

Research Paper

Investigation of heavy metal levels in roadside agricultural soil and plant samples in Adogo, Nigeria

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ABSTRACT

The contamination of soils and plants by heavy metals from automobile sources has become a serious environmental issue. The content of Cd, Cu, Ni, Pb and Zn in the agricultural soils and cassava (*Manihot esculentus*) leaves from Adogo, Nigeria was investigated using atomic absorption spectroscopy (AAS) technique. Samples of soil and cassava leaves were collected from a site located on a highway, and another in a rural area which served as the reference site. Levels of Cd, Cu, Ni, Pb and Zn in soil and cassava leaves were found to be <0.01 , 0.89 ± 0.25 , 0.18 ± 0.03 , 0.44 ± 0.16 , 0.04 ± 0.003 and 0.13 ± 0.0002 , 0.15 ± 0.01 , 0.06 ± 0.005 , 0.07 ± 0.004 , 0.06 ± 0.002 $\mu\text{g/g}$ respectively. The levels of heavy metals in roadside agricultural soils and cassava leaves were higher as compared to reference soil levels, with Pb concentration seven times higher than level in soil and cassava leaves in reference soil. In the absence of any major industry in the sampling sites the Pb metallic level indicates relation to traffic.

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INTRODUCTION

Heavy metals are released from various sources such as municipal wastewater sludge, urban composts, road traffics, atmospheric deposits and agrochemicals such as fertilisers, pesticides, fungicides and so on. Atmospheric emissions tend to be of great concern, because of the quantity, wide spread dispersion, potential and their invisible nature. Environmental pollution of heavy metals from road traffics emissions has attained much attention in the recent past due to their long-term accumulation. Several studies have proved that roadside environments are polluted by heavy metals released during different operations of the road transport. Heavy metals such as Pb, Cd, Cu, and Zn have been reported to be released into the atmosphere during different operations of the road transport (Zhang et al., 2012; Akbar et al., 2006; Sharma and Prasade, 2010; Atayese et al., 2008). Studies on some

heavy metals in scalp hair of traffic wardens in Benin City, Nigeria reported high level of Pb and Zn which is reported to be due to emissions from motor vehicle exhausts and vehicle component wear which they are exposed to (Eruyogho et al., 2007).

The use of leaded gasoline in cars is one of the major sources of Pb pollution in cities around the world (Luilo and Othman, 2006). According to Irami et al. (2009) road traffic is responsible for over a thousand tonnes of Pb each year, as a result of lead additives in petrol. Soils, plants and food are major receptacles for these atmospheric emissions. According to Sharma and Prasade (2010) only 3% of Pb in soil is translocated through the root to the shoot of plants while the rest is through foliage. Research on smoked fish food exposed to highways indicated a relationship between the vehicular traffic volume and the

fish Pb levels (Adekunle and Akinyemi, 2004). This acts as potential threat posed to the health, security and safety of such food items.

These metal pollutants are deposited on adjacent soil where they may be transformed and transported to other parts of the environment such as vegetation (Sharma and Prasade, 2010; Okunola et al., 2008). Plants grown in the neighbourhood of major motorways have been reported to contain metals such as Pb and Cd from motor vehicle emissions (Sharma and Prasade, 2010; El-Gamal, 2000; Luilo and Othman, 2006). Other sources of heavy metals to roadside environments are vehicle component wear, engine oil consumption and corrosion of batteries and other vehicle metallic parts. The average Pb and Cd content of dry cell batteries imported into Nigeria between 1980 and 1998 were 1051 and 107.7 mg kg⁻¹ respectively (Nnorom and Osibanjo, 2006). Studies by Hjortenkrans (2003) gave brake linings and tyres as contributing more than 85% of the total Cu and Pb emissions while Zn contributes more than 85% of the emissions from tyres. Zhang et al. (2012) reported engine oil consumption as the largest emission for Cd, tyres wear for Zn, and brake wear for Cu and Pb. In furtherance bitumen and mineral filler materials in asphalt road surfaces have also been reported to contain different metal species, including Cu, Zn, Cd, and Pb.

