Full Length Research Paper

Levels of trace metals in soil and vegetation along major and minor roads in metropolitan city of Kaduna, Nigeria

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Sample of soil and plant (*Sida acuta burm* F.) were collected from 30 sites of 24 roads. The samples were analyzed for Pb, Cd, Zn, Cu and Mn using flame atomic absorption spectrophotometry. The soil physico-chemical parameter, pH and particle size distribution was also determined. Levels of Pb, Cd, Zn, Cu and Mn in soil were 15.28 – 76.92, 1.96 – 9.80, 41.66 – 237.96, 1.60 – 4.88 and 76.00 – 132.00 mg/kg dry weight, respectively. Results of concentrations in plants ranged were from trace – 32.37, 4.88 – 14.93, 27.78 – 185.19, 1.67 – 3.89 and 20.00 – 110.00 mg/kg dry weight for Pb, Cd, Zn, Cu and Mn, respectively. The soil pH was from 6.22 – 8.44 while sand and loamy sandy textural classes constitute the soil samples. For both experimental soil and plant samples, the mean concentrations were found to follow the decreasing orders; Zn > Mn > Pb > Cu > Cd and Zn > Mn > Pb > Cd > Cu, respectively. Mild correlation between traffic density and metals in samples with the exception of plant Pb content, suggest that automobile emission couple with waste dispose along the roads remain a threat. The findings in general indicate the levels of metals in soil and plant samples were within the EU limits with the exception of Cd. In addition, the high level of Cd appears to reach pollution levels and metal dynamics up the food chain is highly possible.

Key words: Trace metals, soil, plant, metropolitan.

INTRODUCTION

Roadside soils have been shown to have considerable contamination due to both depositions on vehicle - derived metal and to relocation of metals deposited on the road surface (Harrison et al., 1981). Because of the severe adverse environmental and/or ecological and health effects of these heavy metals, there have been many studies on heavy metal contamination in soils along major roads (EPA, 1999; Turer and Maynard, 2003).

Heavy metal pollutants are of significant ecological/environmental concern because they are not biodegradable and have long half - lives in the soil, thus predicating far reaching effects on biological systems including soil microorganism and other soil biota (Adeniyi, 1996; Ram et al., 2000). According to Adeniyi (1996),

these metals also get accumulated when plants and crops cultivated along major roads are consumed by man and animals especially livestock, either directly or indirectly. This accumulation may fast reach lethal levels quickly (Wang and Demshar, 1992).

Several researchers have indicated that need for a better understanding of urban soil pollution (De Kimple and Morel, 2000; Manta et al., 2002), vegetation present on verges of roads (Okonkwo and Maribe, 2004; Chimuka et al., 2005; Awofolu, 2005). Vegetation present on verges of roads is presumably the oldest form of anthropogenic vegetation (Ullmann and Heindle, 1989). Roadside vegetation represents not only a distinct type of synanthropic vegetation, but in areas with high population density and an intense industrial or agricultural landscape, roadside verges are often the only habitats where natural vegetation can develop (Ansari et al., 2003). Although, there have been a considerable number of studies on the concentrations of heavy metals in roadside

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soil and plants, the vast majority have been carried out in developed countries with long histories of industrialization and extensive use of leaded gasoline (Page et al., 1971; Goldsmith et al., 1976; Otte et al., 1991; Mateu et al., 1995).

Kaduna metropolis (Lat. 10.52°N, Long. 7.44°E) located in Kaduna state occupies central portion of Northern Nigeria (Kaduna, 2004). Founded in 1917 as an administrative headquarters of Northern Nigeria, it is presently one of the most important cities in the country. As at 1991 census it had a population of 993,600 but projected to be home to about 1.56 million people (TWG, 2005). Apart from presently being the administrative headquarters of its state, it has experience a high concentration of federal parastatals, industries and has also seen increase in both population and traffic. There-fore, this study was initiated to assess the level of contamination of surface roadside soil (soil have been known to serves as a receptacle for most chemicals released by man, (McEldowney et al., 1993) and plants by some heavy metals along major and minor roads, since there have been no studies about the extent of contamination of roadside ecosystem by priority heavy metal pollutants.

