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Analysis of some heavy metals in *Guiera senegalensis* plants from the vicinity of a Kaolin milling plant in Alkaleri Bauchi State, Nigeria using Neutron Activation Analysis (NAA)

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Abstract

This study was conducted to determine the concentration of heavy metals in samples of Guierasenegalensis from the vicinity of a Kaolin milling plant in Alkaleri Bauchi State. A total of twelve samples were collected at different sampling points within the vicinity of the Kaolin milling plant. 11 elements were analyzed using Neutron Activation Analysis (NAA). The concentrations of elements arein the range of 0.15 ± 0.03-2.60 ± 0.04mg/Kg for Co, 53.0 ± 18.55 - 343.5 ± 7.56mg/Kg for Fe 334.8 ± 1.67 - 1708 ± 102.5mg/Kg for Mn 11.01 ± 2.3 - 43.15 ± 2.9mg/Kg for Zn 2.49 ± 0.09 - 9.04±3.16mg/Kg for Cu 0.14 ± 0.01 - 2.46±0.05mg/Kg for As 0.49 ± 0.17 - 6.69 ± 1.31mg/Kg for V 0.011±0.00 - 0.031±0.00 for Cr 0.003 ± 0.001 - 0.37±0.015 mg/Kg for Sb 0.0065 ± 0.002 - 0.017 ± 0.004mg/Kg for Cd and 13.6 ± 4.76 - 103±26mg/Kg for Ba. The levels of the elements determined are in the order Mn>Fe>Ba>Zn>Cu>V>Co>As>Sb>Cr>Cd. Most of the elements are present in most samples but some were however below the detection limit of the instrument in very few samples. The mean concentration of the elements at different direction showed no significant difference except for Cr (P<0.05).

Keywords: Heavy metals, *guiera senegalensis,* kaolin, NAA, alkaleri, milling plant.

Introduction

Metals form an important class of toxic substances which occur in most occupational and environmental activities. The impact of these toxic agents on human health is currently an area of intense interest due to the ubiquity of exposure[1]. Heavy metals contributions in the biosphere have increased by the anthropogenic activities as a result of industrialization and urbanization.Heavy metals can be classified essential elements which are useful for plant nutrition, they exhibit phytotoxiceffects only in relatively high concentrations (Cu, Fe, Mo, Zn, Co, Ni) and into the non-essential elements like As, Cd, Cr, Hg, Pb and Ti which, due to frequent use in industrial processes, are deposited even in remote ecosystems and exhibit a potential phytotoxic risk[2].Heavy metal toxicity in plants varies with plant species, specific metal, concentration, chemical form, soil composition and pH, as many heavy metals are considered to be essential for plant growth[3]. Anthropogenic activities greatly influenced the availability of heavy metals in the environments[3]. Excessive concentration of heavy metals in the environment is of great concern because of their non-biodegradability. Therefore, their persistence in the environment portends health hazard to plants and animals and consequently trigger ecological imbalance in the ecosystem[4,5]. Some of heavy metals (Fe, Cu and Zn) are essential for plants and animals[6,3]. The availability of heavy metals in medium varies, and metals such as Cu, Zn, Fe, Mn, Mo, Ni and Co are essential micronutrients[7,3], whose uptake in excess by the plant result in toxic effects[8,3]. They are also called as trace elements due to their presence in trace (10 mg kg^{-1}, or mg L^{-1}) or in ultra trace (1g kg^{-1}, or l g L^{-1}) quantities in the environmental matrices. The essential heavy metals (Cu, Zn, Fe, Mn and Co) play biochemical and physiological functions in plants and animals such as participation in redox reaction, and being an integral part of several enzymes[3].

The different types of clay minerals particularly montmorillonite, kaolinite and illite in soil adsorb trace elements[9]. Studies conducted by Bonglaisin *et al* [10] shows that kaolin is contaminated not only with Pb but Cd and Hg as well. The differences in Pb content at district levels is statistically significant P=0.02 (P<0.05). The fate of heavy metals, radionuclides, pesticides, organics, and other contaminants in the environment was partly determined by their physical and chemical interactions with kaolin and other clay materials[11]. In hot and humid milieu, Kaolin develops negative charges between its layers and will attract positive charges (such as heavy metals) resulting to contamination[12,10]. Metal toxicity has high impact and relevance to plants and consequently it affects the ecosystem, where plants form an integral component[3].

Guiera senegalensis, a shrub of the savannah re-gion of west and central Africa is widely used in traditional medicine for the remedy of many ailments/diseases. Its leaves extract is being used against dysentery, diarrhea, gastrointestinal pain and disorder, rheumatism and fever[13,14].

Materials and methods

Samples collection and preparation: Samples of *Guiera senegalensis* was collected from the vicinity of Kaolin milling plants. Samples were collected from twelve sampling sites (Figure-1). The branches about 30-40cm and parts of roots were collected and placed in a polypropylene bag. The sample collected was washed thoroughly with tap water then with distilled water to remove soil and dirt. It was then dried in the lab at room temperature. The dried plant samples were pulverized using porcelain pestle and mortar then sieved with 2 mm mesh.

Sample preparation for NAA analysis: The method described by Jonah *et al.*[15] with some modification was adopted. This consists primarily of weighing and packaging of samples and wrapped in polyethylene bags. Before weighing the samples, the polyethylene bags and rabbit capsules were cleaned by soaking in 1:1 HNO_3 (Nitric acid) for 3 days and washed with de-ionized water to sterilize and oven dried. The plant samples were weighed with a four-digit Melter model weighing balance in the range of 250mg to 300mg encapsulated, heat sealed in a polyethylene material and package finally into a polyethylene vial as adopted for NIRR-1 at Centre for Energy Research and Training ABU, Zaria.

Sample Irradiation: The protocols for sample irradiation were performed in two irradiations stages as described by Jonah *et al.,* Oladipo *et al.*[15,16]. Arrangements of elements with short life are determined using the short live protocol. Samples packaged in the vials are sent to the reactor irradiation sites using the rabbit system (pneumatic transfer system) at a time and the neutron flux was determined by theoretical expression based on estimated activity of the sample[15]. The first irradiation was designed to capture short half-lives radionuclide, the second irradiation was designed to capture long half-life-radionuclide in the inner channel of the Miniature Neutron Source Reactor (MNSR) operating at full power of 30 kW thermal with a neutron flux of flux of 2.5 x 10^{11} n/cm^2 s and irradiation period of 600s.

