

METAL CONCENTRATION OF LIQUID EFFLUENTS AND SURROUNDINGS OF A PHARMACEUTICAL INDUSTRY

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ABSTRACT. Major and trace metals (Mg, Na, K, Ca, Fe, Zn, Cu, Sn, Al, Pb, As, Cr, Cd, Mn and Ti) in liquid effluents, soil sediments and plant parts (roots and leaves) from Tisco Nigeria Limited, Akure, were determined in both open effluent channel and closed direct tank. The plant in the open effluent channel was *Pennisetum purpureum* while the one around the direct tank was *Chloris pilosa*. The correlation coefficient (Cc) of the metals in the open channel gave the values: soil sediments/water (0.61), roots/leaves (0.709); and (0.34), (0.91), respectively, in direct tank. F-test values showed that 67 % of the metals were significantly different ($p < 0.05$) among the samples. The soil sediments would serve as reservoir for all the metals determined. This was also the case for both plant roots with species variation. The plant leaves showed evidence of bioaccumulation of some metals. The high levels of Pb, As and Cd in the samples call for concern as environmental contaminants.

KEY WORDS: Major and trace metals, Liquid effluents, Soil sediments, Leaves, Roots

INTRODUCTION

The pharmaceutical industry comprises of those companies that produce drugs and pharmaceuticals that kill or inhibit disease-causing microorganisms. Tisco Nigeria Limited is a pharmaceutical company that produces disinfectants, antiseptics and other pharmaceuticals.

Industrial effluents, wastes and emissions, contain toxic and hazardous substances most of which can be detrimental to human health [1]. These include heavy metals such as Cd, Co, Hg, Pb, etc. and toxic organic chemicals. Metal contamination from pharmaceutical industries comes from various sources. Some metals involved in such industries are: Na, K, Mg, Ca, Hg in the production of products where reaction vessels are sources of Cu and Fe. For examples: Zn and Na are involved in the production of methyl acetyl ester, $ZnCl_2$ is a condensing agent in the manufacture of 1,3-dihydroxy-4-hexylbenzene and its intermediate is purified/reduced with zinc amalgam, AgCl is involved in the production of vitamin B₁, Pt or Pd and $Na_2S_2O_4$ are involved in producing vitamin B₂, calcium acetate and calcium hydroxide are by-products in the production of chloroform, Cu, Cr and CH_3ONa are involved in the production of vitamin C while brine and Grignard reagents are involved in the synthesis of darvon (d-propoxyphene HCl) [2]. Metal catalysts are also sources of metal contaminants.

Elephant grass, *Pennisetum purpureum* Schumach (Poaceae) is a robust perennial up to 8 inches high and 2.25 cm diameter at the base; commonly occurs near the banks of streams. Spikes, 14-30 mm broad (excl. bristles); leaf-blades up to 40 mm broad; anther tips with a tiny tuft of hairs; rachis densely pubescent; persistent peduncles obscure, involucre subsessile; spikelets 4-7 mm long; lower floret variable. It is common throughout tropical Africa, and widely introduced elsewhere in the tropics [3]. *Chloris pilosa* Schumach (Poaceae) has a lemmas with short ciliate. Spikelet conspicuously cuneate upper lemmas 2, truncate, empty; awns 2, the longest about 3 mm long. An annual grass, 30-60 cm high; common by roadsides and old farm [3].

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The present work evaluated the concentration of both major and trace metals in the effluent channels and their environments in a pharmaceutical industry. This type of work is necessary to alert the public of the hazards it is exposed to if such effluents are exposed or released to the public without treatment and more so when the plants around them bioaccumulate and biotransfer harmful minerals to ruminants that serve as protein sources to human beings.

A study close to this type of work was a case study of environmental risk assessment studies of heavy metal contamination in the industrial area of Kattedan, India. The industries involved were battery manufacturing, metal plating, textile and pharmaceuticals production and others. Samples examined were soils and forage grass as well as human exposure assessment [4]. Some of the metals under study are also known to be deleterious, e.g. Pb causes toxicity in the body when it accumulates, disease caused by Cd poison is known as *itai-itai* while As affects the skin causing skin cancer in its severe form.

