site 1 during the wet season

As can be observed from Figures 1 and 2, the wet season had higher metal levels than the dry season; Fe had the highest levels relative to other selected metals. Also depth 45 - 60 cm had the least metal levels compared to the top soil except for Fe. Metals complexed more effectively with the top soil more than deep soil (depth 45 - 60 cm) probably as a consequence of the top soil being richer in organic matter content than soil at 45 - 60 cm depth which acceded with Behbahaninia *et al"s* (2008) work on metal transport in soil.

Fig 3 depicts metal levels in site 2 during the dry season ranging from 0 - 75 cm depth. The most abundant metal was Zn while Cd was the least abundant. Also shallower soil had higher composition of Pb relative to the deeper soil.

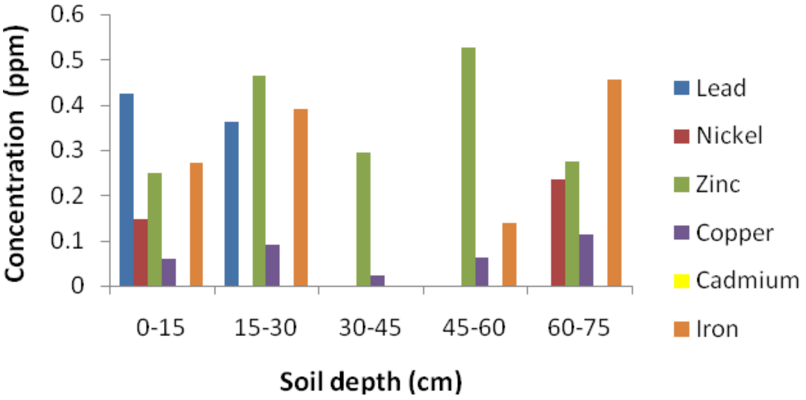

Fig 3. Actual metal levels for site 2 during the dry season

Metal levels at site 2 during the wet season are presented in Fig.4. As can be observed in Fig. 3 levels of Zn decreased relative to the dry season probably due to Zn being washed away by run - off water in the wet season.

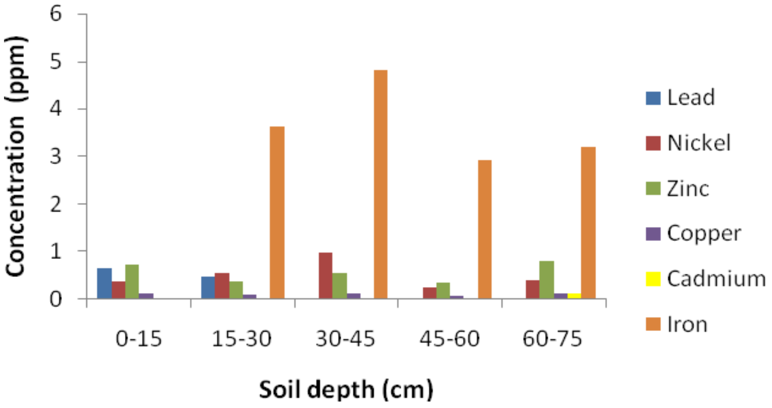

Fig 4. The actual metal levels for site 2 during the wet season

Fig.5 depicts the actual metal levels in site 3 during the dry season ranging from 0 - 75 cm depth. The most abundant metal was Zn while Cd was the least abundant. Nickel levels were also higher in site 3 relative to the other sites.

