ASSESSMENT OF HEAVY METALS CONCENTRATIONS IN PHARMACEUTICAL EFFLUENTS AND SOILS IN MINNA, NIGERIA.

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ABSTRACT

In this study, five heavy metals (Mn, Zn, Cu, Ni, and Cd) were assessed in the effluent from Dana Pharmaceutical Company in Minna Niger state to ascertain their presence and evaluate their concentration. The impacts in the soils receiving the effluents were also examined. Samples were collected from treated and untreated effluents and analysed using Atomic Absorption Spectroscopy (AAS).Soil samples were also collected randomly from three locations on the plot receiving the effluents. The results of effluent analysis revealed that the heavy metals concentrations were beyond the allowable limit despite the consistent effort to bring down the concentration to allowable level. The level of soil contamination was determined using enrichment factor (Ef), degree of contamination (Cdeg) and index of geo-accumulation (Igeo).Enrichment Factor values of heavy metal were found to be above 2 in all sampling site suggesting that the source of these metals are more likely to be anthropogenic.Unlike the Efs, the Igeo values were generally low (< 2) in all cases except for Zn. Degree of contamination calculated for soil samples revealed an extremely high degree of contamination, indicating that the effluent discharge from the industry led to increased concentration of heavy metal in these soils. This study reveals the need for detailed effluent treatment before their discharge to surrounding environment to reduce their potential environmental hazards.

1. INTRODUCTION

Though, industries are contributing factors to economic growth, they have simultaneously given rise to environmental pollution. Anthropogenic activities within urban areas influence biogeochemical cycles and this has led to various irreversible changes in our environment (Odoi *et al.*, 2011). Agricultural soil contamination with heavy metals through repeated use of untreated or poorly treated wastewater from industries is one of the most severe ecological problems in Nigeria (Ram *et al,* 2011). These wastes reduce soil quality, and are a potential cause of environmental degradation (Olaitan *et al,* 2013). Heavy metals presence in wastewater is a matter of concern due to their non-biodegradable nature and long biological half-lives (Sardar *et al,* 2013).

In Nigeria, increase in demand for pharmaceutical products have resulted in an increase in number of pharmaceutical manufacturing companies in the country and hence increased pharmaceutical wastes which are known to contain various degrees of heavy metals (Olaitan *et al,* 2013). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and cause damage to blood composition, lungs, kidneys, liver, and other vital human organs. They are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. (Ram *et. al.,* 2011). Although, some of these heavy metals are required at very low concentration, they constitute serious hazard to the environment at high concentration. The hazardous effects of these metals and the regular release of the industrial effluents into the immediate environment without any assurance of proper treatment and conformity to the acceptable standards have attracted considerable attention globally during the last decades (Sebastian *et al.,* 2012).

Awareness on the impacts of pharmaceutical wastes that are channeled into the fields where farmers cultivate their crops is grossly inadequate. There is tendency for uptake of these metals by crop and eventual transfer into human body system after eating the crops, the concentration of which depends on quantity and quality of effluents (Sardar *et al.,* 2013). It was also reported that uncontrolled input of heavy metals in the soils is undesirable, because once accumulated in the soil, the metal becomes generally very difficult to remove. Subsequent problem is the toxicity to the plant growing on the contaminated soil and uptake by the plants resulting in high metals levels in plant tissues. It has been reported that soil contamination may adversely impact human health when agricultural produce grown in such area is consumed. Heavy metal pollution not only affects the production and quality of crops, but also influences the quality of the atmosphere and water bodies which in turn threatens the health, life of animals and human beings by way of the food chain.

Cadmium is known to cause environmental hazard like kidney damage which has long been described to be the main problem for patients chronically exposed to cadmium (Ahaneku and Sadiq, 2014). Low dosages of cadmium are reported to stimulate ovarian progesterone biosynthesis, while high dosages inhibit it. A subcutaneous injection of cadmium chloride can induce prostate cancer in Wistar rats (Iyaka and Kakulu, 2012), which is proof of the carcinogenic role of cadmium. Copper has a tendency to accumulate in the blood and deplete the brain zinc supplies. Acute symptoms of copper poisoning by ingestion include vomiting, haematemesis, hypotension, melena, coma, jaundice and gastrointestinal distress. Zinc is a bluish-white, lustrous, diamagnetic metal though most common commercial grades of the metal have a dull finish. It is less dense than iron and has a hexagonal crystal structure (Abraham and Parkar, 2008). Zinc acts as a traffic director, overseeing the efficient flow of body processes, maintenance of enzyme systems and cells. Zinc toxicity, which is commonly a fatal cause of severe haemolyticanemia, liver or kidney damage; vomiting and diarrhea. Manganese metal and its common ions are paramagnetic, it tarnishes slowly in air and "rusts" like iron, in water containing dissolved oxygen. Manganese plays the role of activating enzymes (Idris *et al,* 2013).