EXPERIMENTAL

Study area

The soil sediments, liquid effluents and plant samples were collected from Tisco Nigeria Limited, Akure. Akure is in the Akure South Local Government Area of Ondo State, Nigeria. Akure is the capital of both the Local Government and the Ondo State. Tisco Nigeria Limited is located in the industrial area of the town.

Sampling procedure and treatment

The first set of samples was collected from the closed direct tank where liquid wastes generated were generally discharged. The direct tank, which was like a septic tank, was built of staggered blocks which allowed part of the liquid waste to seep through the spaces at the sides. Liquid and soil sediment samples were collected from the tank. Plant samples *Chloris pilosa* Schumacher (Poaceae) were also collected from this place (on the soil over the underground tank). The second set of samples was collected from the open effluent channel where dirt was washed away from production machines. Liquid, soil sediments and plant samples were collected from there. The plant samples *Pennisetum purpureum* Schumacher (Poaceae) (elephant grass) were collected at the open effluent channel. Collections were done on the same day. Liquid samples were collected into clean 1-litre rubber containers while soil samples were collected into polyethylene bags. All the plant samples were in their young vegetative (immature) stages. Sample collections were done in triplicate.

The liquid effluent samples' temperatures were taken immediately at the site of collection, the electrical conductivity was also measured immediately the samples were collected. The liquid samples were stored in the deep freezer until analyses were carried out. The plants and soil sediments were air-dried in the laboratory. After drying, the different soil samples were ground using the laboratory pestle and mortar. The soil samples were sieved using a 850 µm mesh sieve. The soil samples were packed in sample bottles and labelled. This procedure was used for all the soil sediments. The plant samples were separated into leaves, stems and roots. Each part (except stem) was ground using pestle and mortar and the resultant powder packed into well-labelled sample bottles. The labelled and packaged soil and plant samples (roots and leaves) were then kept in a cool dry place pending analyses. The roots and leaves were gently washed in distilled deionised water and water drained in folds of filter paper before final air-drying and processing. Dust was not allowed to settle on the samples during drying.

Physico-chemical analysis

Temperature was measured using a simple thermometer calibrated in °C. Electrical conductivity was measured with CDM 83 conductivity meter (Radio meter A/S Copenhagen, Denmark). 0.5 g of each soil sediment and plant part sample was weighed using Mettler AE 160 balance in 50 mL beakers. 5.0 mL concentrated HCl, HNO₃, HClO₄ and HF were added in that order for each of the samples. The beakers containing each of the samples were placed on the heater for about 3 h [5]. For the effluent samples, 5.0 mL of concentrated hydrochloric acid was added to 250 mL of effluent sample and evaporated to 100 mL. The sample concentrate was left to cool and poured into labelled bottle containers.

Analysis of samples

Atomic absorption spectrophotometer (Perkin-Elmer Model 403 Norwalk, CT, USA) was used to determine the levels of Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Pb, Sn, Ti and Zn while K and Na were determined using a flame photometer (Corning, UK, Model 405) using NaCl and KCl to prepare the standards [6]. Analyses were made in duplicate. For quality control, the detection limits of all the elements were determined before the sample solutions were analysed [7]. The optimum analytical range was 0.5-10 absorbance units with coefficient of variation of 0.05-0.4 %. All determinations were reported on dry weight (DW) basis.

Statistical analysis

Data obtained were subjected to statistical evaluation. Parameters evaluated for were F-test, correlation coefficient, regression coefficient, coefficient of alienation and index of forecasting efficiency. Standard deviations and coefficient of variation percent were also calculated [8].

RESULTS AND DISCUSSION*Physicochemical parameters*

Both the temperature and the conductivity in the open effluent channel were slightly lower than the corresponding values in the direct tank. Temperature (°C) was 28.0 in open effluent channel but 31.0 in direct tank; also the conductivity (μScm^{-1}) was 2.9×100 in open effluent channel but 5.5×100 in direct tank. The temperature was lower in the open channel by 10.7 % while the conductivity was lower by 47.3 %. The heat in the direct tank would have been responsible for higher temperature and higher conductivity since a hotter environment will result into more particles going into solution, hence, higher conductivity. The current conductivity levels were much higher than the levels reported ($3.4\text{-}14.5 \mu\text{Scm}^{-1}$) for a textile effluent [9] and $0.1 \times 100 \mu\text{Scm}^{-1}$ for a cocoa industry liquid effluent [10].