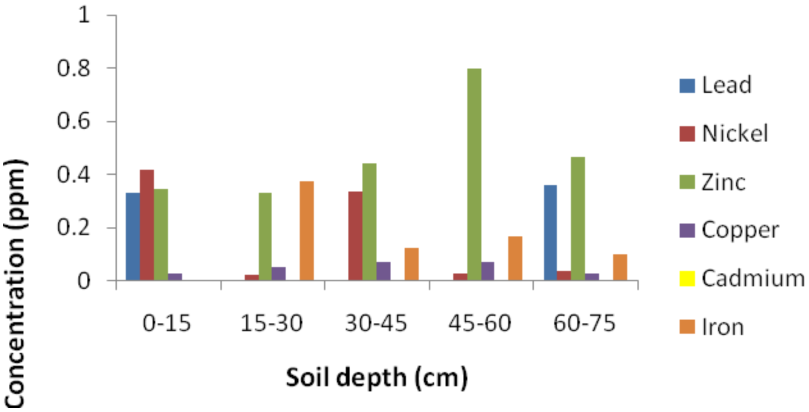

Fig 5. The actual metal levels in site 3 during the dry season

Metal levels at site 3 during the wet season are presented in Fig.6. Levels of Fe in the wet season increased relative to the dry season, whereas, Zn levels remained fairly constant. Rainfall could have increased the rates of formation of organic matter and also led to hydrolysis of carbonates resulting into elevation of pH. Increased pH favoured Fe retention capacity of soil hence concurred with Odat and Alshammari (2011) findings.

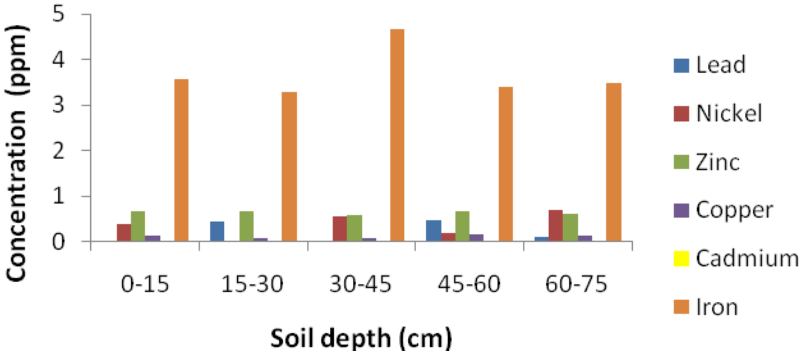

Fig 6. Actual metal levels for site 3 during the wet season

Fig.7 depicts the metal levels in site 4 during the dry season ranging from 0 - 75 cm depth. The levels of Pb were highest at this site relative to the other three sites, probably due to more petroleum spillage. At lower depths, Ni had highest levels relative to the other five selected metals.

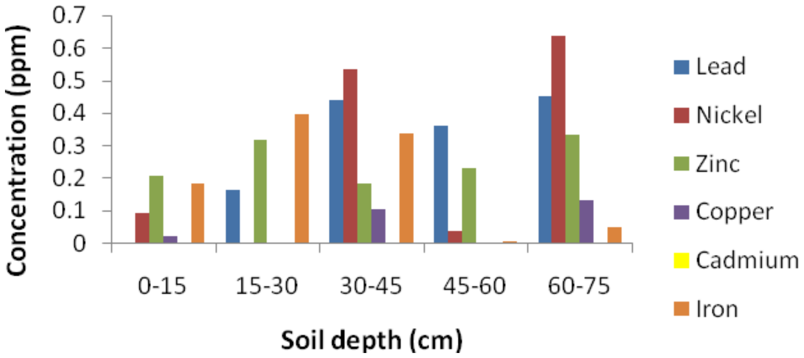

Fig 7. The actual metal levels for site 4 during the dry season

As for Fig 8, the metal levels in site 4 during the wet season ranging from 0 - 75 cm depth are presented. Here, the levels of Fe were higher relative to its dry season. Zinc levels decreased when compared to the dry season. At deeper depth, Ni had higher levels relative to the shallower depth.