The pollution of agricultural soils by heavy metals from automobile sources is a serious environmental issue due to their potential accumulation in bio systems. Heavy metals can enter the body through soil and dust, dermal contact, breathing and food chain. Total heavy metal content of soils is useful for many geochemical applications but often the speciation of these metals is more of an interest agriculturally. Thus environmental risks are reported to be related to the bioavailability of these metals which depends on the speciation of the metals, soil characteristics and the complex interactions between metals and the environment (Yobouet et al., 2010; Matthews-Amune and Kakulu, 2012). The majority of the heavy metals are toxic to the living organisms and even those considered as essential can be toxic if present in excess (Ayodele and Oluyomi, 2011; Luilo and Othman, 2006). The heavy metals can impair important biochemical processes posing a threat to human health (Akbar et al., 2006; Ayodele and Oluyomi, 2011). Pb for example is a nonessential metal with neurological toxin affecting many processes and almost every organ in the human body and affecting children growth (Luilo and Othman, 2006). In furtherance heavy metal toxicity has negative effect on plant such as growth, enzymatic activity, stoma function, photosynthesis activity and so on (Onder et al., 2007; Akbar et al., 2006; Ayodele and Oluyomi, 2011).

Several studies on environmental pollution of heavy metals from automobiles have attained much attention in recent times due to the contamination levels reported in several countries but none has been carried out in the vicinity of Adogo in Kogi State, Nigeria. The present research was undertaken to determine the metallic level of

Cd, Cu, Ni, Pb and Zn in roadside agricultural surface soil and cassava plant to ascertain the influence of transportation activities.

MATERIALS AND METHODS

The study area is Adogo located in Kogi State, Nigeria. The agricultural structure of the area is dominated by small farms with maize (*Zea mays*), cassava (*M. esculentus*), yam (*Dioscorea rotundata*), okro (*Abelmoschus esculentus*) and fodder crops being the staple agricultural produce. These products are likely to represent a high proportion of the potential dietary intake of contaminants by high risk consumer groups (that is those growing a high proportion of their own food). The studied farm is a cassava plant farm land 30 m from the Adogo highway. It lies within longitude 7°29'50.3"N and latitude 6°29'43.3"E. The reference site is a sparsely populated area with low traffic, no industrial activity taking place, lying within longitude 7°41.821'N and latitude 6°20.925'E and 50 m to the road. A total of 150 soil samples (0-15 cm dept) and 150 plant samples were collected from 10 locations in the vicinity of the farms at 50 m interval using a stainless steel knife.

The collected soil samples were air-dried for seventy-two hours, ground in a mortar, passed through a 0.005 mm sieve and stored in clean acid treated polythene bags. Tessier et al. (1979) method for total metal analysis was carried out by digesting 1 g (<0.005 mm) of soil sample with a mixture of 5 ml HF and 1 ml HClO₄. The extract was analyzed using AAS. Same procedure was carried out on soil reference sample.

Soil pH was determined using a soil-water ratio 1: 2.5 (w/v). Soil organic matter was determined using the Walkey-Black wet oxidation method (Udovic et al., 2009). Soil particle size distribution was done using hydrometer method and soil carbonate was determined by the concentrated HCl acid method (Udovic et al., 2009). Cassava plant samples were washed with deionized water, air dried to a constant weight at a temperature of 105°C in an oven. Samples were ground into powder, passed through a 0.02 mm sieve, mixed to homogenize and stored in acid treated polythene bags. Method of 4:1 mixture of HNO₃ and HClO₄ by Kakulu and Jacob (2006) was used for plant digestion. Reagent blank was prepared in similar manner. Spiking of the sample was done using standards of concentration of each studied metal and extracted as above.

Quality control was implemented through three replicate samples, reagent blank, spiking and use of international soil reference sample (Soil Reference Material 989 Netherland). Precision for the determination of heavy metal in plants ranged from 0.30-12% and in soil from 8-12%. Recovery studies gave 80-120% for plants. Analysis of soil Reference Material 989 from Netherland gave Cu 144.5±11.6 and Pb 253.8±13.8 µg/g against the standard values of 153±3.9 and 282±3.6 µg/g for Cu and Pb respectively.