Metal composition

Table 1 depicts the comparisons between the soil sediments, liquid effluent and the plant (roots and leaves) from the open channel. The major metals that were of high concentration were Mg, Na and K particularly in the soil sediments, plant roots and leaves. Following the trail of high concentration values among the trace metals were Fe, Zn, Pb, As and Cd in the samples as enumerated for major metals. All the metals were detected in all the samples but widely varied among the samples as depicted by the values for the coefficient of variation percent (CV %).

While titanium was the least concentrated among the trace metals, calcium occupied that position among the major metals. Also, while iron was the most concentrated trace metal, sodium was the most concentrated major metal.

The magnesium levels were high in the soil sediments, plant leaves and roots but low in the liquid effluent samples with values of 8.75-8.84 ppm. Magnesium is essential for both human beings, other mammals and plants and not known to cause any deleterious effect in its usual concentration. Representative levels of calcium in the soil solution of temperate region soils are 30-300 ppm; our soil results fell within this range. In soils of higher rainfall region, the calcium in solution range from 8-45 ppm with an average of about 33 ppm. Our soil sediment levels were greater than 8-45 ppm which was 84-165 ppm. While both plant roots and leaves were more concentrated in calcium than their soil sediments in *P. purpureum*, both roots and leaves of *C. pilosa* were lower in calcium than the soil sediments. Sodium is required by plants for growth and in man it controls body water balance and has a role in muscle contraction. The sodium level in soil sediments was lower to the levels in the roots and leaves of *P. purpureum* (Table 1); on the other hand, sodium was more concentrated in the plant parts (1524-1627 ppm) of *C. pilosa* than in the soil sediments (1494 ppm) (Table 2). Potassium was lower than sodium in the plant parts and the soil sediments as well as the liquid effluents from the direct tank. Potassium is required for plant growth and useful to man since it is present in all foods. When sodium is absorbed by clay colloids at high concentration it can cause displacement of potassium and calcium, leading to deterioration of soil texture [11]. *Panicum maximum* Jack leaves of 6 weeks old has the following values from literature in ppm: Ca (512.9), Mg (148.7), K (519.7) and Na (205.9) [15].

Table 1. Comparison of metal concentration in samples from open effluent channel (dry weight for soil, plant roots and leaves).

Metal (ppm)	Soil sediments	Liquid effluent	Plant ^a roots	Plant ^a leaves	CV % ^b
Fe	1773	1.19	2002	157	107
Zn	799	2.24	641	445	110
Mn	81	0.26	68	66	68
Cu	74	0.15	44	32	82
Sn	8.0	0.08	20	31	92
Al	33	0.10	26	42	71
Mg	721	8.75	1225	933	72
Na	1629	7.23	1618	1460	67
K	1243	7.45	1504	1459	67
Pb	618	0.54	600	577	67
As	111	1.67	444	534.3	94
Cr	68	0.51	170	130	81
Cd	124	1.27	143	297	86
Ti	3.34	0.085	10.02	16	96
Ca	84	1.10	105	92	67

^aElephant grass (*Pennisetum purpureum* Schumach). ^bCoefficient of variation percent.

Table 2 depicts the comparisons between the soil sediments, liquid effluent and the plant (roots and leaves) from the closed direct effluent tank. The metals were highly varied in the samples as in Table 1. The following trace metals were highly concentrated: Fe, Zn, Pb, As, Mn and Cd while Na, Mg and K were also concentrated among the major metals. Na, Ca, Fe and Ti still occupied their positions as observed in Table 1.

Table 2. Comparison of metal concentration in samples from direct tank and environment (dry weight for soil, plant roots and leaves).