The long irradiation entailed wrapping samples in polyethylene films and stacks packing each inside the 7cm^2 rabbit capsule and heat-sealed for irradiation for 6h at maximum value of thermal neutron flux of 5x10^{11}n/cm^2s. The flux is kept constant by monitoring the neutron flux reading from a fission chamber connected to the micro-computer-controlled room. After the samples have been irradiated they were retrieved via the same pneumatic transfer of the rabbit to the control chamber where they were collected and kept in a glass chamber.Finally the identification of gamma ray of product radio-nuclides through their energies and quantitative analysis of their concentration were obtained by using the gamma ray spectrum analysis software WINSPAN 2004.

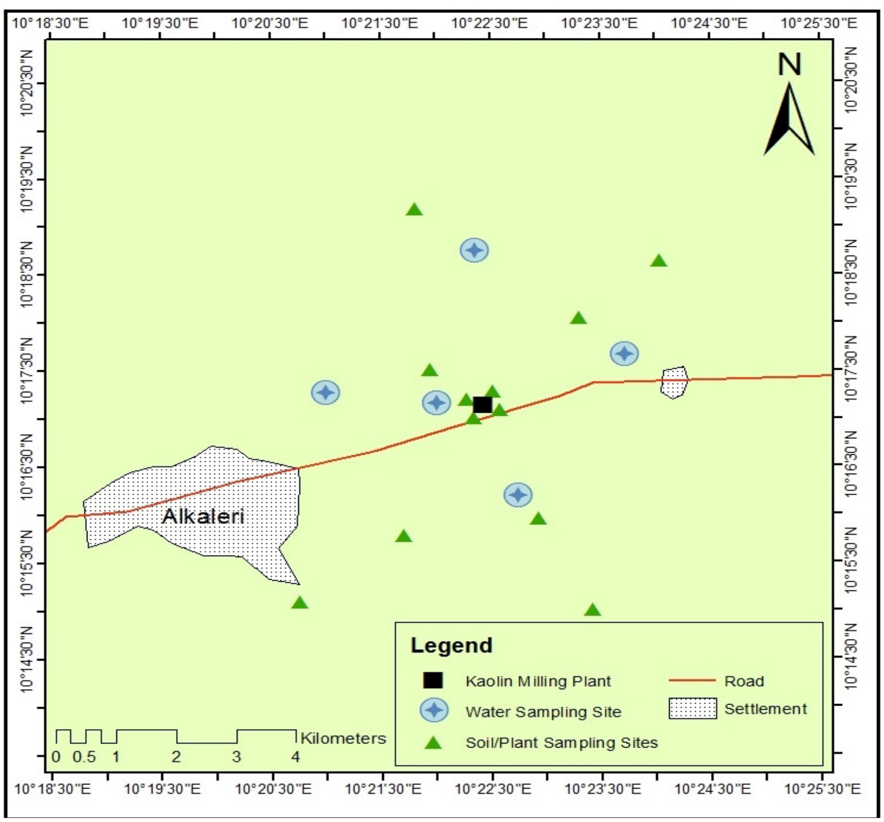

Figure-1: Map of study area showing sampling sites.

Standard reference material SRM 1547 (NIST PEACH LEAVES) was analyzed along with the samples for method substantiation and quality control purposes. From results obtained, it was observed that most of the elemental concentrations are comparable to the certified values. Neutron activation analysis is a non-destructively analytical technique[17]. The instrumental neutron activate analysis technique (INAA) was used for the analysis using NIRR-I at the Centre for Energy Research and Training ABU Zaria.

Results and discussion

Table-1 showed the concentration in mg/Kg of heavy metals analysed in *Guiera senegalensis* in the vicinity of Kaolin milling plant in Alkaleri, Bauchi state. The distribution of the elements is presented graphically in Figures-2-12.

Table-1: Heavy metal Concentration (Mg/Kg) in plant samples in the Vicinity of Kaolin Milling Plant.

Direction from Milling Plant	Distance in Km	Co	Fe	Mn	Zn	Cu	As
Northwest	0	1.29±0.02	102.7±24.5	553.2±5.0	21.8±2.0	4.10±1.4	1.29±0.03
	2	1.92±0.04	78.2±27.3	945.7±6.6	16.9±2.7	BDL	0.14±0.01
	4	2.58±0.04	156.1±46.5	797.3±6.4	25.6±3.6	7.50±2.6	1.26±0.03
Northeast	0	0.41±0.03	123.5±43.2	458.7±4.1	13.1±2.4	2.52±0.9	1.71±0.03
	2	0.88±0.04	343.5±7.6	1708.0±102.5	24.8±2.6	9.04±3.2	0.25±0.03
	4	0.99±0.03	53±18.6	952.8±6.7	11.0±2.3	BDL	0.61±0.02
Southwest	0	2.60±0.04	329.1±67.5	380.0±3.8	43.2±2.9	BDL	1.21±0.03
	2	0.33±0.02	196.9±68.9	412±2.1	15.0±1.9	BDL	0.87±0.03
	4	0.15±0.03	65.6±23	1547±7.7	BDL	BDL	1.66±0.04
Southeast	0	0.72±0.02	207.8±28.9	334.8±1.7	33.9±2.1	BDL	0.78±0.03
	2	0.71±0.02	130.8±37.1	348.3±1.7	33.4±2.6	2.49±0.1	1.02±0.03
	4	2.43±0.04	267.8±40.4	937.9±4.7	15.1±2.9	BDL	2.46±0.05

Table-1(a): Heavy metal Concentration (Mg/Kg) in plant samples in the Vicinity of Kaolin Milling Plant.

Direction from Milling Plant	Distance in Km	V	Cr	Sb	Cd	Ba
Northwest	0	1.12±0.3	0.022±0.007	0.037±0.01	0.038±0.005	80.7±16.9
	2	1.15±0.4	0.011±0.004	0.029±0.01	BDL	103±26.0
	4	BDL	0.031±0.01	0.018±0.01	0.014±0.004	BDL
Northeast	0	1.01±0.2	BDL	0.37±0.02	BDL	61.0±21.3
	2	1.80±0.4	BDL	0.052±0.6	0.006±0.002	BDL
	4	0.49±0.2	BDL	0.009±0.003	0.017±0.004	40.9±14.3
Southwest	0	6.69±1.3	0.019±0.007	0.30±0.01	0.011±0.004	13.6±4.8
	2	2.71±0.7	BDL	0.20±0.02	0.009±0.003	33.0±11.5
	4	6.13±1.4	0.031±0.011	0.08±0.02	BDL	BDL
Southeast	0	1.43±0.5	BDL	0.003±0.001	BDL	71.0±17.0
	2	3.01±0.9	0.017±0.006	0.017±0.006	0.008±0.003	19.1±6.7
	4	BDL	0.024±0.008	0.009±0.003	0.012±0.004	BDL

*BDL Below detection limits. † Concentrations are mean ± Standard error.

