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Heavy Metals Levels in Forage Grasses, Leachate and Lactating Cows Reared around Lead Slag Dumpsites in Nigeria

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ABSTRACT:A field study was conducted around Pb slag contaminated sites in Ibadan, Nigeria to assess the intake of trace metals by cows reared around the contaminated sites as indication of heavy metals contamination. Levels of Pb, Cd, Cu and Zn in blood, milk and faeces were determined in 20 cows exposed to the sites and 20 reference cows from uncontaminated areas. Chemical analysis of pasture grasses and leachate from the contaminated sites showed high levels of Pb. Range and mean levels of Pb, Cd, Cu and Zn in the forage grasses are: 209-899 (425 ± 79.0), ND-1.87 (0.94 ± 0.23), 4.01-8.78 (6.26 ± 0.62) and 17.4-202 (79.2 ± 23.5) mg/kg respectively. The mean values of 8.81±0.06, 0.041±0.003, 0.20±0.01 and 1.00±0.004 mg/L were obtained l for leachate Pb, Cd, Cu and Zn. Difference in blood and milk Pb was highly significant ($p<0.01$) between the two groups of animals. Mean, median and range blood Pb concentration of 349±82.0, 312, <DL-1380μg/L, milk Pb concentrations of 347 ± 144, 313, <DL-630μg/L and faecal Pb concentrations of 2.08 ± 1.46, 2.00, 0.25-6.75 mg/kg were found in test animals whereas Pb was not detected in the tissues of the control animals. Analyses of blood, milk and faeces were found to be good indicators of environmental exposure to Pb. Test cows accumulated significantly higher levels of Zn in milk than in blood. Reverse is the case for Pb and Cu. The high concentration of Pb detected in both environmental and biological samples implies the need for sound management of hazardous waste.

Key words: Lead slag, Heavy metals, Lactating cows, Forage grasses, Leachate

INTRODUCTION

Slag is a solid waste produced as by-product during metallurgical processes. An example of slag is solid waste emanating from production of lead for auto battery manufacturing. Huge amount of this waste generally accompanies production of automobile battery either from primary or secondary sources. The slag apart from being contaminated with Pb, has been reported to contain other elements such as As, Ag, Au, Ba, Bi, Cd, Cr, Co, Cu, Mo, Ni, Sb, Se, Te, V, Zn, B, Br, Cl, K, Na, Mg, Sn, Nd, Zr, Br and Rb either as by-products or co-products (Saikia *et al.,* 2008; Ettler *et al.,* 2004). The slag, if dumped openly can lead to emission of Pb and other toxic heavy metals by the agents of wind and rain, thereby contaminating soil, plant, surface and groundwater with resultant negative effects living organisms.

Inorganic pollution and its consequent adverse effects on organisms have been widely studied all around the world (Ekmekyapar *et al.,* 2012; Mhadhbi *et al.,* 2012; Nasrabadi *et al.,* 2010; Davis *et al.,* 2012; Okuku and Peter, 2012; Ghaderi *et al.,* 2012).

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Contamination of animals reared in the vicinity of metallurgical processing industries with toxic metals such as lead (Pb) and cadmium (Cd) and trace elements like copper (Cu) and zinc (Zn) have been reported (Smith *et al.,* 2010; Patra *et al.,* 2008; Swarup *et al.,* 2005; 2006; Palacios *et al.,* 2002). Lead and Cd have been labeled as major environmental pollutants since they are easily transferred into the food chain and they are not known with any significant biological functions. They rather produce varied harmful effects in animals and man on exposure, which may result in undesirable biochemical and physiological alterations. Plasma hormonal changes and abnormal liver function have been observed in cows that were exposed to Pb and Cd in industrial areas (Swarp *et al.,* 2007). Copper and Zn on the other hand are trace elements which are required at certain concentrations for normal metabolic processes. Copper and Zn could be toxic when ingested in excess (Bidewell and Livesey, 2002; Minervino *et al.,* 2009) and when deficient can lead to impairment of biological activities (Guyo *et al.,* 2009; Sharma *et al.,* 2005).