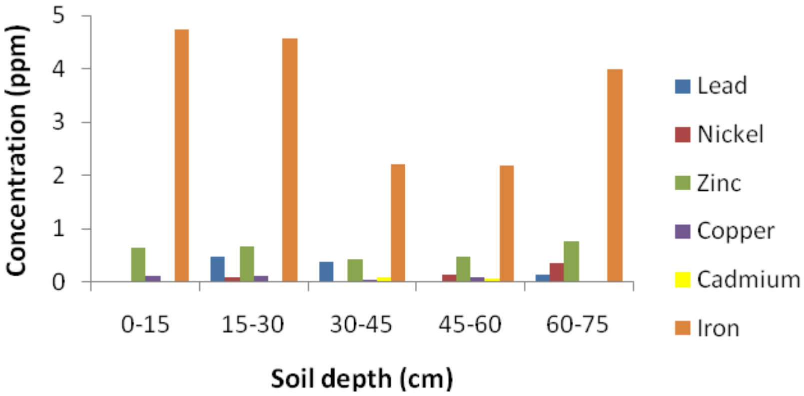

Fig 8. The actual metal levels for site 4 during the wet season

Table 2. The metal in petroleum standards by the COQG in ppm

	Pb	Zn	Ni	Cu	Cd	Fe
Acceptable mean levels	0.13	2 .00	5.70	None	0.10	7.00
Site 1 mean levels - Dry	0.10	0.34	0.23	0.06	0.02	0.15
Site 1 mean levels - Wet	0.08	0.47	0.22	0.05	0.00	2.26
Site 1 Mean levels	0.09	0.40	0.23	0.06	0.01	1.21
Site 2 mean levels - Dry	0.16	0.36	0.08	0.07	0.00	0.25
Site 2 mean levels - Wet	0.22	0.56	0.52	0.11	0.02	2.92
Site 2 Mean levels	0.19	0.46	0.30	0.09	0.01	1.59

Site 3 mean levels - Dry	0.14	0.48	0.17	0.05	0.00	0.15
Site 3 mean levels - Wet	0.20	0.65	0.37	0.12	0.01	3.68
Site 3 Mean levels	0.17	0.56	0.27	0.09	0.00	1.92
Site 4 mean levels - Dry	0.28	0.26	0.26	0.05	0.00	0.20
Site 4 mean levels - Wet	0.21	0.60	0.13	0.08	0.03	3.54
Site 4 Mean levels	0.24	0.43	0.19	0.07	0.02	1.87

From Table 2 Pb (0.13 ppm), Zn (2.00 ppm), Ni (5.70 ppm), Cu (none), Cd (0.10 ppm) and Fe (7.00 ppm) are the acceptable mean levels. Lead exceeded COQG permissible mean level of 0.13 ppm at sites 2, 3 and 4 while other elements were within the acceptable range.

It is evident that site 4 had the highest mean level of Pb ranging from 0.21 ppm (dry season) to 0.24 ppm (wet season). The mean concentration levels were higher in comparison with the acceptable level of 0.13 ppm. On average the mean Pb levels increased at site 1 from mean levels of 0.08 ppm in wet season to mean levels of 0.28 ppm in site 4 during the dry season. Large amounts of oil spillage, the type of soil and soil pH in site 4 could have led to higher levels of Pb relative to site 1.

For Zn, the mean levels were below the acceptable limit of 2.00 ppm. The mean levels ranged from 0.26 ppm (site 4 dry) to 0.65 ppm (site 3 wet). It can therefore be inferred that the mean Zinc values increased from the dry season to the wet season since oil spillage slows down the transport of metals by run offs (Bada & Olanrire, 2012). The mean values for Ni were, however, below the acceptable limit of 5.70 ppm with site 2 having the lowest level of 0.08 ppm during the dry season whereas the wet season had the highest value of 0.52 ppm. This could be because Ni is readily hydrated and binds less firmly to soil.

For Pb, there was a correlation between the mean levels for the four sites. Sites 1 and 4, respectively, had mean levels decreasing from highest of 0.23 ppm and 0.26 ppm in the dry season to lowest of 0.22 ppm and 0.13 ppm, respectively, in the wet season. On the other hand, the mean levels tended to increase from the dry season to wet season in sites 2 and 3. Proximity of sites 1 and 4 to each other could have resulted in the two sites experiencing similar anthropogenic activities. Alternatively, the two sites could be having the same soil composition. The same scenario could be true for soils in sites 2 and 3.