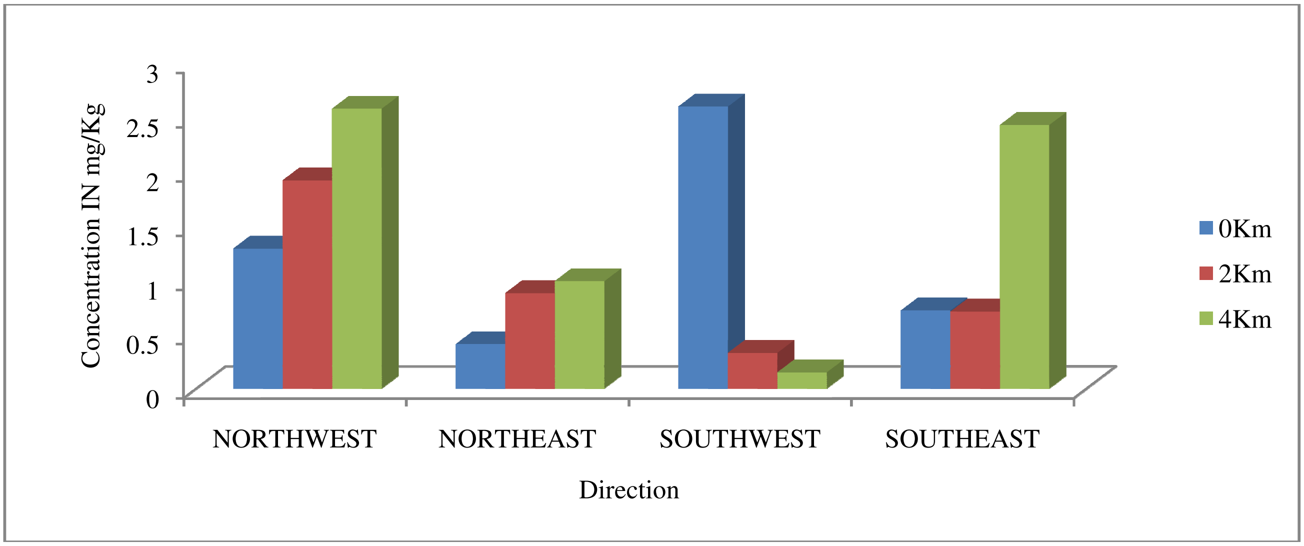

Figure-2: Distribution of Co in plant samples within the vicinity of Kaolin milling plant.

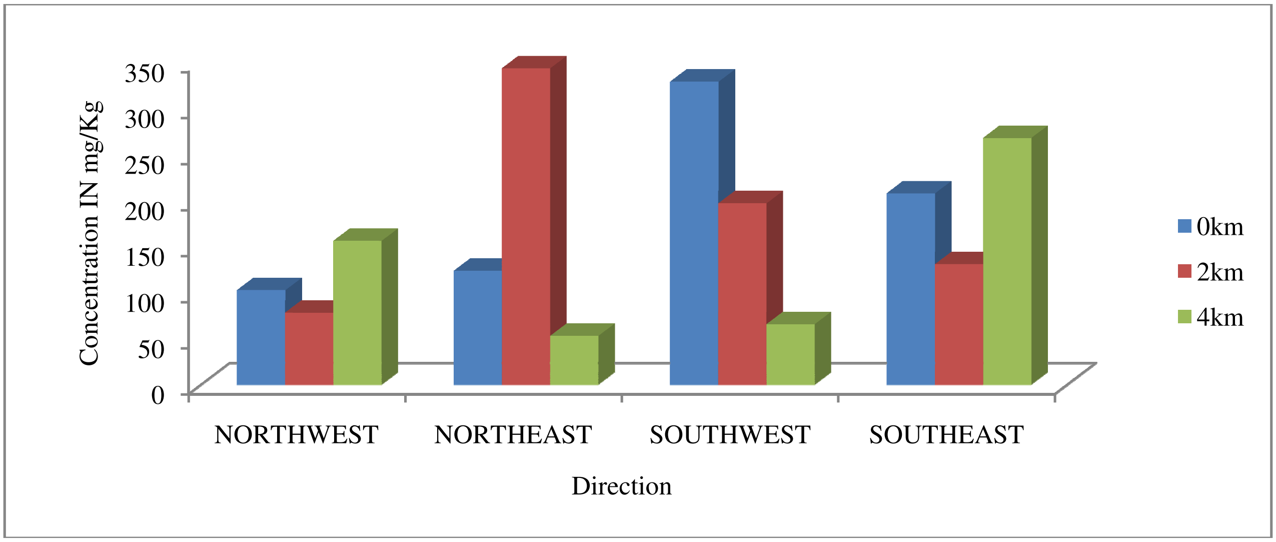

Figure-3: Distribution of Fe in plant samples within the vicinity of Kaolin milling plant.