The slag produced by a defunct auto battery manufacturing company was indiscriminately dumped in open space in some villages in Ibadan, Nigeria. Soil and plants from one of the abandoned dumpsite have been documented to contain high levels of heavy metals especially Pb (Ogundiran and Osibanjo, 2008; 2009). Therefore, monitoring heavy metals especially Pb accumulation in animals such as cows reared around the contaminated areas is essential. The study thus aimed at assessing the intake of trace metals by cows reared around Pb slag contaminated site as indication of heavy metals contamination and the probable routes of exposure.

MATERIALS & METHODS

This research was conducted in 2010. The study areas were Lalupon and Ile-Igbon located in Lagelu local Government area of Ibadan, Oyo State. Lalupon waste dumpsite lies between latitude 7° 27' 42"N and longitude 4° 04' 10"E as shown in the location map Fig. 1 and has a population of about 10,000 people. The residential area is some meters away from the dump site. The dump site is characterised with plants averagely growing in the vicinity of the slag and leachate especially during wet season. Ile-Igbon contaminated site on the other hand lies on latitude of 7° 28' 47" N and longitude of 4° 04' 39"E. It is a rural agricultural settlement with population of over 300 persons. The site consists of broken glasses, battery slag, battery scraps, poultry waste, saw dust and ashes. The site is occupied by some plants species while residential areas are located at close distances from the slag. Leachate is found on the site especially during the wet season. Bodija cattle ranch was used as control site. Bodija market chosen as the control site is a commercial area which housed an abattoir. The abattoir within the market is located on the latitude 7^{o} 26^{1} 03^{11} N and longitude 3^{0} 54^{1} 58^{11} E. The animals sold at this market were mainly from northern parts of the country and were believed to be free from contamination.

The research was carried out with twenty lactating cows that grazed at the auto battery slag dumpsites and twenty control lactating cows from Bodija cattle market. The sampling sites and the geographical locations of the sampling areas are shown in Fig. 1 and Table 1respectively. All the sampled cows were from small private ranch most of which have spent their lifetime in the studied areas. Herd of cattle rearing around the contaminated sites have free access to the sites and are known to regularly drink leachate from the waste during wet season and graze on the foraging grasses which grow naturally on the sites. Samples of foraging plants, leachate and feed were collected and analysed heavy metal levels in order to evaluate possible transfer of heavy metals from plant, feed, and leachate present on the site to the grazing animals.

In 2010, blood and milk were sampled from cows from the studied areas and from control cows before slaughtering with the aid of Veterinary doctors. Blood sample was collected by venipuncture, using syringe and needles into acid- treated polyethylene bottles that contain Ethylene Diamine TetraAcetic acid (EDTA) as anticoagulant. The milking of the cow was carefully done into sterile polyethylene bottles during the early hours after discarding the first few drops of milk. Samples were kept frozen until analyses. Aboveground faeces from a particular cow from which milk and blood samples were obtained were carefully collected into polyethylene bottles pre-washed with nitric acid using hand glove, avoiding reaching the soil surface. Four pooled samples of different species of above-ground foraging grasses were collected from the contaminated sites into polyethylene bags. The grasses eaten by the cattle were selected based on their availability on the contaminated sites. They were identified at Botany Department Herbarium Unit University of Ibadan, Nigeria, thereafter, the samples washed under running tap to remove adhered soils. Feed samples given to the animals at the cattle market before slaughtering were collected individually from various points in polyethylene bags and bulked to make one sample. The faeces, plant and feed samples were oven dried for 48 hrs at 80^{o}C and milled to < 2mm. Ingestion of heavy metals by the animals through drinking of contaminated leachate was also investigated by analysing pooled leachate sample collected in an acid-treated polyethylene bottles from the sites.

Table 1. Geographical coordinates of sampling points

Study Location	Sampling Location	Latitude	Longitude
Ile-Igbon	Leachate Sample	7° 29' 00"	4° 04' 50"
Ile-Igbon	Plant Sample	7° 28' 46"	4° 04' 47"
Ile-Igbon	Cattle farm	7° 28' 34"	4° 04' 40"
Lalupon	Plant Sample	7° 27' 25"	4° 04' 24"
Lalupon	Leachate Sample	7° 27' 16"	4° 04' 08"
Lalupon	Cattle farm	7° 27' 19"	4° 04' 17"
Bodija	Cattle ranch	7^{o}26'03"	3^{o} 54' 58"