The lowest mean value of Cu was 0.05 ppm in site 1 during wet season with the highest mean level being 0.12 ppm in site 3 during the wet season. In general, the mean levels had a small variance as can be seen from the difference between the lowest and highest value which was less than 0.07 ppm. For Cd, the highest mean level was in site 4 during the wet season of 0.03 ppm. The Cd levels were, however, much below the maximum acceptable level of 0.10 ppm. Cadmium binds firmly to soil more than the other selected metals and this explains why Cd levels were comparatively lower for all the sites and this was supported by ATSDR (2004). All the sites showed that the mean levels for Fe were higher during the wet season than dry season. The highest mean level was found in site 1 with a value of 2.26 ppm while the lowest being in site 3 of 0.15 ppm. The metal levels were, however, below the acceptable value of 7.00 ppm.

Two-Sample t-tests for Impact of Seasonal Variations on Metal Levels

The mean of Pb samples from the wet season had higher levels in ppm (mean = 0.18, standard error of mean = 0.04797), relative to the dry season (mean = 0.17, standard error of mean = 0.04107). Statistically the difference in mean Pb levels between the seasons was insignificant with t(38) = 0.12, p=0.451, r = 0.0195. This observation agreed with Omono and Kakulu (2012) and Ewa *et al.* (2013) who reported that Pb in the wet season was higher than the Pb levels in the dry season and equally the seasonal difference was less significant in their findings.

On average, Ni samples from the wet season had higher concentration (mean = 0.31, standard error =0.05644), than those of dry season (mean = 0.18, standard error = 0.04745) as evidenced from the two sample t -test appendices and the seasonal difference was statistically significant t (38) = 1.69, p = 0.049, r = 0.264. This concurred with the results of Delbari and Kulkarni (2011) and Odat and Alshammari (2011) findings that reported Ni levels during rainy season exceeded those in the dry season, nonetheless, the mean differences were significant from their observations.

Zinc samples from the wet season had higher levels on average (mean = 0.57, standard error = 0.03157), than those of dry season (mean= 0.36, standard error = 0.03132). The difference between the wet and dry season was significant t (38) = 4.74, p = 0.001, r = 0.372. These findings concurred with Odat and Alshammari (2011) and Delbari and Kulkarni (2011) who reported significantly higher mean levels of Zn in the wet season relative to the dry season.

Copper samples from the wet season had higher concentration (mean = 0.09, standard error = 0.008798), than those of dry season (mean = 0.06, standard error = 0.008655). The difference was significant t (38) = 2.44, p=0.01, r = 0.136. These results are supported by those reported by Odat and Alshammari (2011) and Delbari and Kulkarni (2011) that Cu in the rainy season was higher than in the dry season.

Cadmium samples from the wet season had higher concentration (mean = 0.02, standard error = 0.007112), than those of dry season (mean = 0.01, standard error = 0.004961). The relative mean level differences between dry and wet season was statistically less significant t (38) = 1.11, p= 0.136, r = 0.032. These findings agreed with those reported by Omono and Kakulu (2012) and Achudume and Olawale (2009) who asserted that Cd in the rainy season was insignificantly higher than the dry season. They reported higher values of Cd than the findings in this study.

As for Fe, samples from the wet season had higher concentration (mean = 3.19, standard error = 3.318), than those of dry season (mean = 0.19, standard error = 0.039). The difference was significant t(38) = 1.90, p = 0.033, r = 0.087. These conformed with Odat and Alshammari (2011) and Delbari and Kulkarni (2011) who established that Fe in the rainy season was significantly higher than in the dry season.

From the two - sample t - test, all the selected metals from the wet season had higher mean levels than the dry season. This is attributable to rainfall that could have increased the organic matter content and the soil pH during the wet season. Odat and Alshammari

(2011) deciphered that increased alkalinity and organic matter content improves metal retention ability of soils.

At the same time, metals bind differently to various soil types and the binding ability could be enhanced in presence of water if the soil is rich in clay content. This justifies why the levels of metals were higher during the rainy season (Delbari & Kulkarni, 2011). Further to the above explanations, a number of factors generally affect the metal sorption abilities on soils. Among these are: rainfall distribution, erosion, soil drainage, redox potential, texture and organic matter and clay content. Increased rainfall could enhance microbial - mediated processes like decomposition of biological matter leading to increased organic content. Organic matter formed is a good adsorbent for metals in soil (Omono & Kakulu, 2012).