Table 1. Physico-Chemical parameters of the studied soil.

	Sand (%)	Silt (%)	CO ₃ ²⁻ (%)	Clay (%)	TOM %	pH
Agricultural Soil	70.24	13.28	4.77	16.48	2.36	6.90
Reference	78.24	7.28	4.72	14.48	3.17	8.3

TOM-Total Organic Matter.

Table 2. Concentration of heavy metals in soil and cassava crop (µg/g dry weight).

Metal/Site	Soil		Plant	
	Agricultural Soil	Reference	Cassava crop	Reference
Cd	<0.01	0.07±0.01 (0.06-0.08) ^a	0.13±0.0002 (0.1298-0.1302) ^a	0.03±0.002 (0.028-0.032) ^a
Cu	0.89±0.25 (1.14-0.64) ^a	0.05±0.02 (0.03-0.07) ^a	0.15±0.01 (0.14-0.16) ^a	0.01±0.002 (0.018-0.012) ^a
Ni	0.18±0.03 (0.15-0.21) ^a	0.09±0.004 (0.086-0.094) ^a	0.06±0.005 (0.055-0.065) ^a	0.01±0.004 (0.006-0.014) ^a
Pb	0.44±0.16 (0.28-0.60) ^a	0.06±0.001 (0.059-0.061) ^a	0.07±0.004 (0.066-0.074) ^a	0.01±0.003 (0.007-0.013) ^a
Zn	0.04±0.003 (0.037-0.043) ^a	0.05±0.001 (0.049-0.051) ^a	0.06±0.002 (0.058-0.062) ^a	0.02±0.01 (0.01-0.03) ^a

a = range

RESULTS

The physiochemical properties of the studied soil are shown on Table 1. The agricultural soil is mainly sandy, neutral and moderately high in carbonate with low percentage of organic matter. The levels of heavy metals in soil and cassava leaves samples are given in Table 2. Cd content in soil ranged <0.01-0.07±0.01, Cu 0.05±0.02-0.89±0.25, Ni 0.09±0.004-0.18±0.03, Pb 0.06±0.001-0.44±0.16 and Zn 0.04±0.003-0.05±0.001 µg/g. These levels fit in the typical ranges of the average concentration in the Earth's crust (Yobouet, 2010). These levels are not as high as the ranges reported in roadside soils of England (Pb 25.0 - 1198.0 µg/g, Zn 56.7- 480.0 µg/g, Cd 0.3-3.8 µg/g and Cu 15.5 -240.0 µg/g) which were higher than natural background levels reported for British soils (Akbar et al., 2006). In agricultural soil Cu concentration was recorded highest followed by Pb.

Cd content in cassava leaves was 0.03±0.002-0.13±0.0002, Cu 0.01±0.002-0.15±0.01, Ni 0.01±0.004-0.06±0.005, Pb 0.01±0.003-0.07±0.004 and Zn 0.02±0.01-0.06±0.002 µg/g. In cassava leaves, Cu concentration were recorded highest followed by Cd.

DISCUSSION

Heavy metals are emitted from various sources into the

atmosphere. Most studies have used soil and plant samples to monitor their metallic levels (Luilo and Othman, 2006; Alam, 2008; El-Gamal, 2000). The metallic levels of the studied soil and plant were generally low and higher than the reference samples. These observations indicate some level of contamination possibly from aerial deposition of metal particulates in road side environment from extraneous sources. These sources could be due to the addition of artificial fertilizer and pesticides in agricultural soil, traffic volume, highways layout, contributions of the stone material used in road pavement climate and anthropogenic activities. Other possible influences on the metallic levels observed are, frequent farming activities which could mix the farmland top soil spatially and result in uneven distribution of heavy metal, the crops in agricultural soil may have various abilities to assimilate heavy metal soil contaminants and the local terrain and factors such as rain runoff and drainage, wind direction and speed, and other non-crop plants might change the heavy metal contaminants' distribution patterns. According to El-Gamal (2000) the mobilization pattern can be attributed to the nature of the element and the physico-chemical properties of the soil. Increase in metallic levels at a distance beyond 35 m off the road edge is reported to be attributed to geological and/or biological decomposition of leaf litters (Luilo and Othman, 2006). Zhang et al. (2012) findings indicate that trees growing linearly along roadways can effectively reduce the heavy metals' concentrations

in the roadside farmland. Continuous deposition of these heavy metals indicates potential health risk for human through the food chain.