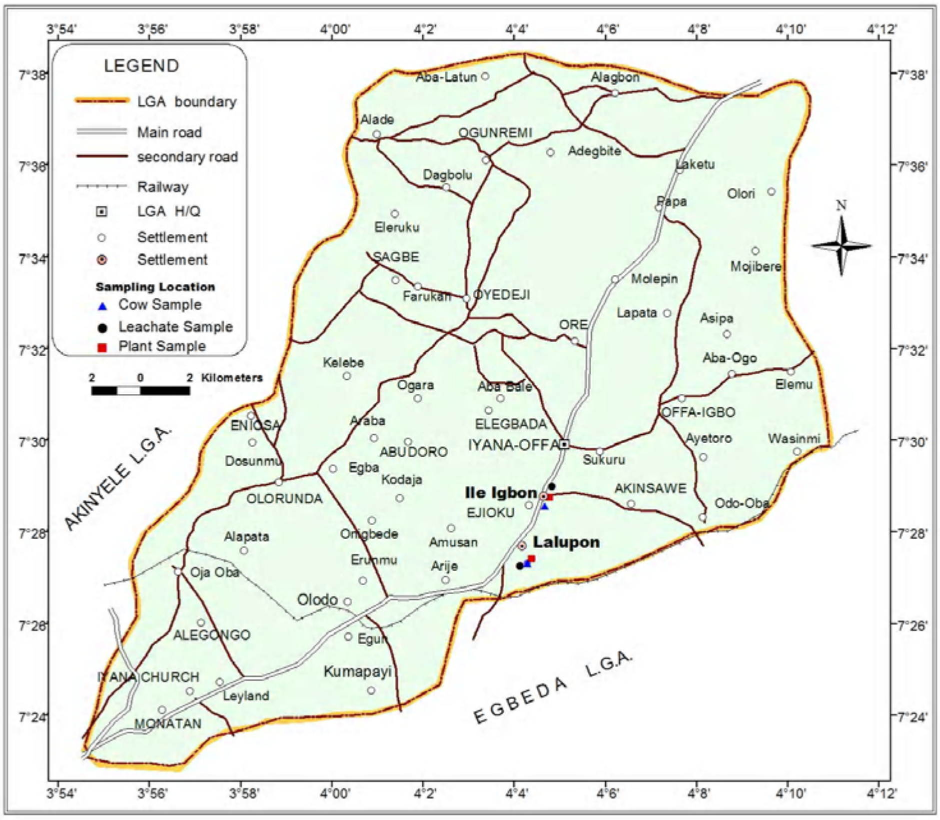

Fig. 1. Location map of Ibadan showing the sampling sites, Lalupon and Ile Igbon

All glassware used were soaked in detergent solution overnight, rinsed thoroughly under running tap, soaked in dilute nitric acid for 24 hrs and washed thoroughly with deionised water. 10% duplicate analysis was carried out along with the digestion process as the quality control. Wet ashing procedure was chosen for the oxidation of blood, milk, faeces, plant and feed samples. The method of Ataro et al. (2008) was adopted for digestion of liquid samples. 4 mL each of thawed and homogenized whole blood, milk and leachate samples were digested using 20 mL concentrated HNO_3 (65 %) at 150°C for 30 minutes on a tectator (digestion Apparatus), until clear solution was obtained indicating the end of digestion. The digests were allowed to cool, filtered and then diluted to 25 mL in a standard flask. 2.0 g of < 2 mm fraction of oven dried faeces, plants and feed samples were digested with 20 mL of conc. HNO_3 at 200°C until clear solution was obtained. Lead, Cd, Cu and Zn concentrations in blood, milk, faeces, plants, feed and leachate were quantified by flame atomic absorption spectrophotometry (AAS) using a Buck scientific Atomic Absorption machine model 210 VAP instrument with an air-acetylene flame . The wavelength of Cd, Pb, Cu and Zn were 228.9, 283.2, 324.7, 213.9nm respectively. The values were expressed in µg/ml of blood or milk or leachate and mg/kg of faeces or plant feed. 10% duplicate analyses were carried out along with the digestion process to control the accuracy of the methods of analysis. Blind samples which are solutions of pure analytes with known concentrations were inserted into the sample digests to assess the performance of the instrumental analyses. Instrumental and procedural blanks were also analyte to indicate contamination. Accuracy and precision of the analysis were good in all cases, confirming the validity of the method used.