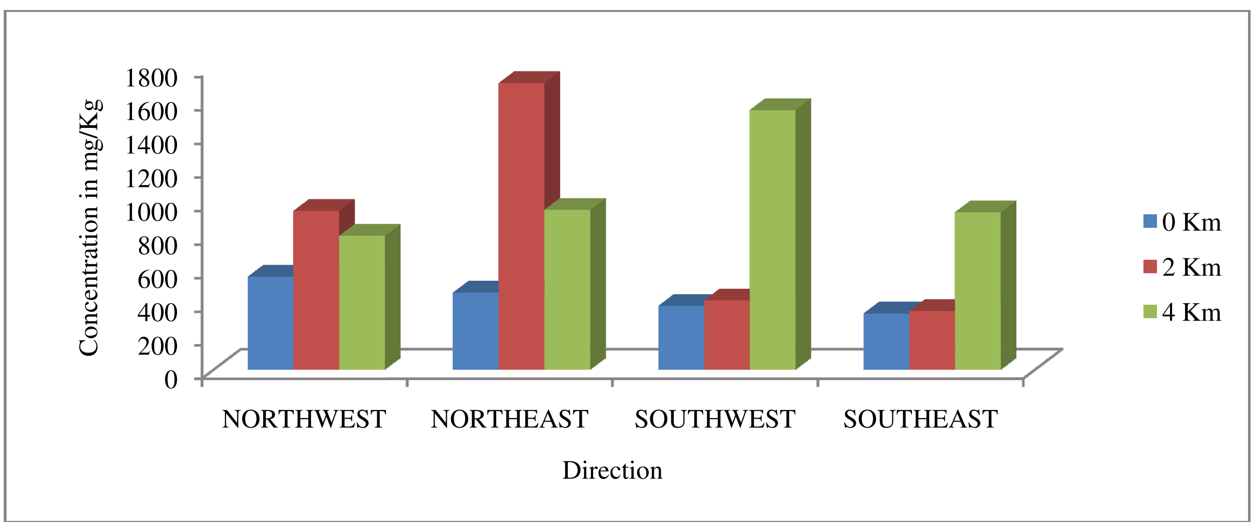

Figure-4: Distribution of Mn in plant samples within the vicinity of Kaolin milling plant.

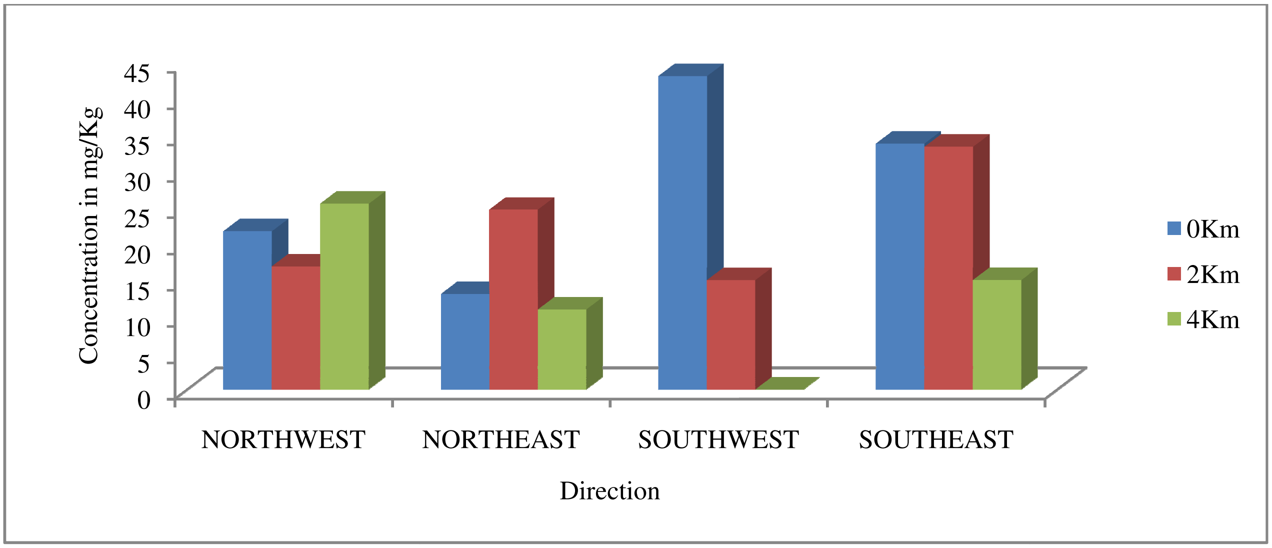

Figure-5: Distribution of Zn in plant samples within the vicinity of Kaolin milling plant.

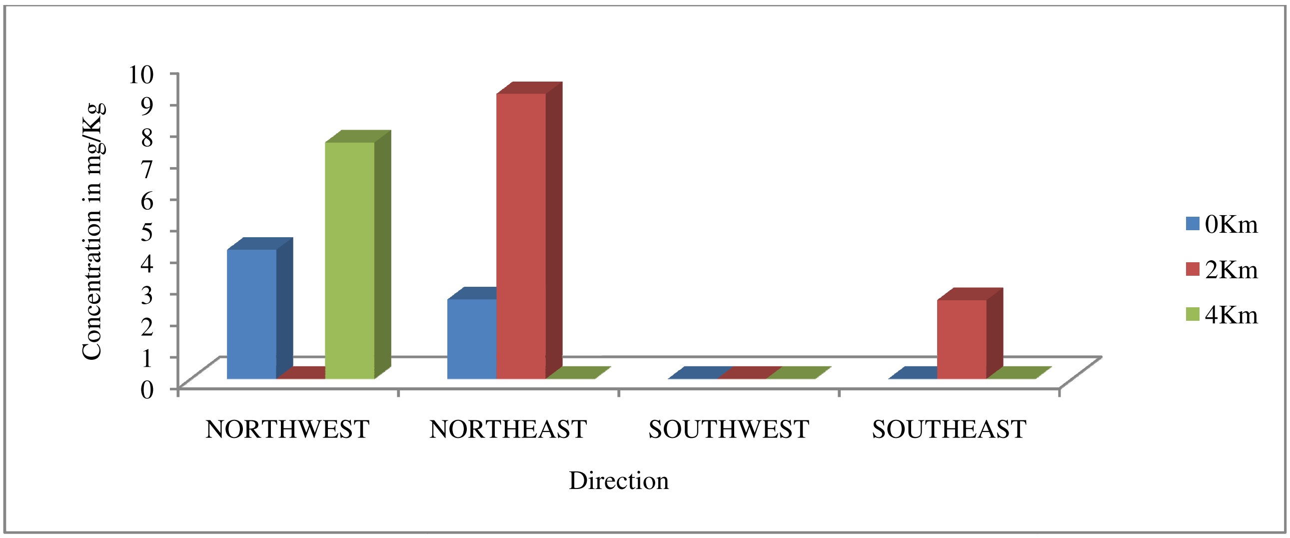

Figure-6: Distribution of Cu in plant samples within the vicinity of Kaolin milling plant.