MATERIALS AND METHODS

Study area and sampling

Sample was collected from twenty points of fourteen major and minor tarred roads in the months of May, 2006. The map of sampl-ing sites in ascending other (Ungwan Dosa, Rabah (KSMC), Isa Kaita/Malali, Race coarse, Kassim Ibrahim, Barau Dikko/Hospital, Stadium, Barnawa, Kadpoly(CES) Barnawa, Sabo/Prison, Bypass (PZ), Bypass-Kurumashi, Govt. College-Kurumashi, Bypass-Ungwan-Ma'azu, Kassim Ibrahim house/Amusement-Park, Poly (Tundun-Wada), Bypass-Trikania, Makera-Nassarawa, Bypass-Kakuri and Angwan Romi). 10 roads were selected as the reference site for soil and plant sampling, representing low traffic roads (<2000 vehicle per day). The low traffic sites were located in no commercial and industrial activities area as shown in Figure 1. Surface soil samples of an approximate varied distance of 3 m from each road was collected with the aid of stainless spoon, washed with soap and rinsed with distilled water after each sampling (Awofolu, 2005). 10 individual sub-samples of 20 g were collected from each side of the road of the sampling site. The samples for each sampling location were mixed properly to give a composite sample mixture. Enough soil samples was collected from the composite sample of each site, placed in a cellophane bag (Bam-gbose et al., 2000), labeled and taken to the laboratory for pre-treatment and analysis. The soil sampling spots was cleared of debris before sampling (Chimuka et al., 2005).

Fresh leaves of the same species (*Sida acuta burm* f.) were randomly taken from the vicinity of the sampled area where soil were collected, using a clean stainless steel pair of scissors (Okonkwo and Maribe, 2004), placed in a paper bags, labeled and taken to the laboratory for pre-treatment and analysis.

Sample preparation

Plants samples were properly rinsed with distilled - deionized water to remove any attached soil particles, cut into smaller portions then

Table 1. Mean (%) recoveries and standard deviation (±)of heavy metals from spiked samples.

Metals	Soil	Plant
Pb	88.9 ± 9.6	94.4 ± 19.3
Cd	96.7 ± 11.5	90.0 ± 0.0
Zn	97.3 ± 1.2	96.7 ± 0.5
Cu	95.7 ± 2.8	97.1 ± 0.5
Mn	87.5 ± 0.0	91.7 ± 0.5

placed in large clean crucible where they are oven dried at 100°C for 48 h. The dried plant samples were grinded into fine particles using clean acid washed mortar and pestle. The procedure according to Awofolu (2005) was used for digestion of plant sample. 0.5 g of sieved leaf samples were then weighed into 100 ml beaker. A mixture of 5 ml concentrated concentrated trioxonitrate (IV) acid and 2 ml perchloric acid was added and this was digested on low heat using hot plate until the content was about 2 ml. The digest was allowed to cool, filtered into 50 ml standard flask using 0.45 um Millipore filter kit. The beaker was rinsed with small portions of double distilled water and then filters into the flask. Triplicate diges-tion of each sample was carried out together with blank digest without the plant sample.

Soil samples from each site was homogenised and air - dried in a circulating air in the oven at 30°C to a constant weight and passed through a 2 mm sieve. 5 g of soil samples were placed in 100 ml beaker. 3 ml 30% hydrogen peroxide was added following a previously described procedure by Sharidah (1999). This was left to stand for 60 min. until the vigorous reaction ceased. 75 ml of 0.5 M solution of HCl was added and the content heated gently at low heat on hot plate for about 2 h. The digest was then filtered into 50 ml standard flask. Triplicate digestion of each sample together with blank was also carried out. Then the quantitation of metallic content of digested samples was carried out with the flame atomic absorp-tion spectrophotometry model AA 650.

Physico - chemical parameters

The pH and electrical conductivity were measured using a soil sample added to distilled deionized water in a ratio 1: 2 (soil: water) on a volume basis (Hendershot et al., 1993). Particle size distribu-tion was determined by the hydrometer method as described by Bauyoucos (1951).