All the statistical analysis and calculations were done using Microsoft excel 2007. Range, arithmetic mean, standard deviation were calculated. For statistical analysis of non-detectable concentrations the value of the detection limit was assigned. The data was analyzed using Paired sample T- test to find out the statistical difference between the mean values of heavy metal concentrations in the contaminated and the control animals. Also, F- test was used to evaluate the statistical difference between the accumulation of heavy metals in blood and milk.

RESULTS & DISCUSSION

The concentration of heavy metals present in the grass samples from the two studied sites and animal feed from the control area are shown in Tables 2 and 3 respectively. The plants and the feed contained all the four heavy metals, Pb, Cd, Cu and Zn although at varied concentrations. Range and mean levels of Pb, Cd, Cu and Zn in the forage grasses are: 209-899 (425± 79.0), ND-1.87 (0.94± 0.23), 4.01-8.78 (6.26±0.62) and 17.4-202 (79.2±23.5) mg/kg respectively. In the feed from the control site, the concentrations of Pb, Cd, Cu and Zn are 1.24, 0.63, 10.5 and 25.8 mg/kg respectively. The concentrations of Pb were several folds higher in the plants from the contaminated sites than in the feeds. Furthermore, the Pb levels in the plants were higher than the recommended limits of 0.5-10 mg/kg in normal plant (Boularbah *et al.,* 2006; Kabata-Pendas and Pendas, 2001). Lead levels which range from 30-300mg/kg have been considered phytotoxic to plants. Concentrations of Cd, Cu and Zn are within the recommended limits of 0.05-2.0, 5.0-20.0 and 10-150 mg/kg respectively (Boularbah *et al.,* 2006; Charya *et al.,* 2008; Kabata-Pendas and Pendas, 2001).There is a few studies which also demonstrated contamination of forage plants by metallurgical activities. Swarup et al. (2005) reported lead concentration in fodder collected from around Pb/Zn smelter and from non-industrialized area as 29.06±11.32 µg/g and 2.08±0.22 µg/g, respectively. Radostits et al. (2000) also reported that the pasture near smelter unit contained 325 µg/g of Pb.

Lead contents in leachate samples from both the contaminated sites were high. The mean values of 8.81±0.06, 0.041±0.003, 0.20±0.01 and 1.00±0.004 mg/L were obtained in leachate for Pb, Cd, Cu and Zn. Generally, concentrations of heavy metals in leachate are usually compared with water quality standards (Oman and Junestedt, 2008). The concentrations of Cd, Cu and Zn measured in the leachate samples were below the drinking water standards while those of Pb were several folds higher than the standards (USEPA 2009, WHO, 2006) as shown in Table 3.

Animals and human get exposed to non-permissible levels f heavy metals mainly through ingestion of contaminated food and water. In order to explain the possible routes of exposure of the sample cows to heavy metals, forage grasses and natural leachates from the contaminated sites were analysed. Sporobolus pyramidalis, Imperata cylindrica, Panicum maximum, and Andropogon tectonum, were the forage grasses which occurred abundantly on the two sites. All the samples analyzed indicated high level than the normal value of Pb in plant, agreeing to gross contamination of the sites with lead. It could be observed from the results of heavy metals concentrations in forage grasses that major source of the heavy metals particularly Pb in the sample cows was ingestion of contaminated plants. Transfer of Pb to cattle through consumption of contaminated plants was also corroborated in literature (Swarup *et al.,* 2005). Leachate Pb contents are abnormally high as revealed by the water quality standards suggesting possible intake of Pb by the cows that ingest the leachate. It is important to note from the results of this work that improper disposal of metallurgical wastes could lead to contamination of forage plants and water with consequent transfer to ruminants.

Biological samples such as blood, milk, air and fingernails have been used as indicator of heavy metal contamination (Moses and Prabakaran, 2011). Milk and milk products have been linked with health benefits which stems from its components such as protein,