Though, a number of work has been done on the heavy metal assessment of soil in Minna city. For instance, Ahaneku and Sadiq, (2014) assessed quantity of heavy metals in Minna agricultural soils while Iyaka and Kakulu, (2012) evaluated concentrations of heavy metals in Minna top soil. However, no research has been documented on the effect of effluent from Pharmaceutical firms on the neighbouring soil. The soil is used for agricultural purposes, which means a possibility of heavy metal consumption by man through food chain. It is important to critically assess possible presence and concentration of heavy metals in the discharged effluents as part of environmental supervision and ecosystem evaluation with a view to providing a robust data base. The state of soil also needs to be assessed because the soil serves as reservoir for all the metals present in these effluents. The objectives of this work were to determine the concentration of some heavy metals in the effluents of the Pharmaceutical Company and the soil using established indices.

2. MATERIALS AND METHODS

2.1 Study Area

The study site was Maitumbi industrial layout in Minna, located between latitude 9° 38' 4.20" and longitude 6° 35' 1.27" in Niger State.

2.2 Effluents and Soil Sampling

The study involved sampling of effluents (treated and untreated) from Dana Pharmaceutical Industry. The company mainly discharges its partially treated and untreated effluent to the environment.

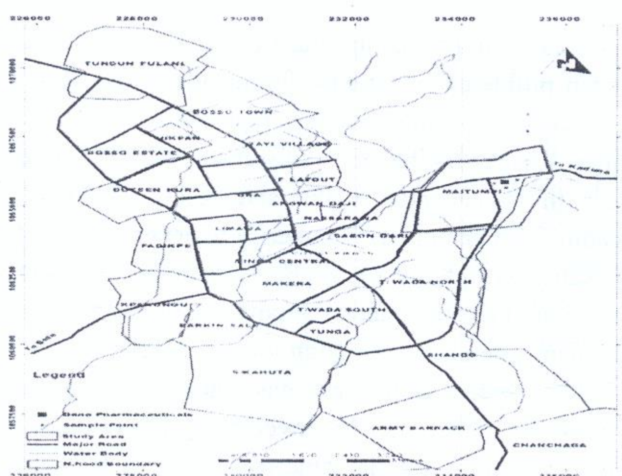

Figure 1: Map of the Study Area.

Soils samples were taken from study site, where these effluents are channeled through. Samples were collected monthly between February 2014 and May, 2015. The collected effluent samples were labeled and taken to laboratory to analyze for copper, cadmium, lead, zinc, iron and manganese. During each month of collection, a composite soil sample of 4-5 kg, were collected at a depth of 0-15 cm from each of the selected sites (Figure 1) with the help of a stainless steel soil auger. Soil samples were collected from three different locations of the site, especially along the line of flow, and were taken to the laboratory and prepared for the analyses (Ahaneku and Sadiq, 2014). Liquid samples were collected into clean 0.75-litre plastic containers while soil samples were collected into polyethylene bags. During effluent analysis, 100 ml each of the sample was digested using 20 ml concentrated nitric acid in a 250-ml conical flask placed in a fume cupboard to ensure removal of organic impurities and prevent interference during analysis. The samples were heated at 150^0C on a hot plate until the solution reduced to about 20 ml (Abraham and Parker 2008). This was allowed to cool and made up to mark (100ml) with distilled water before filtering into a volumetric flask, it was then taken to AAS – ACCUSYS 211 Atomic Absorption Spectrophotometer for further analysis. (Abraham and Parker 2008).

2.2.1 Effluents and Soil Analysis

For soil analysis, collected soil sample was air dried over pre-cleaned Pyrex petri dishes. Then 2–3 g dry soil samples were digested in about 15 ml of three parts per chloric acid (3:1) for approximately 4–5 hours using a hotplate maintaining a heating temperature of approximately 110 °C. The samples were next placed in a 100 mL Pyrex glass beaker and diluted with distilled water up to 50 ml. The solution was filtered and the filtrates were analyzed using Atomic Absorption Spectrophotometer (AAS). Data obtained were subjected to statistical analysis and soil data were processed using three established indices to know the degree of soil contamination.