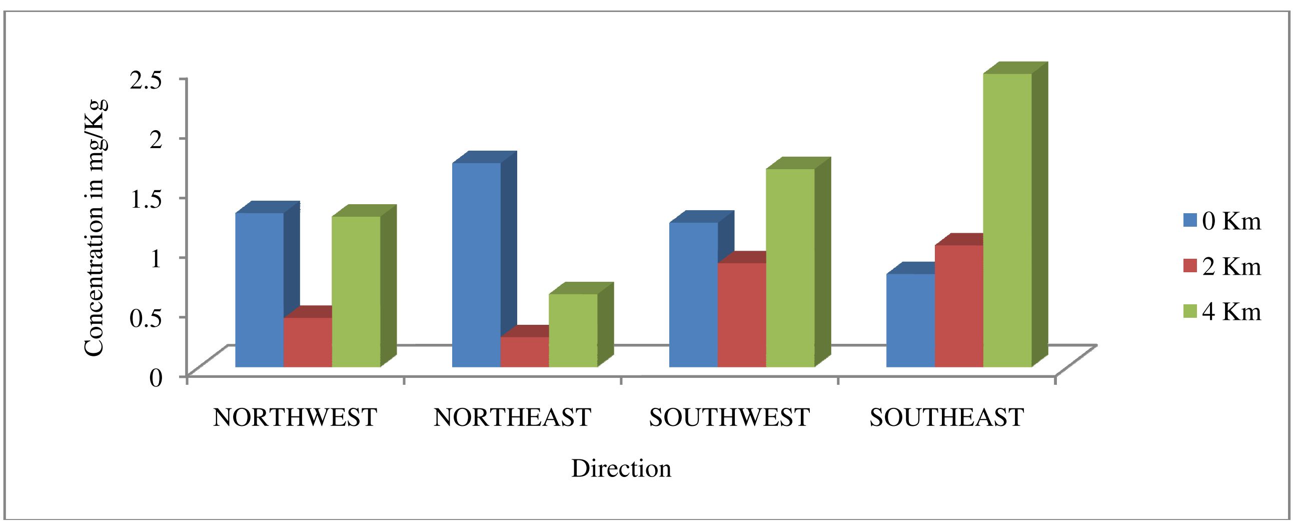

Figure-7: Distribution of As in plant samples within the vicinity of Kaolin milling plant.

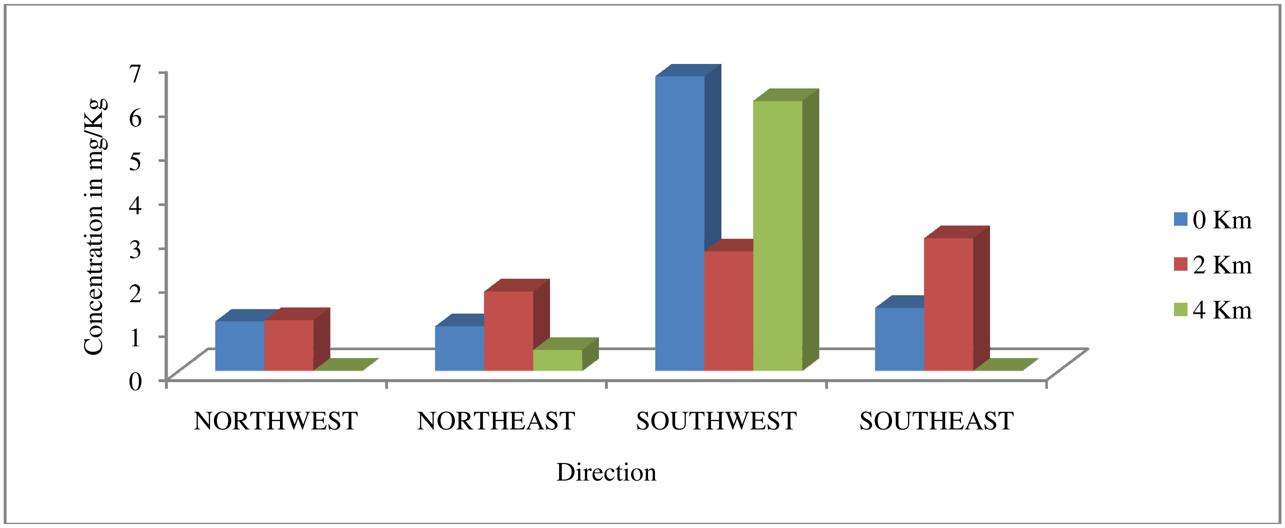

Figure-8: Distribution of V in plant samples within the vicinity of Kaolin milling plant.

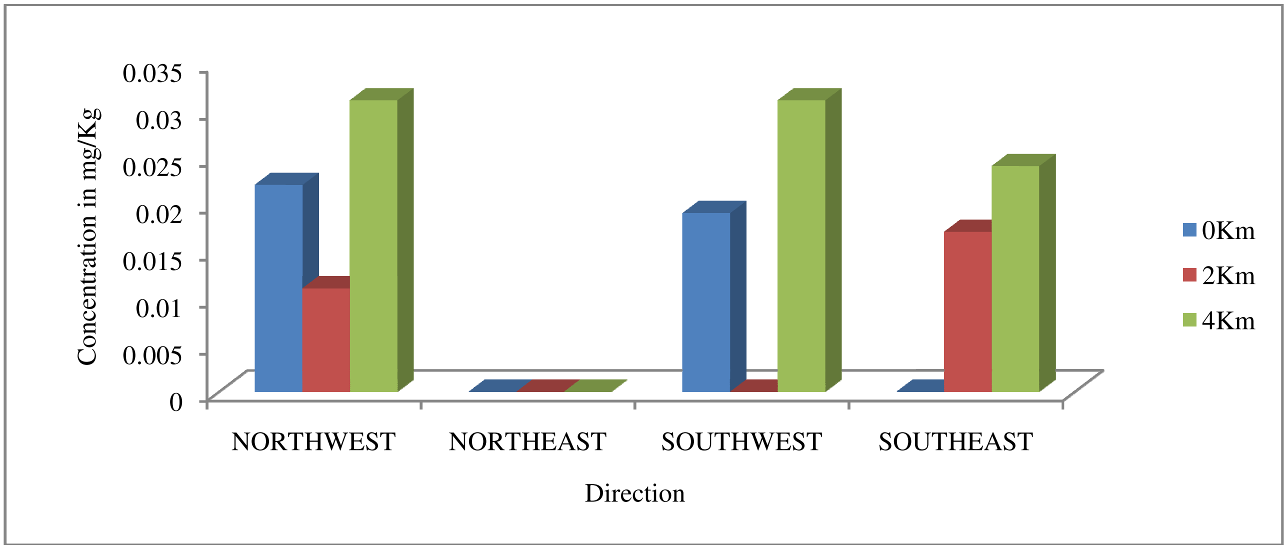

Figure-9: Distribution of Cr in plant samples within the vicinity of Kaolin milling plant.