Table 2. Heavy metal concentrations of plant samples from the studied sites

Common name	Botanica name	Heavy metals concentrations (mg/kg)	Heavy metals concentrations (mg/kg)	
			Lalupon	Ileigbon
Antropogon Tectonium Grass	*Antropogon Tectonium*	Lead	418	209
		Zinc	44.2	39.7
		Copper	5.84	7.64
		Cadmium	1.53	1.13
Elephant Grass	*Imperata cylindrica*	Lead	521	214
		Zinc	96.3	152
		Copper	5.9	4.23
		Cadmium	1.87	ND
Sporobolus Grass	*Sporobolus pyramidalis*	Lead	479	899
		Zinc	60.9	202
		Copper	8.15	8.78
		Cadmium	0.528	1.33
Spear Grass	*Panicum maximum*	Lead	291	369
		Zinc	20.8	14.7
		Copper	5.55	4.01
		Cadmium	0.935	0.163

Table 3. The concentration of heavy metals (mg/kg) in feed from control site

Cu	Pb	Zn	Cd
10.4	1.24	25.8	0.06

vitamins, antioxidants, highly absorbable Ca, mineral among others (Bhat and Bhat, 2011). But as nutritious as milk is, the presence of toxic minerals in it can make it a potential hazard to man. Cow blood and milk were chosen as the indicator of heavy metal contamination of the sites for the following reasons. Firstly, research has been conducted on soil and plants from the sites to evaluate the impacts of the slag on the environment (Oguniran and Osibanjo, 2008, 2009). Hitherto, no research has been reported on heavy metal status of the animals that are reared around these sites. Analysis of blood was employed to estimate exposure and potential health problems for grazing livestock. Secondly, milk lead concentration is a potential public health concern, particularly for growing children. Furthermore, the safety implications for community living around the contaminated sites with respect to consumption of milk products such as cheese emanated from animals exposed to high Pb contents was predicted.

Presented in Table 4 are the mean (± SD) milk, blood and faeces Pb, Cd, Cu and Zn levels measured in both the contaminated and reference lactating cows. The large standard deviation observed for both blood and milk Pb showed that there was high variation in the levels of Pb among the animals. The concentrations of Cd in the tissues of test animals were below the detection limit of the instrument whereas in control animals both Cd and Pb levels were below the detection limits. Pb was detected in blood, milk and faeces of all the sample animals where the concentrations ranged from <80.0-1380 μg/L (349±82.0μg/L) in blood, <80.0-630 μg/L (347±144μg/L) in milk and from 0.25-6.75 mg/kg (2.08±1.46 mg/kg) in faeces. 70 % of the sample animal had blood Pb higher than the detectable limit of the instruments. 40 % of the animals had blood Pb concentration above the maximum limit of 260μgPb/L. Normal blood Pb concentrations for ruminants has been mentioned to be generally below 260μgPb/L (Smith *et al.,* 2010). Researchers have recorded higher blood and milk lead levels in animals raised around contaminated sites. Swarup et al. (2005) documented high levels of Pb which ranged from 170 to 1,220 μg/L (756±69 μg/L) and 130 to 2,700 μg/L, 844±113 μg/L in blood and milk collected from animals reared in the vicinity of a lead zinc smelter. Blood and milk Pb levels of 1,180 and 1,560 μg/kg respectively were reported in cattle after 2 weeks of accidental exposure from the licking of burnt storage batteries (Oskarsson *et al.,* 1992). Bilandzic et al. (2011)

Table 4. The mean (±SD) concentrations of heavy metals in leachate and regulatory standards

Parameters measured	Concentration (mg/L)		
	Leachate concentrations	USEPA PWQS 2009	WHO WQS, 2006
Pb	8.81±0.06	0.015	0.01
Cd	0.041±0.003	0.005	0.003
Cu	0.20±0.01	1.3	2.0
Zn	1.00±0.004	5.00*	3.0

*USEPA Secondary water quality Standard

reported milk Pb level ranging between 1.0-370.0 μg/L. All the values of Pb in the sample animals exceeded maximum residue levels (MRLs) of 20μg/kg for Pb in milk established by Codex Alimentarius Commission (Ataro *et al.,* 2008). Accumulation of Pb in blood and milk samples were statistically evaluated to find out if the experimental differences in analytical results are significant. There is a significant difference ($p<0.05$) in the accumulation of Pb in blood and milk of the animal. Fcal = 2.76>Ftab=2.17. Blood contained higher concentrations of Pb. Data on metal concentrations in cow's faeces or published normal levels with which to compare the results are sparse. However, the non-detectable levels of Pb in the faeces of the control animals imply faecal contamination of the sample animals. It is also worth mentioning that the faecal Pb indicates that a portion of the absorbed Pb was not only eliminated through the milk but also through the digestive system of the animal.