RESULTS AND DISCUSSION

Quality control test

Table 1 shows the quality control test conducted on soil and plant samples in order to verify the efficiency of sample treatment procedure. The high percentage reco-very shown, validated the sample treatment procedure used in the present study. Generally, all samples from the thirty (30) sites were dominated by high average % sand fractions followed by % clay and finally % silt. The varia-tion in particle size pattern indicate that sand is poorly sorted and the poor sorted nature of the various particle size indicate that these soils were not formed from the natural process of weathering of the underlying parent material but rather from deposited particles (Okoronkwo et al., 2006).
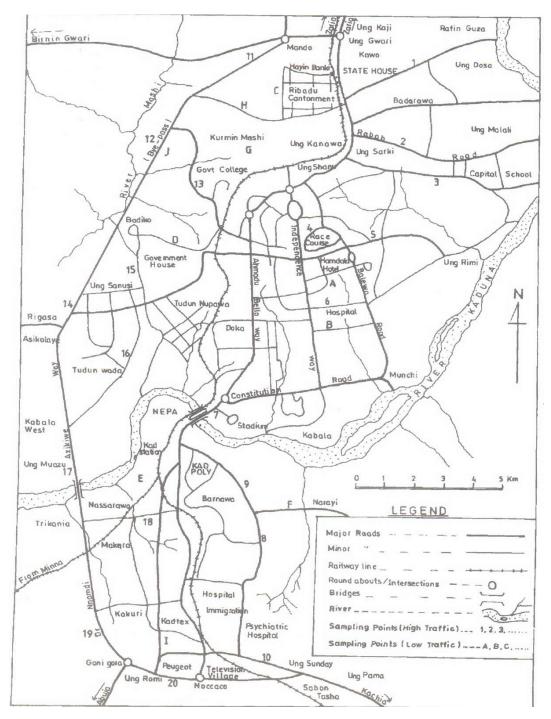
Figure 1. The road network in Kaduna Metropolis showing the sampling points.

Soil pH generally plays an important role in metal bio-availability, toxicity and leaching capability to surrounding areas especially in summertime (Chimuka et al., 2005). Heavy metals are mostly more soluble and leached out in acidic pH (Alloway, 1995). In this present study, the pH values were indicative of an alkaline environment except site I of pH 6.22, hence the presence of soluble salt (Landon, 1996; Tan, 1996). Such pH values are common to areas that receive low rainfall (Brandy and Weil, 1996) where leaching tends not to be very intense and the base forming cations are left to dominate the exchange complex in the place of Al^{3+} and H^+ ions.

Trace Metal levels in soil

Heavy metal contents in roadside soils varied significantly

Table 2. Mean and standard deviation (±) of heavy metal content in soil at selected sites.