Metal (ppm)	Soil sediments	Liquid effluent	Plant ^a roots	Plant ^a leaves	CV %
Fe	1815	0.50	777	197	117
Zn	568	2.998	363	297	76
Cu	126	0.15	64	52	85
Sn	15.4	0.10	20	12	71
Al	42.0	0.22	57	40	70
Mg	775	8.84	985	1272	71
Na	1494	7.66	1524	1627	66
K	828	7.06	1455	1526	74
Pb	515	1.008	371	300	73
As	107	2.22	327	556	99
Cr	33	0.51	133	170	96
Cd	304	1.41	280	197	70
Ti	19	0.085	6.55	17	83
Ca	165	0.91	112	84	76
Mn	184	0.34	104	47	95

^aPoaceae (*Chloris pilosa* Schumach).

The correlation coefficient (Cc), regression coefficient (Rc), coefficient of alienation (C_A) and the index of forecasting efficiency percent (IFE %) were, respectively 0.709, 0.519, 0.705 and 29.5 % in roots and leaves in the open effluent channel; 0.61, 0.00302, 0.79 and 21.0 % in soil sediment and water from open effluent channel; 0.34, 0.05, 0.94 and 6.0 % in soil sediment and water from direct tank. The roots and leaves metal levels from the open effluent channel has Cc (0.709) with an Rc (0.519) meaning that for every one unit increase in the concentration of any given metal in the root, there would be a corresponding 0.519 increase in leaves. Also while the C_A was high (0.705), the IFE was low (29.5 %) meaning that the reduction in the error of prediction of relationship between the root and the leaf metal levels was low. Table 1 also indicates that the roots of *Pennisetum purpureum* were more concentrated in Fe, Zn, Mn, Cu, Mg, Na, K, Pb, Cr and Ca, while the leaves showed some levels of bioaccumulation for Sn, As, Al, Cd and Ti. Table 1 also contained the comparison between metal levels in soil sediments and liquid effluent from the open effluent channel. The Cc was 0.61 with a low Rc value (0.00302), high C_A (0.79) and low IFE (21 %). The Rc value showed that the soil sediments was a good reservoir of all the metals determined while the major metals were mostly better concentrated in liquid effluent, this could have been due to the higher solubility of those metals in water. Table 2 compared the metal levels in the soil sediments and the liquid effluent in the closed direct tank. Both the Cc (0.34) and Rc (0.05) and IFE (6 %) were low but have high C_A (0.94 or 94 %) making prediction of relationship the most difficult among the results. Table 3 compared the metal levels in roots and leaves of *Chloris pilosa*. The Cc (0.91) was the highest among all the results, the C_A (0.41) was the lowest while the IFE (59 %) was also the highest. This would make prediction easy. The roots were better concentrated in Fe, Zn, Mn, Cu, Sn, Al, Pb, Ca and Cd while the leaves, contained more Mg, Na, K, As, Cr and Ti. Table 4 depicts the F-test values of the data obtained. 66.7 % of the metals were significantly different (p < 0.05) in the concentrations in the samples with trace metals being 40 % significant and major metals being 26.7 % significant.

Table 3. Correlation coefficient (Cc), regression coefficient (Rc), coefficient of alienation (C_A) and index of forecasting efficiency (IFE) in roots and leaves in the open effluent channel.

Metal	Roots	Leaves	Cc	Rc	C _A	IFE
Fe	2002	157				
Zn	641	445				
Mn	68	66				
Cu	44	32				
Sn	20	31				
Al	26	42				
Mg	1225	933				
Na	1618	1460	0.709	0.519	0.705	29.5 %
K	1504	1459				
Pb	600	577				
As	444	534				
Cr	170	130				
Cd	143	297				
Ti	10.02	16				
Ca	105	92				

Table 4. F – test values of obtained data.

Metal	Fe	Zn	Mn	Cu	Sn	Al	Mg	Na	K	Pb	As	Cr	Cd	Ti	Ca
F-calc.	8*	9*	4	8*	4	6	24	174*	44*	7.3*	69*	22	3.3	2.8	7.2*

*Significant at 0.05 confidence level.