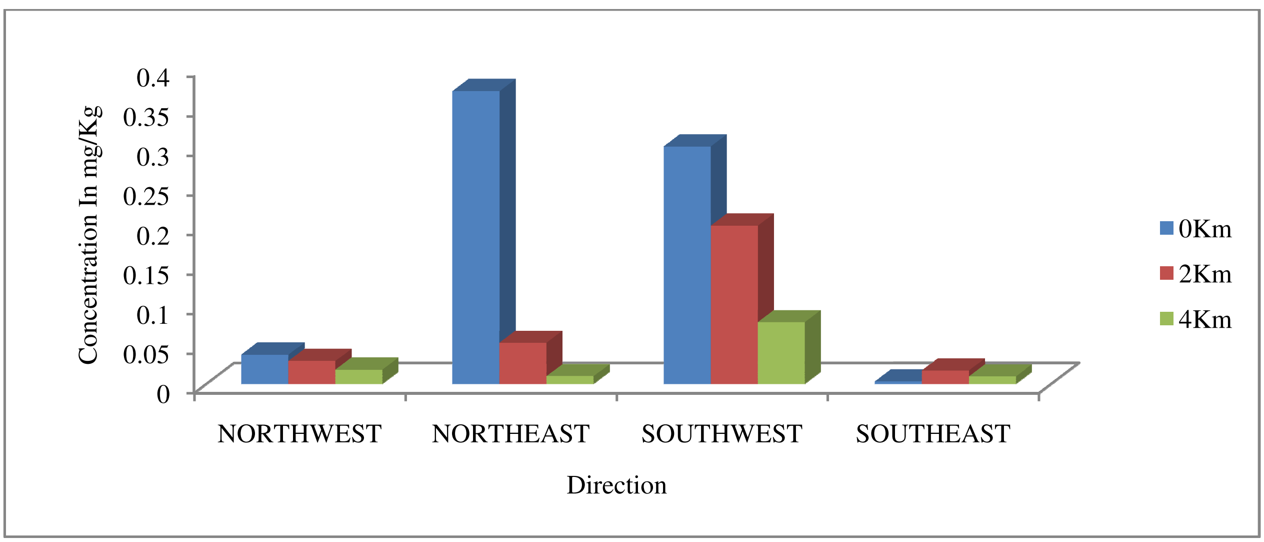

Figure-10: Distribution of Sb in plant samples within the vicinity of Kaolin milling plant.

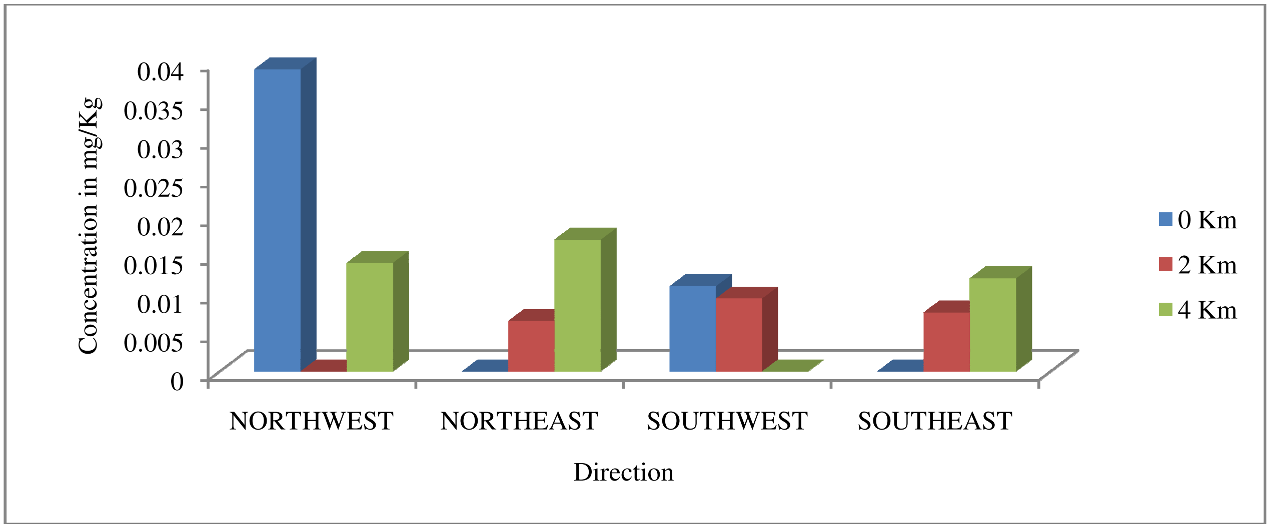

Figure-11: Distribution of Cd in plant samples within the vicinity of Kaolin milling plant.