Site	Pb (Soil)	Cd (Soil)	Zn (Soil)	Cu (Soil)	Mn (Soil)
1	34.62 ± 2.31	3.90 ± 0.37	84.26 ± 24.20	3.90 ± 0.07	103.20 ± 0.36
2	46.15 ± 0.17	1.96 ± 0.22	77.82 ± 0.94	5.40 ± 0.10	84.00 ± 0.27
3	35.38 ± 0.09	5.82 ± 0.19	75.93 ± 0.35	4.80 ± 0.06	105.00 ± 0.33
4	17.69 ± 0.19	5.86 ± 0.04	45.37 ± 0.16	2.14 ± 0.19	95.00 ± 0.30
5	15.38 ± 0.16	5.88 ± 0.23	85.19 ± 0.19	16.00 ± 0.17	102.50 ± 0.58
6	23.08 ± 0.12	5.68 ± 0.25	176.60 ± 0.36	10.40 ± 0.11	117.00 ± 0.27
7	30.77 ± 0.54	5.88 ± 0.04	237.96 ± 40.54	14.40 ± 0.26	100.00 ± 0.44
8	30.92 ± 0.31	3.90 ± 0.12	69.44 ± 19.53	10.08 ± 0.14	130.00 ± 0.35
9	38.46 ± 0.09	3.92 ± 0.18	147.22 ± 9.28	48.00 ± 2.43	89.00 ± 0.23
10	23.08 ± 0.14	3.90 ± 0.14	132.77 ± 0.06	41.60 ± 0.40	76.00 ± 0.13
11	24.28 ± 0.07	3.63 ± 0.13	71.30 ± 0.09	15.20 ± 0.04	123.00 ± 0.22
12	36.20 ± 0.16	4.88 ± 0.24	130.56 ± 1.41	48.00 ± 0.92	132.00 ± 0.18
13	61.54 ± 0.13	4.71 ± 0.11	143.52 ± 0.82	13.60 ± 0.09	90.00 ± 013
14	46.16 ± 0.23	5.82 ± 0.10	126.85 ± 0.09	43.20 ± 0.07	94.50 ± 0.33
15	61.54 ± 0.13	5.86 ± 0.04	144.63 ± 9.44	32.00 ± 0.21	99.00 ± 0.33
16	46.16 ± 0.12	6.80 ± 0.16	137.96 ± 3.59	16.80 ± 0.05	94.00 ± 0.13
17	53.85 ± 0.26	4.88 ± 0.02	106.48 ± 4.38	22.40 ± 0.03	92.00 ± 0.27
18	69.23 ± 0.07	3.83 ± 0.32	139.82 ± 4.51	26.40 ± 0.05	96.00 ± 0.28
19	49.28 ± 0.05	3.92 ± 0.11	62.74 ± 0.09	31.00 ± 3.10	117.00 ± 0.09
20	30.77 ± 0.06	4.90 ± 0.56	105.56 ± 0.18	9.60 ± 0.09	120.00 ± 0.17
A	23.08 ± 0.25	2.02 ± 0.09	86.12 ± 0.59	4.00 ± 0.26	118.00 ± 0.17
B	53.85 ± 0.15	2.92 ± 0.08	78.70 ± 0.52	1.60 ± 0.11	86.50 ± 0.13
C	38.46 ± 0.20	1.96 ± 0.03	84.44 ± 0.98	8.21 ± 0.16	93.00 ± 0.22
D	30.76 ± 0.20	2.62 ± 0.28	41.66 ± 2.48	3.16 ± 0.02	101.50 ± 0.10
E	15.28 ± 0.04	2.92 ± 0.21	117.60 ± 2.19	36.00 ± 1.50	105.00 ± 0.27
F	76.92 ± 0.05	3.36 ± 0.94	140.74 ± 0.16	4.00 ± 0.68	82.00 ± 0.18
G	38.46 ± 0.20	7.80 ± 0.09	64.81 ± 0.24	27.66 ± 0.27	105.00 ± 0.44
H	23.08 ± 0.23	3.90 ± 0.09	56.24 ± 0.14	2.12 ± 0.19	116.00 ± 0.18
I	46.15 ± 0.24	9.80 ± 0.03	76.86 ± 0.13	2.40 ± 0.05	90.00 ± 0.18
J	23.08 ± 0.22	2.92 ± 0.02	45.28 ± 0.05	3.41 ± 0.05	88.00 ± 0.27

from site to site as shown in Table 2. Pb contents in soil ranged from 15.28 – 76.92 mg/kg. Cd contents in soil ranged from 1.96 – 9.80 mg/kg. The result shows that site F that ranked low in traffic density had the highest Pb contents in soil. On the other hand, Pb was lower than EU upper limit of 300 mg/kg (EC, 1986) and was at lower concentrations than the maximum tolerable levels proposed for agricultural soil, 90 – 300 mg/kg (Kabata-Pendias and Dudka, 1984). The observed highest Pb concentration of site F that experience low traffic, suggest long accumulation of some level of Pb, probably from vehicle emissions, since there are no industrial activities within the area. The Pb obtained in the present study substantially exceeds reported background values of 25 mg/kg Pb in soil (Canadian Environmental Quality, 1992).

One of the sources of Pb obtained in the soil samples in the present study may have come from the deposition of Pb following emission from vehicle. Most of the sites investigated had Cd either within or above the recommended 1 – 3 mg/kg limit given by EU. Highest concentration of Cd in site I on the other hand may have result from automobile industry located along the site. However, the sources of Cd in the urban areas are much less well defined than those of Pb, but metal plating and tyre rubber were considered the likely sources of Cd (Hewitt and Rashed, 1988). In the absence of any major industry in the sampling sites, the levels of Cd could be due to lubricating oils and/or old tyres that are frequently used, and the rough surfaces of the roads which increase the wearing of tyres. The concentration of zinc in soil

Table 3. Mean and standard deviation (±) of heavy metal contents in plant at selected sites.