Sand and clay fractions are the dominant soil parameters and the agricultural soil is moderately high in carbonate. Soil pH of 6.90 indicates that the soil is neutral. Soil pH and other soil properties are especially important in soil processes, responsible for solubility of heavy metals in soil and their transportation (Matthews-Amune and Kakulu, 2012). According to Sipos et al. (2005) findings high carbonate content enhances the pH of soil and Pb distribution within the soil phases is mostly determined by the organic matter, the percentage and mineralogical characteristics of the soil clays and carbonate content of the soil.

Pb concentration in soil ranged 0.06 ± 0.001 - 0.44 ± 0.16 $\mu\text{g/g}$. The concentration of Pb in soil was seven times higher than the level in the reference soil. Oztas and Ata (2002) reported soils within 40 m off the motorway having at least 2 to 6 times higher amounts of Pb than the background level. Several reports have been given on the use of Pb as an antiknocking agent in gasoline which results in its release during emissions from fossil combustion (Sharma and Prasade, 2010; Akbar et al., 2006; Oztas and Ata, 2002; Onder et al., 2007). Pb content of leaded gasoline in Nigeria ranges 0.60 to 0.80 g/l (Kakulu, 2003). In addition, wearing down of vehicle tyres can also introduce Pb to the roadside soil (Sharma and Prasade, 2010; Zhang et al., 2012). Its distribution is dependent on wind direction, the oxidation of parent material and sulphide ores, anthropogenic materials and deposition due to alkalinity of soil (Iorfa, et al., 2011; El-Gamal, 2000; Oztas and Ata, 2002).

Pb is reported as one of the heavy metals with highest affinities for soils moreover it becomes stabilized on the surface of soil through hydrolysis reactions (Sipos et al., 2005). There are several reports that Pb accumulates within the top few centimetres of soil with discharge from automobiles reported to be confined within a zone of 33 m wide, measured from the road edge (Sharma and Prasade, 2010; Manno et al., 2006; Atayese et al., 2008). Previous studies on speciation of the studied agricultural soil in Adogo (Matthews-Amune and Kakulu, 2012) gave Pb levels to be highest in the exchangeable phase. The presence of mobile forms of Pb indicate toxic risk both in the food chain and its migration downwards the soil profile. Levels of Pb concentration in soil ranging from 25.0 to 1198.0 $\mu\text{g/g}$ have been reported on roadside soil in England, 0.00 to 50.10 $\mu\text{g/g}$ in India, 78.4 to 832 $\mu\text{g/g}$ in Tanzania 9.27 ± 0.23 to 45.92 ± 22.06 $\mu\text{g/g}$ and 47-151 $\mu\text{g/g}$ on major highway in Lagos, Nigeria (Akbar et al., 2006; Atayese et al., 2008; Luilo and Othman, 2006; Sharma and Prasade, 2010; Othman et al., 1997).

Cd concentration in soil ranged from <0.01 - 0.07 ± 0.01 $\mu\text{g/g}$. Pagotto et al. (2001) reported similar low level of Cd in samples in the immediate vicinity of French major highway, Akbar et al. (2006) reported Cd concentration

ranging from 0.3 to 3.8 $\mu\text{g/g}$ in England, Onder et al (2007) research reported levels lower than the general soil level of 0.1 $\mu\text{g/g}$, 0.3 – 1.33 $\mu\text{g/g}$ in studies by Atayese et al. (2008) on heavy metal contamination of soil on major highway in Lagos, Nigeria while Okunola et al. (2008) reported Cd concentrations levels which were higher than FAO/WHO recommended limits in Kaduna Metropolis, Nigeria. In the absence of any major industry in the sampling sites, the levels of Cd could be due to engine oil consumption and the wearing of tyres. Such findings have been reported previously (Sharma and Prasade, 2010; Atayese et al., 2008; Zhang et al., 2012). With the high percentage of Cd ($26.93 \pm 9.10\%$) in the exchangeable and carbonate phases of the studied agricultural soil ($42.52 \pm 4.91\%$) (Matthews-Amune and Kakulu, 2012) there is potential for its release and further derived processes of migration and toxicity.