2.3 Determination of Soil Contamination

Several methods of calculation have been put forward to quantify the degree of metal enrichment in soil sediments. For instance, Fakayode and Owolabi (2013) proposed pollution impact scales to convert the calculated numerical results into broad descriptive bands of pollution which range from low to high intensity. Soil contaminations are assessed using various indices, including the enrichment factor (EF), index of geo-accumulation (Igeo), normalized enrichment factor, contamination factor (Cf) and degree of contamination (Cd) along with proposed modifications. In this work, the enrichment factor (EF), index of geoaccumulation, contamination factor (Cf) and the modified degree of contamination (mCd) were used to determine the contamination status of sediment. These methods provide a measure of the degree of overall contamination in surface layers in a particular sampling site as compared to other methods.

2.3.1 Determination of Enrichment Factor (EF)

The enrichment factor (EF) was based on the standardization of a tested element against a reference one. It is calculated as;

$$EF = {Cn}/{CR} \qquad \text{(i)}$$

Where, EF is ratio between the measured metal concentration (Cn) and the average metal concentration in shale. (CR). According to Singh and Taneja, (2010) five contamination categories are generally recognized on the basis of the enrichment factor. For instance, EF < 2, depletion to mineral enrichment; 2 ≤EF < 5, moderate enrichment; 5 ≤EF < 20, significant enrichment; 20 ≤EF < 40, very high enrichment; and EF > 40, extremely high enrichment.

2.3.2 Determination of Index of Geo- accumulation (Igeo)

The index of geo-accumulation (Igeo) actually enables the assessment of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediments (Krzyzstof *et al*, 2004). It is applied to the assessment of soil contamination on the basis of the following:

$$I_{geo} = \log_2 \frac{Cn}{1.5Bn} \qquad (2)$$

where Cn is the measured concentration of the element in the pelitic sediment fraction (<2 μm) and Bn is the geochemical background value. The scale for Igeo contamination level is presented in Table 2.

2.3.3 Determination of Contamination Factor (Cf) and Degree of Contamination (Cd)

The assessment of soil contamination was also carried out using the contamination factor (Cf), and degree of contamination (Cd).The contamination factor (CF) gives an indication of the level of contamination, was computed for the soil sediments using the concentration of the heavy metals and their corresponding values in the world average shale. It was calculated as follows:

$$Cd = \sum_{i=1}^{n} Cf \qquad (3)$$

The judgment table contamination factor is similar to that of Igeo.

Table 1: Index of Geoaccumulation (Igeo) for Contamination Levels in Soil

Igeo Class	Igeo Value	Contamination Level
0	Igeo ≤0	Uncontaminated
1	0 ≤ Igeo ≤1	Uncontaminated/Moderately contaminated
2	1 ≤ Igeo ≤2	Moderately contaminated
3	2 ≤ Igeo ≤3	Moderately/strongly contaminated
4	3 ≤ Igeo ≤4	strongly contaminated
5	4 ≤ Igeo ≤5	Strongly/extremely contaminated
6	Igeo ≥5	extremely contaminated

Source: Krzyzstof *et al,* 2004).

A modified equation for a generalized approach to calculating the degree of contamination is given as Modified degree of contamination and is given as equation 4 and the judgment table is presented in Table 2.

$$mCd = \sum_{i=1}^{i=n} \binom{n}{k} Cf^{i} \quad (4)$$

Table 2: Different modified degree of contamination (mCd) for soil

McD	Judgment
mCd< 1.5	
1.5 ≤mCd< 2	Low degree of contamination
2 ≤mCd< 4	Moderate degree of contamination
4 ≤mCd< 8	High degree of contamination
8 ≤mCd< 16	Very high degree of contamination
16 ≤mCd< 32	Extremely high degree of