Our results depicted in Tables 1 and 2 showed that soil sediments and the two plant species showed high levels of Pb, Cd and As. The plant samples could obtain the metals from two sources viz: uptake from the soil and rain water washing (precipitation) on the plants. The rate of trace element movement among tissues varies greatly, depending on the plant organ, its age, and the element involved. Research had shown that Cd, Pb and Zn absorbed by the tops of brome grass were not likely to move readily to the roots whereas Cu was very mobile [12]. Airborne Pb, a major source of Pb pollution, is also readily taken up by plants through foliage. Nigeria still uses leaded petrol which is a major source of airborne Pb. Pb values from different countries show that amounts for soil types range from 10-67 ppm and average 32 ppm. High Pb levels (above 100 ppm) have been reported for Denmark, Japan, Great Britain and Ireland and most probably reflect the impact of pollution. Most non-contaminated soils in Nigeria have Pb range of 0.0-90 ppm [14] whereas baseline values of this metal in most world soils should not be much higher than 20 ppm [12] showing that our soils are polluted. Unlike our results in the grasses for Pb and Cd, no detectable levels of the metals were found in reference [14]. The As content of certain contaminated soils has already been built up to as high as 0.2 % (2000 ppm). Grasses from a semiarid climatic zone (Kazakhstan, USSR) contain an elevated amount of As, from 1.1-5.4 ppm (DW) showing our samples to be highly polluted [12].

While the soil sediments would serve as reservoirs of those metals, the plants were often cut (particularly *Pennisetum purpureum*) and used as fodder for ruminants. *P. purpureum* has also been put into other uses viz: In East Africa a growing practice is not to apply chemical fertilizers direct to a crop such as coffee, but to apply the fertilizers to a grass which is then cut and applied to the coffee as a mulch: in this way the uptake of the added fertilizer is improved [13]. On forest soils in Ghana, maize and cassava yields, after 7 years of continuous cropping, were severely reduced by potassium deficiencies when the potassium saturation percentage had fallen to 1.2 % [13]. However, *P. purpureum* fallow included in the rotation, resulted in a potassium saturation percentage of 2.4 % and no drop in yields through potassium deficiency [13]. The fact

that both *P. purpureum* and *C. pilosa* were bioaccumulators of lead, cadmium and arsenic metals, they should not be used where their minerals could be re-circulated to contaminate human diet resources when the plants are coming from polluted sources.

The tin levels were low in the samples analysed: 0.08-0.10 ppm (liquid effluents), 8.0-15.4 ppm (soil sediments), 19.6-25.8 ppm (roots) and 12.0-42.0 ppm (leaves). These values were generally higher than we got in a Crown Caps Industry: 3.9 ppm (*Nicotiana tobacum*), 7.8 ppm (metal dump site soil) and 12.5 ppm in the paint effluent [16]. Chapman [17] cited the common range of Sn in soils as 1-11 ppm and reported that Sn ranges in grass from 0.2-1.9 ppm (DM), all these are lower than our results. Sn is very toxic to both higher plants and fungi.

There was species variation in the concentration of aluminium by the two plants but both values were lower than the level in *N. tobacum* (69.2 ppm) [16]. Because of the presence of aluminium in soils and rocks, there are natural traces of the element in nearly all foods [16]. Al content from various grass tops (DW) ranged as follows: grass, timothy tops 6.5-23.5 ppm, grass from tetany pasture 60-14,500 and another grass sample with 50-3,410 ppm [12].

Titanium was generally low in all the samples with biological accumulation in the roots and leaves of *P. purpureum* whereas the plant values were less than the soil sediments in the direct tank environment. Titanium is not known to be a contaminant. Our copper values were lower in the plant parts than in the soil sediments in both effluent sites. Also the roots were more concentrated in copper than the leaves. This meant copper excretion to xylem and phloem saps was low. Copper is needed by both plants and animals for their metabolisms. The threshold value of 100 ppm Cu was exceeded by the soil sediments in direct tank. Literature values of Cu in grass tops from contaminated sites (ppm DW) are 21 (Great Britain) and 20-70 (Canada) for 1.6-5.8 km distance from a smelter [12]. The iron levels were generally high in the soil sediments and the plant parts. The iron level in soil sediments (1773 ppm) was lower than in the roots (2002 ppm) but higher than in the leaves (157 ppm) of *P. purpureum* in the open effluent channel; there was a slight reverse in the direct tank: soil sediments (1815 ppm), roots (777 ppm) and leaves (197 ppm) in *C. pilosa*. The concentration of iron in soil solutions within common soil pH levels ranges from 30-550 μgL^{-1} , whereas in very acid soil it can exceed 2000 μgL^{-1} . The appropriate content of iron in plants is essential both for the health of the plant and for the nutrient supply to man and animals. The natural iron content of fodder plants ranges from 18-1000 ppm dry weight (DW). The nutritional requirement of grazing animals is usually met at the iron concentration range 50-100 ppm (DW) in forage. All our iron levels in the leaves were higher than the limit of 100 ppm (DW) in forage. Both *C. pilosa* and *P. purpureum* showed evidence of bioaccumulation of chromium in both their roots and leaves but *C. pilosa* showed better accumulation. *Panicum maximum* has an Fe value of 95.2 ppm [15] which was lower than our results. Chromium is essential to life. Anthropogenic sources of Cr are responsible for the elevated content of this metal in plants. Mean Cr concentration in grass near city streets is as high as 17 ppm (DW) [12]. The levels of manganese in the two soil sediments were correspondingly higher than the levels in the roots and leaves of the two plants. Worldwide background contents of manganese range 17-334 ppm in grass and 25-119 ppm in clover. Our results were within these limits. The critical manganese deficiency level for most plants ranges from 15-25 ppm (DW) whereas the toxic concentration is about 500 ppm (DW) [12].