The general high blood Pb levels observed in this study are indicative of the degree of exposure of cattle reared around the studied contaminated sites to environmental Pb. Non-detection of Pb in the faeces of the controls as against the high levels in the sample also supported contamination of the cows in the vicinities of the wastes. These high levels of Pb can connote danger to the animals' physiological and metabolic systems. Based on the maximum residue levels (MRLs) of 20 μg/kg for Pb in milk as established by Codex Alimentarius Commission (Ataro *et al.,* 2008), it could be inferred that the milk from these animals were contaminated with Pb. This implies that there is potential danger to the community in the vicinity of the cattle farms if consume products resulting from the milk. The Pb contents in the faeces apart from revealing the Pb contamination status of the animals also depicts the potential risks for the population inhabiting the vicinities of the studied sites in terms of sporadic soil contamination as the animals drop their wastes during passage.

Copper was detected in both the sample and control animals. The cows reared around the contaminated sites had mean blood, milk and faeces Cu concentrations of 984±250 µg/L, 185±91.8 µg/L and 14.0±2.51 mg/kg respectively which were significantly lower ($P<0.01$) than the control values of 17960±5600 µg/L, 29200±8370 µg/L, 56.5±13.5 mg/kg. In a similar way to Pb, levels of Cu in blood were significantly higher ($p<0.05$) than levels in milk for both sets of animals. F-test analysis ($F_{cal} = 7.41 > F_{tab}=2.17$) also showed a significant difference ($p<0.05$) between the Cu levels in the blood and milk of the animal. In sample cows, faeces Cu levels were lower than what were excreted in the faeces of the control animals.

The range 713-1490 of µg/L obtained for blood Cu in sample animals falls within a concentration range of 600-1500 µg/L which has been suggested as a critical blood Cu concentrations in cattle (Erdogan *et al.,* 2004), suggesting contamination of the animals.

The copper concentrations observed in blood and milk of reference animals were much more than those found in raw cow milk and blood from many countries (Triphathi *et al.,* 1999; Patra *et al.,* 2008; Bilandzic *et al.,* 2011). However, Bilandzic *et al.,* (2011) also reported Cu concentration as high as 17,077 µg/L in raw milk from Croata. Coni et al. (1995) reported mean Cu concentrations which ranged from 873 to 12100 µg/kg in raw milk samples collected from seven Italian livestock farms.

Zinc was detected in both the sample and reference cows. The cows reared around the contaminated sites had mean blood, milk and faces Zn concentrations of 1210±804 µg/L, 1740±1200 µg/L and 83.6±16.9 mg/kg respectively while the control cows had values of 17960±5600 µg/L, 29200±8370 µg/L ; 56.5±13.5 mg/kg in blood, milk and faeces respectively. Levels of Zn in blood and milk of the control animals were significantly higher $p< 0.01$ than the sample animals. Coni et al. (1995) as well reported mean Zn concentrations which ranged from 21, 600 µg/kg to 41,500 µg/kg in cow's raw milk samples collected from seven Italian livestock farms . Zn concentrations which ranged from 2,460±220 to 5,730±580 µg/ L were also measured in fresh milk from Brazil (do Nascimento *et al.,* 2010). Other workers too measured relatively high levels of Zn in raw cow milk (Licata et al. 2004; Martino *et al.,* 2001; Triphathi *et al.,* 1999).

Unlike Pb and Cu levels in sample animals, both the analytical data and statistical evaluation indicated that Zn levels in the milk were significantly ($p<0.05$) higher than the levels in the blood. However, for control animals Zn levels were higher in the blood than in the milk ($F_{cal} = 0.26 < F_{tab}=0.46$, $p<0.05$). Zhang et al. (2010) also reported lower Zn levels in the blood of cows with subclinical ketosis when compared with healthy cows. In contrast to what was observed with faeces Cu, the level of Zn excreted in faeces of the sample cows were much higher than the levels excreted in the faeces of the control animals ($T_{cal}= 6.29 > T_{tab} = 2.09$, $p<0.05$).