One Way ANOVA for Depth

From one way ANOVA [F(4, 35) = 0.43, *p* = 0.7827] for Pb, that is, variation along different depths decreased though the effect of decreasing Pb levels was less significant. This was in agreement with Aniket (2011) findings that levels of Cr, Zn, Co, Ni, Ba, Al, Cu, Mo, B, Pb, Cd, Sr decreased with depth and similarly the decrease was less significant.

When subjected to the same statistical treatment, Zn levels increased with depth albeit the increase with depth was not statistically significant [*F*(4,35) = 0.51, *p* = 0.7263]. These results did not agree with Carroll *et al*. (2002) and Chunhacherdchai *et al*., (2011) findings, they established that the levels Zn decreased with depth of soil. The difference could be due to the nature of organic matter present at deeper soil that complexed more effectively with Zn than at the shallower soil (Shirdast *et al*., 2010).

Unlike Pb and Zn, one way ANOVA statistic infers a significant effect of variation of Ni levels with depth [*F*(4,35) = 3.83, *p* = 0.0109]. Nickel levels significantly increased with depth implying that Ni was less firmly bound to soil and thus ground water could be at great risk of Ni contamination in the study area. These results acceded with Chunhacherdchai *et al*., (2011) findings that at deeper depth, levels of As, Ag and Ni were higher than at shallower depths. Evidenced by one way ANOVA [F*(*4, 35) = 0.14, *p* = 0.9641], the levels of Cu did not significantly vary with depth because Cu binds firmly to soil, nonetheless, these findings disagreed with those reported by Behbahaninia *et al*., (2008). Olubunmi and Olanipekun (2010) affirmed that Copper binds firmly to soil and has little vertical movements in soil.

There was no statistically significant differences between the Cd levels at different depths ANOVA [*F*(4,35) = 0.68, *p* = 0.6076]. Cadmium prefers to bind to top most soils with insignificant vertical movements to deeper soil. This concurred with Ogboi (2012) who obtained higher Cd levels than the findings in this study. From one way ANOVA [F*(*4, 35) = 0.36, *p* = 0.8330], decrease in Fe levels with depth was statistically insignificant. This was in agreement with Shirdast *et al*. (2010) findings that levels of Fe and Mn levels in shallower depth were higher than in deeper depth.

One-Way Analysis of Variance for Metals at Different Sites

Although differences in levels existed for Pb at different sites, these differences were not statistically significant as evidenced from one-way ANOVA [$F(3,36) = 0.71$, $p = 0.5509$]. This could be due to sites having similar chemical composition and thus same abilities of stabilizing metals in soil Onojake and Okonkwo (2011) in Nigeria.

There was statistically insignificant differences between the Zn levels in the samples collected from the different sites ($F(3,36) = 1.45$, $p = 0.2442$). The levels of Zn in the control site were relatively lower than the experimental sites. When subjected to the same statistical method, differences between Ni levels from sites 1 to 4 were insignificant ($F(3,36) = 0.38$, $p = 0.7656$) since the sites were in the same locality thus their soils could be similar. The levels of Cu in the control site were relatively lower than the experimental sites. Differences between the levels from sites 1 to 4 were not statistically significant ($F(3,36) = 0.94$, $p = 0.4309$). As a consequence of the sites being in the same geographical area, their soils could be similar at metal retention. These results are backed up by the findings of Essiett *et al*. (2010) in Nigeria.

Cadmium was below detection for most sites. There was no statistically significant difference between the Cd samples collected from the different sites as determined by one-way ANOVA ($F(3,36) = 0.47$, $p = 0.7056$). The sites could be having identical soil composition which permitted almost equal movement of Cd. The levels of Fe at the control site were relatively lower than the experimental sites. Differences between Fe levels from site to site were, however, statistically insignificant ($F(3,36) = 0.92$, $p = 0.4415$). Soils are usually rich in Fe which is the second most abundant element on earth. Oil spillage didn‘t significantly increase the Fe levels in soil (Sheffer, 2005).