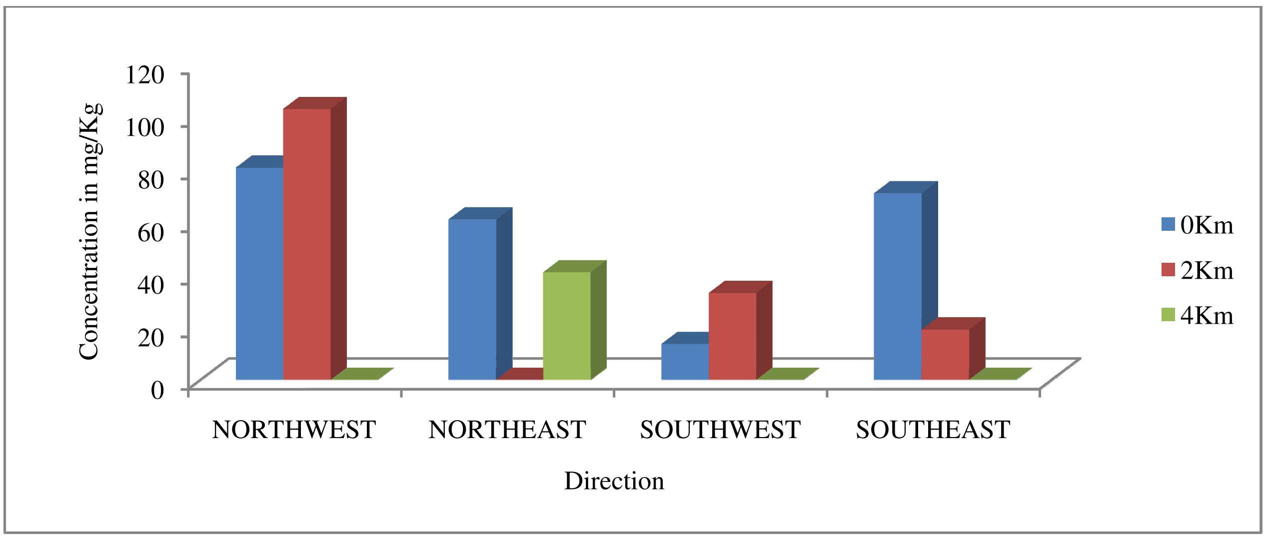

Figure-12: Distribution of Ba in plant samples within the vicinity of Kaolin milling plant.

Figure-2 show the distribution of Co in plant samples within the vicinity of Kaolin milling plant. Co has a mean concentration of 1.25±0.90mg/Kg with variability coefficient of 72%. The highest concentration of Co (2.60±0.04mg/Kg) was found in the sample at 0 km Southwest while the lowest concentration of Co (0.15±0.03mg/Kg) was found in the sample at 4 Km Southwest. The mean concentration of Co in all the directions showed no significant difference ($P < 0.05$). In plants, Co complex is found in the form of vitamin B12[3]. Excess Co has adverse effect on shoot growth and biomass[18,3] and also significantly decreased water potential and transpiration rate[3]. Misra and Mani[19] gave the concentration of Co in plants as 0.05-0.5µg/g[3].The concentration of Co in the plant samples analysed was in range of 0.15±0.03mg/Kg to 2.60±0.04mg/Kg.

Figure-3 showed the distribution of Fe in plant samples within the vicinity of Kaolin milling plant. Fe has a mean concentration of 171.3±99.3mg/Kg with variability coefficient of 58%. The highest concentration of Fe (343.5±7.56mg/Kg) was found in the sample 2 km Northeast and the lowest concentration (53.0± 18.55mg/Kg) was in the sample 4 km Northeast. The mean concentration of Fe in all the directions showed no significant difference ($P<0.05$). Iron as an essential element for all plants has many important biological roles in the processes as diverse as photosynthesis, chloroplast development and chlorophyll biosynthesis. Iron is a major constituent of the cell redox systems such as heme proteins including cytochromes, catalase, peroxidase and leghemoglobin and iron sulfur proteins including ferredoxin, acontiase and superoxide disumutase[3]. Misra and Mani[19] gave the concentration of Fe in plants as140 µg/g[3]. The samples analysed showed the concentration of Iron range of 53.0±18.55mg/Kg to 343.5±7.56mg/Kg. The concentration of Fe in *Guiera senegalensis* leaf extract according to Mohammed[14] is given as 497.36 mg/Kg.

Figure-4 showed the distribution of Manganese in plant samples within the vicinity of Kaolin milling plant. Mn has a mean concentration of 783.9±461.4mg/Kg with variability coefficient of 59%. The highest concentration of Mn (1708±102.5mg/Kg) was found in the sample 2 km Northeast while the lowest concentration (334.8±1.67mg/Kg) was found in the sample 0 km Southeast. The mean concentration of Mn in all the directions showed no significant difference (P<0.05). Manganese is an essential element for plants, intervening in several metabolic processes, mainly in photosynthesis and as an enzyme antioxidant-cofactor[20]. Nevertheless, an excess of this micronutrient is toxic for plants. Mnphytotoxicity is manifested in a reduction of biomass and photosynthesis, and biochemical disorders such as oxidative stress[20]. Misra and Mani[19] gave the concentration of Mn in plants as 15-100µg/g [3]. The concentration of Mn in all the samples analysed were farabove this value.

Figure-5 showed the distribution of Zinc in plant samples within the vicinity of Kaolin milling plant Zn has a mean concentration of 21.14±11.8 mg/Kg with a variability coefficient of 56%. The highest concentration of Zn (43.15± 2.9mg/Kg) was detected in the plant sample collected at 0 Km Southwest and the lowest concentration of Zn (11.01±2.3mg/Kg) was found in the sample at 4Km Northeast. Zn was not detected in sample collected from 4Km Southwest. The mean concentration of Zn in all the directions showed no significant difference (P<0.05). Zinc is an essential element for all living organisms[21]. It plays an important role in catalyzing biochemical reactions by participating in the formation of an enzyme-substrate system, protein translation, gene copying and multiplication of a genetic chain[22,21]. Zinc is responsible for disturbing the functions of mitochondria[22,21].Misra and Mani[19] gave the concentration of Zn in plants as 8-100µg/g[3]. The concentration of Zn in the plant samples analysed was in range of 11.01±2.3mg/Kg to 43.15± 2.9mg/Kg. The concentration of Zn in *Guiera senegalensis* leaf extract according to Mohammed[14] is given as 43.70 mg/Kg.

Figure-6 showed the distribution of Copper in plant samples within the vicinity of Kaolin milling plant. Cu has a mean concentration of 2.14±3.20mg/Kg with variability coefficient of 149%. Highest concentration of Cu (9.04±3.16mg/Kg) was found in the sample 2Km Northeast and lowest concentration (2.49±0.09mg/Kg) was in the sample 2km Southeast. Cu was detected in 5 samples while the concentrations in 7 samples were below detection limit. The mean concentration of Cu in all the directions showed no significant difference (P<0.05). Copper (Cu) is considered as a micronutrient for plants[23,3] and plays important role in CO_2 assimilation and ATP synthesis. Cu is also an essential component of various proteins like plastocyanin of photosynthetic system and cytochromeoxidase of respiratory electron transport chain[24,3]. Excess of Cu in plants is cytotoxic, induces stress and causes injury to plants. This leads to plant growth retardation and leaf chlorosis[25,3]. Misra and Mani[19] gave the concentration of Cu in plants as 4.15µg/g [3]. Two samples were found to be above this value, those at Northeast, 2 Km (9.04±3.16mg/Kg) and Northwest 4 km (7.494 ±2.62mg/Kg). The concentration of Cu in *Guiera senegalensis* leaf extract according to Mohammed[14]is 19.80 mg/Kg.