Cu concentration in agricultural soil ranged from 0.05 ± 0.02 - 0.89 ± 0.25 $\mu\text{g/g}$ and was recorded highest of all the studied metals. Break dust have been recognized as a carrier of Cu which is used in brakes to control heat transport (Manno et al., 2006; Hjortenkrans, 2003; Zhang et al., 2012). Soil Cu content has been reported to differ according to the soil type and pollution source (Onder et al., 2007). Cu is usually present in soils within the range of 0 to 250 $\mu\text{g/g}$ (Akbar et al., 2006). The observed level is lower than 15.5-240.0 $\mu\text{g/g}$ reported in roadside soil of England (Akbar et al., 2006).

Zn concentration in agricultural soil ranged 0.04 ± 0.003 - 0.05 ± 0.001 $\mu\text{g/g}$. Normal concentrations of zinc in soil range from 1 to 900 $\mu\text{g/g}$ (Akbar et al., 2006). The observed level is lower than Zn 56.7- 480.0 $\mu\text{g/g}$, reported in roadside soil of England. Zn is used in brake linings because of their heat conducting properties and as such released during mechanical abrasion of vehicles, and from engine oil combustion and tyres of motor vehicle (Manno et al., 2006; Akbar et al., 2006; Hjortenkrans, 2003; El-Gamal, 2000). Ni concentration in soil ranged from 0.09 ± 0.004 - 0.18 ± 0.03 $\mu\text{g/g}$. Ni is absorbed easily and rapidly by plant (Hjortenkrans, 2003). According to Onder et al. (2007) airborne particles emitted by brakes and wears from vehicles tyres can contain considerable amounts of Ni.

There were spatial differences in metallic levels between the soil and cassava leaf. Metallic levels of the studied metals in soil were higher than the observed levels in the cassava leaves except for Cd. The higher level of Cd on cassava leaves could be due to direct foliar deposition from agrochemicals. Okunola et al. (2008) gave similar report attributing the higher level to be due to foliar absorption of these metals via atmospheric emission. Other researchers have reported heavy metal content of soil to be higher than that in plant samples collected near high ways (Luilo and Othman, 2006; Onder et al., 2007). The observed difference in metallic levels between the soil and cassava leaves indicates that only a fraction of the total metal content in the agricultural soil was taken up by the plants. This is in agreement with previous studies (Luilo and Othma, 2006;

Atayese et al., 2008; Othman et al., 1997). Heavy metal levels in plants are determined not only by the concentration in the soil but also by the physico-chemical properties of the soil such as pH, cation exchange capacity (CEC), electrical conductivity (EC) and organic matter content of the soil (Luilo and Othman, 2006; Sharma and Prasade, 2010; Atayese et al., 2008; Onder et al., 2007).

The metallic level of the cassava leaves on agricultural soil was higher than the levels in the reference leaves. The relatively high heavy metal level in cassava leaves on agricultural soil could be mostly due to the transportation activities, which is considered one of the major sources of heavy metal contamination. There is report that growth stage and physiology of the plants indirectly affect the metal contents in the plants (Luilo and Othman, 2006). In this study plants were sampled randomly irrespective of their growth stage and therefore there is a possibility that the relative proportion of mature and young cassava leaves in the composite samples were different from one sampling point to another. This could affect the metallic levels of the cassava leaves. The observed metallic levels in cassava leaves were below the FAO/WHO limits guideline values for heavy metal levels in food.

Conclusion

The influence of road traffic emission on the agricultural soil was evaluated by considering variation in the levels of metals in soil and cassava leaves. There was substantial contamination with metals in both soil and cassava leaves. In the absence of any major industry in the sampling sites these observations suggest that motor vehicles on the roads were the point sources of these metals to the roadside soils and cassava leaves. Agricultural farms should not be close to highways to prevent excessive build up of heavy metals in the food chain. Thus regular monitoring of heavy metals in soil and plants is essential.

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