Comparison of Metal Levels with COQG Permissible Limits

In this section, the actual metal levels are compared relative to the Crude Oil Quality Group (2004) allowable limits. The essence of comparison is to assess whether the quality of petroleum products is threatened by the presence of higher metal levels. Table 2 presents a comparison between the actual metal levels relative to the COQG permissible levels. As observed in Table 2, the actual and the mean metal levels for sites 1 to 4 are closer to the acceptable metal standards by the COQG (2004) in ppm.

Correlation Coefficient for Effect of Petroleum Spillage on Metal Levels

There existed a significantly positive correlation between mean metal levels and petroleum spillage. In terms of metals, Pb mean levels impacted on Ni with $r = 0.67$, $p = 0.012$. This shows that the levels of Pb and Ni were co-determined implying that petroleum spillage which could have contributed to increased levels of Pb in soils and hence could have led to increased Ni levels in soil. The Zn mean levels impacted on the Cu mean levels, $r = 0.73$, $p = 0.006$. To the same extent, Ni and Cu mean levels were co-determined with $r = 0.69$, $p = 0.009$. The same scenario applies to Ni and Cu or Cu and Zn. This therefore implies that the mean levels of Ni and Pb, Zn and Cu, Ni and Cu were linearly interdependent and petroleum spillage could have contributed to their increased levels in soil. This was in consonance with Agbogidi and Eruotor (2012), Radulescu *et* *al*. (2012), Onojake and Okonkwo (2011), Essiett *et al*. (2010) and Vasquez-Duhalt (1989) who reported that petroleum spillage increased metal levels in soils. Agbogidi and Eruotor (2012) affirmed that metal pollutants accumulate with time in areas of petroleum spillage leading to higher mean levels at petroleum contaminated plots relative to uncontaminated sites. Vasquez-Duhalt (1989) averred that Pb, Zn, Cu, Cd and Ni are among the elements added to petroleum to modify its properties and therefore petroleum spillage increases metal levels in soils.

CONCLUSIONS

The results of the study showed that there was contamination of soil by the metal pollutants in the four sites. There was strong positive correlation between metal levels and petroleum spillage implying that petroleum contains metal pollutants. Virtually the mean levels for experimental sites S_2,S_3 and S_4 were higher than the control site (S_1) implying that petroleum spillage increased levels of metal pollutants in soil. There were differences in metal levels from site to site, the differences were, nonetheless, statistically insignificant. Cadmium was not detected for most of the sites.

The study showed that the levels of Pb and Fe decreased with depth while levels of Ni and Zn increased with depth. The downward movement of Ni was statistically significant and could contaminate ground water in the area. Copper was less mobile with limited variation of Cu levels with depth signifying firm binding on soil.

The mean levels of Pb at S_2, S_3 and S_4 exceeded the standards set by the crude oil quality group of 0.13 ppm, whereas levels of Fe, Zn, Cd and Ni were within the acceptable thresholds. Metal pollution surged up during seasonal change from dry to wet season. The levels of Zn were highest during the dry season relative to other metals determined. The increased levels of metals during the wet season could be as a result of increased soil pH and rates of formation of organic matter due to rainfall and petroleum spillage.

RECOMMENDATIONS

A preventive approach should be employed through regular assessment of Pb enrichment of the petroleum fuels in Kenya. Even though from the study Zn, Cd, Ni and Fe were within the acceptable levels, continuous discharge of contaminated petroleum oil to soil may lead to accumulation of these metal pollutants. There is need for thorough pre-treatment of petroleum products to minimize the levels of toxic metals before releasing them for use.

The effect of soil types on adsorption of metals should be studied to understand which soil types promote faster transfer of pollutants within soil strata and even to plants growing on them. Other pollutants originating from petroleum oil like SO_2, benzene, toluene, chlorinated hydrocarbon and metal species should also be investigated as their movement and accumulation in air is potent to health and could even impact the climate. Comparisons should also be made between metal levels in used oil and unused oil in order to compare the elements present in both. These comparisons should aid in understanding the significance of automobile wear and tear on soil pollution.

Since most metals accumulated in the top soil and some in the deeper soils, studies should be done on the metal retention and release by different contents of organic matter in soil. Organic matter should also be amended to make sorbents for remediation of metal polluted soils.

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BIO-DATA

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