In the zinc, the soil values were higher than the plant part values; also, the zinc levels in the roots were correspondingly higher than in the leaves. This could mean that the excretion of zinc from root cells into the xylem and phloem saps where zinc occurred in greater levels could have been low. The zinc concentrations in soil solutions range from 4-270 μgL^{-1} . Itoh *et al.* [18] reported the maximum of 17000 $\mu\text{g ZnL}^{-1}$ of solution and this value is, apparently, for highly contaminated soils. However, in natural but very acid soils (pH < 4), zinc concentration in solutions is reported to average 7137 μgL^{-1} . Mean total zinc contents in surface soils of different countries and of the USA range from 17-125 ppm. Grand mean zinc for worldwide soils may be

calculated for 64 ppm. Obviously, soils in Tables 1 and 2 were contaminated; this could lead to important environmental problem. In grasses zinc ranged from 12-47 ppm (DW) and in clovers ranged from 24-45 ppm (DW) [12]. These values were lower than our results (Tables 1 and 2) meaning that our plants were contaminated by zinc.

From the range values obtained for metals in the plant parts and soil sediments, index of bioaccumulation were calculated [12] and the results gave the degree of accumulation (Tables 5 and 6). The results showed plant differences in the bioaccumulation of metals, the plant parts (roots and leaves) also showed differences in metal accumulation. From Tables 5 and 6, the better plant for monitoring pollution might be *C. pilosa* (roots and leaves) whereas both *P. purpureum* and *C. pilosa* (roots and leaves) were luxury accumulators of As.

Table 5. Bioaccumulation^a of metals by *Pennisetum purpureum* from soil sediments.

Metal	Index of bioaccumulation ^b (roots)	Degree of accumulation (roots)	Index of Bioaccumulation (leaves)	Degree of accumulation (leaves)
Fe	0.43	Slight	0.11	Slight
Zn	0.64	Medium	0.53	Medium
Cu	0.51	Medium	0.41	Slight
Sn	1.28	Intensive	0.78	Medium
Al	1.36	Intensive	0.95	Medium
Mg	1.27	Intensive	1.64	Intensive
Na	1.02	Intensive	1.09	Intensive
K	1.76	Intensive	1.84	Intensive
Pb	0.72	Medium	0.58	Medium
As	3.06	Intensive	5.20	Intensive
Cr	4.08	Intensive	5.20	Intensive
Cd	0.92	Medium	0.65	Medium
Ti	0.34	Slight	0.87	Medium
Ca	0.68	Medium	0.51	Medium
Mn	0.57	Medium	0.25	Slight

^aRatio in plant /soil. ^bIndex of bioaccumulation: 10^{-3} - 10^{-2} (lack), 10^{-2} - 10^{-1} (slight), 10^{-1} -1 (medium), 1- 10^1 (intensive).

Table 6. Bioaccumulation^a of metals by *Chloris pilosa* from soil sediments.