Site	Pb (Plant)	Cd (Plant)	Zn (Plant)	Cu (Plant)	Mn (Plant)
1	30.21 ± 0.01	9.76 ± 4.88	64.81 ± 42.43	3.33 ± 1.67	45.00 ± 8.66
2	28.69 ± 0.00	9.76 ± 0.00	55.56 ± 18.51	1.67 ± 0.00	20.00 ± 10.00
3	24.24 ± 0.03	9.76 ± 8.45	55.56 ± 32.07	1.67 ± 0.00	45.00 ± 13.23
4	20.05 ± 0.08	4.88 ± 0.00	27.78 ± 24.50	1.67 ± 0.00	20.00 ± 13.23
5	24.13 ± 0.06	9.76 ± 4.88	55.56 ± 9.26	1.67 ± 0.00	40.00 ± 18.03
6	21.27 ± 0.25	9.76 ± 4.88	55.56 ± 16.03	5.00 ± 1.67	55.00 ± 13.23
7	30.87 ± 0.00	14.63 ± 0.00	185.19 ± 9.26	1.67 ± 0.00	40.00 ± 13.23
8	30.40 ± 0.44	9.74 ± 8.45	46.30 ± 0.00	3.34 ± 2.89	55.00 ± 17.32
9	30.40 ± 0.00	9.76 ± 4.88	46.30 ± 9.26	3.33 ± 1.67	30.00 ± 5.00
10	30.56 ± 0.00	9.76 ± 0.00	101.85 ± 9.26	1.67 ± 0.00	30.00 ± 10.00
11	32.37 ± 0.24	9.76 ± 0.00	55.56 ± 32.07	3.34 ± 2.89	55.00 ± 8.66
12	31.56 ± 0.00	9.76 ± 4.88	46.30 ± 24.49	3.89 ± 2.55	110.0 ±18.03
13	30.03 ± 0.06	4.88 ± 0.00	95.68 ± 10.69	1.67 ± 0.00	25.00 ± 13.23
14	30.21 ± 0.01	4.88 ± 0.00	98.76 ± 5.35	1.67 ± 0.00	45.00 ± 5.00
15	29.29 ± 0.01	9.76 ± 0.00	83.33 ± 18.52	3.33 ± 1.67	50.00 ± 5.00
16	30.21 ± 0.01	4.88 ± 0.00	98.76 ± 14.14	1.67 ± 0.00	33.33 ± 20.82
17	30.51 ± 0.01	4.88 ± 0.00	83.33 ± 9.26	1.67 ± 0.00	40.00 ± 5.00
18	19.74 ± 0.01	9.76 ± 0.00	101.85 ± 0.00	1.67 ± 0.00	40.00 ± 5.00
19	31.33 ± 0.23	4.88 ± 0.00	46.30 ± 33.38	3.33 ± 1.67	95.00 ± 8.66
20	29.53 ± 0.06	4.88 ± 0.00	83.33 ± 27.78	1.67 ± 0.00	50.00 ± 5.00
A	5.03 ± 0.06	9.76 ± 8.45	52.47 ± 5.35	1.67 ± 0.00	55.00 ± 5.00
B	4.10 ± 0.00	9.76 ± 4.88	55.56 ± 0.00	1.67 ± 0.00	45.00 ± 10.00
C	6.23 ± 0.02	14.63 ± 4.88	46.30 ± 0.00	1.67 ± 0.00	50.00 ± 13.23
D	0.00 ± 0.00	9.76 ± 0.00	33.95 ± 35.05	1.67 ± 0.00	50.00 ± 13.23
E	0.00 ± 0.00	11.38 ± 2.81	83.33 ± 18.52	1.67 ± 0.00	55.00 ± 5.00
F	7.73 ± 0.45	9.76 ± 0.00	92.59 ± 18.52	1.67 ± 0.00	25.00 ± 8.66
G	0.00 ± 0.00	9.76 ± 0.00	37.04 ± 32.07	1.67 ± 0.00	50.00 ± 5.00
H	0.00 ± 0.00	9.76 ± 0.00	33.95 ± 5.35	1.67 ± 0.00	70.00 ± 17.32
I	10.20 ± 0.00	14.63 ± 4.88	46.30 ± 0.00	1.67 ± 0.00	40.00 ± 5.00
J	0.00 ± 0.00	14.63 ± 9.76	27.78 ± 0.00	1.67 ± 0.00	30.00 ± 13.23

samples ranged from 41.66 (site D) – 237.96 mg/kg (site 7). The lowest value of Zn obtained in this study is lower than the reported value of 4.75 – 16.16 mg/kg in 'uncontaminated' soil in another area of the country (Alexander and Pasquini, 2004). However, the range of Zn in the study is lower than 300 – 530 mg/kg reported in a similar study (Harrison et al., 1980). Since no major industry exists in the study area such as metal smelting, primary sources of Zn may assume are probably the attrition of motor vehicle tyre rubber exacerbated by poor road surfaces, and the lubricating oils in which Zn is found as part of many additives.