Figure-7 showed the distribution of Arsenic in plant samples within the vicinity of Kaolin milling plant. As has a mean concentration of 1.10±0.65mg/Kg with a variability coefficient of 59%. The highest concentration of As (2.46±0.05mg/Kg) was found in the sample collected from 4 km Southeast while the lowest concentration (0.14±0.01mg/Kg) was found in the sample collected from 2km Northwest. The mean concentration of As in all the directions showed no significant difference (P < 0.05). Misra and Mani[19] gave the concentration of As in plants as 0.02-7µg/g[3] The concentration of As in all samples fall within this range. Arsenic is a well known carcinogenic element that can harm not only human health but, plant and bacteria as well. Replicated experiments confirmed that Arsenic accumulates in the different tissues in different parts of the plant and, adversely affects the growth and productivity of the plants[26].

Figure-8 showed the distribution of Vanadium in plant samples within the vicinity of Kaolin milling plant. V has a mean concentration of 1.61±1.71mg/Kg with variability coefficient of 106%. The highest concentration of V (6.69±1.31mg/Kg) was found in the sample collected at 0 km Southwest and the lowest concentration (0.49±0.17mg/Kg) was found in the sample collected at 4 km Northeast. V was not detected in 2 samples; samples collected at 4 Km Northwest and 4 Km Southeast. The mean concentration of As in all the directions showed no significant difference (P<0.05). The effect of V on plant growth has also been reported in soybean. It was found that if the concentration of V added to the fluvo-aquic soil exceeded 30 mg/kg soil, significant decrease in yields of shoots and roots were obtained, seedling leaves were yellow and withered[27,28].

Figure-9 showed the distribution of Chromium in plant samples within the vicinity of Kaolin milling plant. Cr has a mean concentration of 0.013±0.012 mg/kg with variability coefficient of 92%. The highest concentration of Cr (0.031±0.01mg/Kg) were found in samples collected at 4 km Northwest and 4 km Southwest while the lowest concentration of Cr (0.011±0.00 mg/kg) was found in the sample collected at 2 km Northwest. Concentration of Cr was below detection limit in 5 out of the 12 samples analyzed. The mean concentration of Cr showed significant difference (P<0.05) between the mean concentration of Cr in Northwest radius and Northeast radius while there was no significant difference between the mean of other directions. Misra and Mani[19] gave the concentration of Cr in plants as 0.2-1µg/g[3]. The concentrations of Cr in all the samples were below this value.

Figure-10 showed the distribution of Antimony in plant samples within the vicinity of Kaolin milling plant. Sb has a mean concentration of 0.093±0.13mg/Kg with coefficient of variability 139%. The highest concentration of Sb (0.37±0.015

mg/Kg) was found in the sample collected at 0 km Northeast and the lowest concentration (0.003±0.001mg/Kg) was found in the sample collected at 0 km Southeast. The mean concentration of As in all the directions showed no significant difference (P<0.05). Sb can damage plants, including growth retardation, inhibition of photosynthesis, decreases in the uptake of certain essential elements and decreases in the synthesis of certain metabolites[29]. The excessive accumulation of Sb can be toxic to plants and can inhibit their growth[29]. The levels of 5–10 mg kg^{-1}Sb in plant tissues have been suggested to be excessive or toxic[29,30]. Misra and Mani[19] gave the concentration of Sb in plants as 0.02- 0.06µg/g[3].

Figure-11 showed the distribution of Cadmium in plant samples within the vicinity of Kaolin milling plant. Cd has a mean concentration of 0.0096±0.011mg/Kg with variability coefficient of 114%. The highest concentration of Cd (0.017± 0.004mg/Kg) was found in the sample collected at 4 km Northeast and the lowest concentration (0.0065±0.002mg/Kg) was found in sample collected at 2 km Northeast. Concentration of Cd was below detection limit in 4 out of the 12 samples analyzed. The mean concentration of Cd in all the directions showed no significant difference (P <0.05). Cd is a non essential element that negatively affects plant growth and development[31]. Cd can alter the uptake of minerals by plants through its effects on the availability of minerals from soil or through reduction of soil microbes[32,31]. Misra and Mani[19] gave the concentration of Cd in plants as 0.1- 2.4 µg/g[3]. The concentrations of Cd in this work are far below the concentration of Cd in Misra and Mani[19]. Cd concentration from 10-20 mg/Kg in plant tissue is expected to result in 10 percent loss in crop yield[33]. Concentration in leaf tissue that is excessive or toxic to various plant species range from 5 to 30 mg/Kg[33].

Figure-12 showed the distribution of Barium in plant samples within the vicinity of Kaolin milling plant Ba has a mean concentration of 35.2±36.1mg/Kg with a variability coefficient of 102%. The highest concentration of Ba (103±26 mg/Kg) was found in the sample collected from 2 Km Northwest and the lowest Ba concentration (13.6±4.76mg/Kg) was found in the sample collected at 2 Km Southwest. The concentration of Ba was below detection limit in 4 samples. The mean concentration of Ba in all the directions showed no significant difference (P < 0.05). The availability of Ba to plant is greatly influenced by pH of the soil, with Ba more available under acidic conditions[33]. The concentration of Ba in leave tissue that has been reported as excessive or toxic to various plant species is 500 mg/Kg[33]. A concentration of 500 mg/Kg has been proposed by Efroymson*et al*. as a benchmark screening value for Ba phytotoxicity[33].

Conclusion

Greater numbers of heavy metals analyzed have highest concentration at 0Km and 2Km radii of the milling plant (4 elements each) while 3 elements have highest concentration at 4 Km radius. This implies that the heavy metals are predominant at distance of 0-2Km from the milling plant. Despite the activities of the milling plant, many other factors may contribute to increase in concentration of heavy metals in the samples of *Guiera senegalensis* from the vicinity of the milling plant. These factors influence the uptake of metals they include temperature, soil pH, soil aeration, competition between plant species, the type of plant, it size, the root system, the availability of the elements in the soil, the type of leaves, soil moisture and plant energy supply to the roots and leaves[35,3].

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