Source: Krzysztof *et al.*, 2004

3. RESULTS AND DISCUSSION

The presence of the following metals was detected. Mn, Cu. Zn, Ni and Cd, and the various concentrations level of these heavy metals was observed to vary. Figures 2, 3 and 4 show that heavy metals were beyond allowable limit by WHO, (2003) and FAO, (2000). The receiving soil and water stands the risk of contamination which in turn will have harmful effect on water and crop cultivated on this soil. Ahaneku and Sadiq, (2014) reported a similar case after analyzing effluents from some pharmaceutical industries in Niger state and recommended that the effluents be impounded and treated inside a lagoon before releasing it to water-courses or being pumped for agricultural re-use. Analysis of Variance (ANOVA) conducted at $p>0.05$ on the treated and untreated effluents revealed that there is no significant difference between the concentrations of the treated and untreated samples and this may be used to conclude that the treatment being carried out on the effluents is not good enough to reduce heavy metals concentration below the allowable limits. Abraham and Parker (2008) have also reported that coagulation, sedimentation and mechanical filtration being carried out one the effluent are physical treatment. Chemical treatment needs to be carried out on effluents from pharmaceuticals firm to safe the people nearby from dangers of heavy metals.

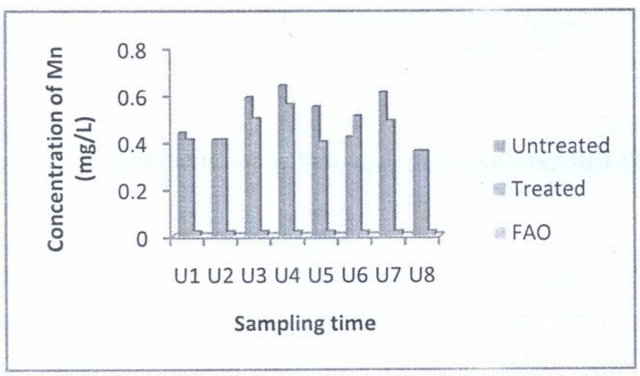

Figure 2: Variations of Manganese Concentrations in Effluent Samples

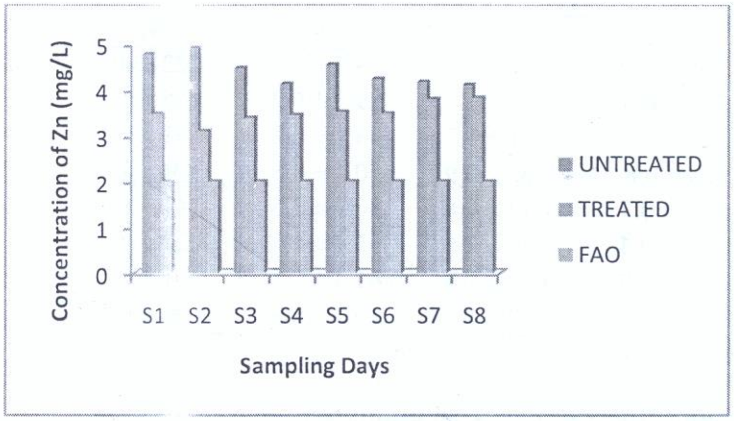

Figure 3: Variations of Zinc Concentrations in Effluent Samples

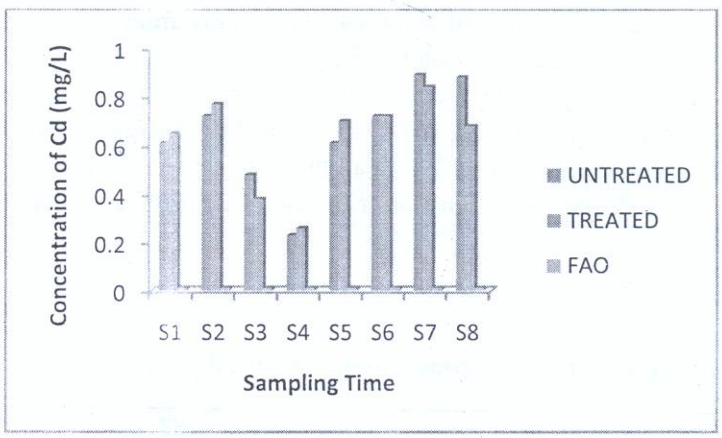

Figure 4: Variations of Cadmium Concentrations in Effluent Samples

The results of soil analysis for heavy metals are presented in Table 3. It is observed that the concentrations of all the heavy metals tested are more in the soil than in the effluent. This may be as aresult of accummulation due to long time dischare of the effluents on the soil. Fakayode and Owolabi (2013) has reported a similatr case for heavy metals and he attributed the accummulation to poor decay rate of major heavy metals and their very high half life. He concluded by discouraging continous discharging of heavy metals-containing effluent on the same spot since the contents are not capable of biodegradation. He however suggested an intemmintanet dischage.