The mean ranged of Cu in surface soil ranged from 1.60 – 48.00 mg/kg. Cu is derived from engine wear, from thrust bearings, bushing and bearing metals, which are common along roadside in the study sites. However some studies show much higher contamination levels (Ndiokwere, 1984; Ho and Tai, 1988), but the results obtained is higher than 18.00 and 1.48 mg/kg reported by Kakulu (2003) and Awofolu (2005) respectively in a similar study.

Soil generally contains 200 – 3000 mg/kg of Mn with an average value of 600 mg/kg (Lindsay and Novell, 1979). In the present study, amount of Mn ranged from 76.00 – 132 mg/kg. The highest level of Mn obtained in this study was lower than 408 mg/kg reported by Ho and Tai (1988). The levels of Mn in soils were relatively low, implying contamination of the metal, if present, has been

mild (Albasel and Cottenie, 1985).

Correlation calculation performed on the heavy metals in soil showed that significant positive correlation are present between Zn and Cu, Pb and Cu. Insignificant positive correlation were found between Zn and Pb, Zn and Cd, Zn and Mn, Cu and Cd, Pb and Cd, Cd and Mn while insignificant negative correlation were found between Cu and Mn, and Pb and Mn. However, the insignificant positive or negative correlations between metals indicate that the appearance of local high concentration for one metal by possible contamination does not necessarily indicate high values for other metals. It may also indicate different sources or biogeochemical behaviours.

Trace metal composition of plants, *(sida acuta burm. f)*

Mean and standard deviation of mean of Pb, Cd, Zn, Cu and Mn in plant samples collected from different site of sampling period are presented Table 3. Plants leaves are known to reflect the elements inputs for a known exposure time (Alfani et al., 2004). The highest content of Cu was found in plants from site 12. Normally, plant metal levels for Cu, Zn and Pb vary in the range of 5 – 20 mg/kg dry wt, 25 – 200 mg/kg dry wt and 1 – 12 mg/kg dry wt, respectively (Fleming and Parle, 1977). High level of Pb and Zn in plant has been reported in similar studies (Ho and Tai, 1988; Otte et al., 1991). Cu levels in plant were generally lower than the tolerable range reported by Fleming and Parle (1977) in uncontaminated soil. However the level of Cd in this study was higher than < 2 mg/kg reported by Ho and Tai (1988) and Awofolu (2005) in similar studies. Indication shows that ruminant that wonders and grazes along roadside feed on these plants and metal accumulation in their bodies is highly probable, indirectly entering the food chain. Also Mn obtained in plants was generally lower than 218 mg/kg reported by Ansari et al. (2003), implying that contamination of the metal, if present has been mild.

Chambers and Sidle (1991) found that metal levels highly vary when related to soil metal levels and, according to Fleming and Parle (1977), the uptake of heavy metal varies widely depending on the plant species being studied. They also found that metal uptake was controlled by such variable as pH, organic matter content and soil type. Generally, most of heavy metals were less available to plants under alkaline conditions, than under acid conditions (Hess, 1971). However, the present results show opposite pattern to the expected, with the fact that Cd plant level were found higher than soil levels in all of the plant analyzed with the exception of few ones. This indicates that Cd uptake by plant is not restricted at these sites by pH or other factors. The high Cd content in plant appears to be due to a direct deposition and foliar absorption more than the translocation from roots to the upper part of the plants.

Conclusion

For the soil sample, the mean concentration of the five metals for this study were found to follow decreasing order; Zn > Mn > Pb > Cu > Cd, while in plant samples they were found to follow decreasing order; Zn > Mn > Pb > Cd > Cu. Results obtained in this study generally revealed the presence of metals in plants and soils along roads in Kaduna metropolis. Most probable sources of these metals are from motor vehicles, wastes from petroleum products such as lubricating oil that are dumped along these roads and from industrial emissions via atmospheric deposition, although further study is needed to confirm these.

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