Metal	Index of bioaccumulation ^b (roots)	Degree of accumulation (roots)	Index of Bioaccumulation (leaves)	Degree of accumulation (leaves)
Fe	1.13	Intensive	0.09	Lack
Zn	0.80	Medium	0.56	Medium
Cu	0.59	Medium	0.43	Slight
Sn	2.50	Intensive	3.85	Intensive
Al	0.79	Medium	1.28	Intensive
Mg	1.70	Intensive	1.29	Intensive
Na	0.99	Medium	0.90	Medium
K	1.21	Intensive	1.17	Intensive
Pb	0.97	Medium	0.93	Medium
As	4.0	Intensive	4.81	Intensive
Cr	2.50	Intensive	1.92	Intensive
Cd	1.16	Intensive	2.40	Intensive
Ti	3.0	Intensive	4.81	Intensive
Ca	1.25	Intensive	1.09	Intensive
Mn	0.84	Medium	0.81	Medium

a,b = see Table 5.

CONCLUSIONS

All the metals analysed were detected in all the samples. It is interesting to note that the surroundings of the closed direct effluent tank and the open gutter containing used machine wash (open effluent channel) had their grasses containing high levels of the metals. The metals could probably come from two sources: the liquid effluents and the airborne contaminants all within the pharmaceutical industry.

REFERENCES

1. Federal Environmental Protection Agency (FEPA) *Guidelines for Environmental Pollution Control in Nigeria*, FEPA: Lagos; **1991**; pp 19-194.
2. Austin, G.T. *Shreve's Chemical Process Industries*, 5th ed., Mc Graw-Hill Book Company: New York; **1984**; pp 795-929.
3. Hutchinson, J.; Dalziel, J.M.; Hepper, F.N. *Flora of West Tropical Africa*, Vol. III Part 1, Crown Agents: London; **1968**; pp 399-400, 459-463.
4. Sekhar, K.I.; Chary, N.I.; Kamala, C.I.; Vairamani, M.I.; Anjaneyulu, Y.2; Balaran V.3; Sorlie, Jan4 *Human and Ecological Risk Assessment* **2006**, 12, 408.
5. Udo, E.J.; Ogunwale, A.J. *Laboratory Manual for the Analysis of Soil, Plant and Water Samples*, University of Ibadan: Ibadan; **1978**; pp 70-76.
6. Association of Official Analytical Chemists (AOAC) *Official Methods of Analysis*, 15th ed., AOAC: Washington DC; **1990**; section 968.08.
7. Varian Techtron *Basic Atomic Absorption Spectroscopy – A Modern Introduction*, Varian Techtron: Springvale, Australia; **1975**; pp 104-106.
8. Steel, R.G.D.; Torrie, J.H. *Principles of Procedures of Statistics*, McGraw-Hill: London; **1960**; pp 7-30.
9. Adeyeye, E.I.; Ayejuyo, O.O. *Pak. J. Sci. Ind. Res.* **2002**, 45, 10.
10. Adeyeye, E.I.; Ajibade, P.A.; Temola, A.F. *Int. J. Environ. Stud.* **2005**, 62, 171.
11. Sutcliffe, J.F.; Baker, D.A. *Studies in Biology No. 48: Plants and Mineral Salts*, Edward Arnold: London; **1974**; pp 1-25.
12. Kabata-Pendias, A; Pendias, H. *Trace Elements in Soils and Plants*, 2nd ed., CRC Press: Boca Raton, Florida; **1992**; pp 1-365.
13. Ahn, P.M. *West African Soils*, Oxford University Press: Oxford; **1970**; pp 232-253.
14. Adeyeye, E.I. *Bull. Chem. Soc. Ethiop.* **2005**, 19, 23.
15. Olowu, O.P.A. *Ph.D. Thesis*, Federal University of Technology, Akure, Nigeria; **2005**; pp 1-234.
16. Adeyeye, E.I.; Oluwamuye, D.A. *Material Sci. Res. India* **2004**, 2, 79.
17. Chapman, H.D. (Ed.) *Diagnostic Criteria for Plants and Soils*, University of California; Riverside, California; **1972**; p 793.
18. Itoh, S.; Tokumaga, Y.; Yumura, Y. *Bull. Veg. Ornamental Crops Res. Sm.* **1979** (Ja), 5a, 145.