It is interesting to observe the different behaviour of Cu and Zn in the blood and milk of the animals. While Cu levels were higher in the blood, Zn levels were higher in the milk of the animals. Blood concentrations of Cu and Zn have been demonstrated to be closely associated with the health status of cows. Zhang et al. (2010) also reported lower Zn levels in the blood of cows with subclinical ketosis when compared with healthy cows. The deficiency of Cu in the cow milk and the depletion of Zn in the cow blood may be attributed to the exposure of the animals to elevated levels of Pb which interfered with normal Cu and Zn absorption system. Cu retained in the blood of the animal can be deposited in the organs such as liver and kidney leading to all sorts of chronic copper poisoning (Minervino *et al.,* 1999). The results obtained also propose that absorption of trace essential metals in cows may not only depend on the total amount in their feeding, but also on the levels of toxic metals that are co-present in the body of the animals.

Levels of Cu and Zn observed in the control animals were extremely higher than those of the sampled animals. Although the reasons for this sharp difference in concentrations observed cannot be clarified with certainty. There are two possibilities. The elevated levels may be suggestive of administration of uncontrolled mineral supplements by the cattle rearers, in addition to the forage grasses in order to meet the Cu and Zn requirements of the animals. For example, analyses of different mineral mix supplements from some dairy farms in China yielded mean Cu and Zn concentrations of 559.9 ±375.5 and 3060 ± 2170 mg/kg respectively (Li *et al.,* 2005).Secondly, the environment around the slaughter house might be the source. In Nigeria, used rubber tires are usually burnt to process the animals. The residues from the burnt tires which are known to contain high levels of Cu and Zn are disposed off in an illegal dumpsite in the vicinity of the slaughter house where the animals graze before they are slaughtered. This demonstrates that particular attention has to be paid to the trace Cu and Zn levels in Nigerian cattle. There is paucity of data on toxic and trace metal concentrations in raw blood and milk in cows in Nigeria. Hence, there are no reports in Nigeria to compare the results of the heavy metals concentrations in the control cows with. In future studies, blood and milk samples from cattle in Nigeria should be analysed to ascertain the trace metals, especially Cu and Zn levels.

CONCLUSION

The study showed elevated concentrations of Pb in all plants and leachate from Pb slag contaminated

Table 5. Concentrations of Pb (μg/L), Cu, Zn (mg/L) in milk, blood and faeces (mg/kg) of cows reared in secondary Pb slag contaminated and uncontaminated areas

	Cows from Pb slag contaminated				Cows from uncontaminated areas			
	N	Mean ±SD	Median	Range	N	Mean ±SD	Median	Range
Pb								
Milk	20	347±144	313	<DL-630	20	<DL	<DL	<DL
Blood	20	349±82.0	312	<DL-1380	20	<DL	<DL	<DL
Faeces	20	2.08±1.46	2.00	0.25-6.75	20	<DL	<DL	<DL
Cd								
Milk	20	<DL	<DL	<DL	20	<DL	<DL	<DL
Blood	20	<DL	<DL	<DL	20	<DL	<DL	<DL
Faeces	20	<DL	<DL	<DL	20	<DL	<DL	<DL
Cu								
Milk	20	185±91.8	166	63.0-388	20	14500±7840	13180	2490-26900
Blood	20	984±250	844	713-1490	20	17880±7600	18760	2499-31870
Faeces	20	14.0±2.51	14.7	6.53-17.8	20	36.2±16.9	33.2	12.5-87.4
Zn								
Milk	20	1799±267	1739	350-4200	20	17960±5600	18100	8740-28700
Blood	20	1210±804	1350	106-2940	20	29200±8370	30290	13740-44400
Faeces	20	83.6±16.9	79.8	41.9-115	20	56.5±13.5	57.4	30-77.5

Detection limits for Pb, Cd, Cu and Zn are 0.08, 0.01, 0.005 and 0.005 mg/L respectively

sites, suggesting a definite adverse impact on the environment and stressing the need to control open dumping of hazardous waste on land. In addition, it is important to note from the results of this work that improper disposal of metallurgical wastes could lead to contamination of forage plants with consequent transfer to ruminants. Analysis of blood, milk and faeces indicated that Pb concentrations can be abnormally raised for animals that continuously graze Pb slag contaminated sites. High levels of Pb in blood and milk can be potential threat to the animals' health and source of transfer to human. The high concentration of Pb detected in both environmental and biological samples implies the need for remedial action on Pb slag contaminated sites. Furthermore, there is need for proper management of metallurgical wastes in order to safeguard the environment and preserve human health.

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