Table 3: Concentration of Heavy Metals in Receiving Soil

Concentrations of heavy metal in treated effluent (mg/kg) n=24

	Mn	Cu	Zn	Ni	Cd
T1	3.86 ± 1.0	8.75 ± 1.1	73.5 ± 3.8	4.22 ± 0.8	7.24 ± 1.8
T2	3.79± 0.9	8.66 ± 1.1	89.3 ± 6.2	4.45 ± 1.1	6.24 ± 1.4
T3	4.27 ± 0.3	7.61 ± 1.7	73.1 ± 6.2	6.91 ± 1.1	7.81 ± 2.1
T4	3.68± 0.8	8.62 ± 0.9	70.4 ± 4.8	2.36 ±0.1	8.23 ± 0.9
T5	3.64 ± 0.7	7.42 ± 0.6	80.2 ± 2.5	5.41 ± 0.4	3.59 ± 0.4
T6	3.28 ± 0.4	8.49 ± 1.6	63.4 ± 1.2	5.22 ± 0.4	6.24 ± 0.6
T7	2.59 ± 1.0	6.52 ± 1.3	61.4 ± 2.1	4.01 ± 0.5	7.67 ± 1.8
T8	3.04 ± 0.3	7.50 ± 1.1	60.3 ± 6.4	4.43 ± 0.1	7.60 ± 1.1

Values are given as means of triplicates, T= treated

Enrichment Factor and Index of Geo - accumulation

Results obtained for enrichment factors in the soils around the study area are presented in Table 4. Results for EF for heavy metals in sampled soils were in the range of 3.23 - 6.87mg/kg forCu; 23.77 – 42.9 mg/kg for Zn; 2.39 – 2.42mg/kg for Ni and 2.00 - 2.29 mg/kg for Cd. According to Iyaka and Kakulu, (2012) EF values ranging between 0.5 and 2 indicate that the occurrence of the metal is due to natural processes, whereas ratios greater than 2 are considered as enrichment mainly from anthropogenic inputs. In the present study, EF values for all the heavy metals were found above 2 which suggest that source of these metals are more likely to be anthropogenic. Index of geo accumulation (Igeo) ranges from 1.11 to 2.2 for Cu, 3.99 to 4.89 for Zn, -1.83 to -1.94 for Ni, and 0 to 0.22 for Cd. The *I*geo results revealed values that are generally low (< 2) in all cases except for Zn. In all the soils, the metals, based on table 4 fall within Igeo class strongly to moderate contamination (Zn and Cu) and uncontaminated to moderate contamination (Ni and Cd).

Table 4.Enrichment factor and Index of geoaccumulation of soil sample

Element	S1	S2	S3
Enrichment factor			
Cu	3.23	6.87	4.67
Zn	23.77	42.90	31.50
Ni	2.42	2.39	2.41
Cd	2.29	2.00	2.81
Index of geoaccumulation			
Cu	1.11	2.20	1.64
Zn	3.99	4.84	4.39
Ni	-1.83	-1.94	-1.88
Cd	0.22	0.00	0.00

The assessment of soil contamination was also carried out using the contamination factor (C_f) and modified degree of contamination (mCd) as shown in Table 5. The C_f is the single element index, the sum of contamination factors for all elements examined represents the Cd of the environment, mCd produces an overall average value for a range of pollutants.

Table 5: Contamination factor and Modified degree of contamination of soil sample

Sample point	Contamination factor				sumCd	mCd
	Cu	Zn	Ni	Cd		
S1	4.11	64.30	0.40	2.05	70.83	17.71
S2	6.28	91.81	0.49	0.00	98.58	24.65
S3	9.92	1.29	0.26	1.29	12.76	3.19
Baseline	2.13	0.8	8.56	0.63		

From the results, it was evident that effluents from pharmaceutical company carries appreciable amounts of heavy metals and this concur with the reports from other researchers (Idris *et al.*, 2013 and Olaitan *et al.*, 2013). Both the treated and untreated effluent still exhibits a high degree of contamination. The presence of heavy metals in the environment is a potential threat to soil, water quality, plants, animals and human life.

Continuous and long-term release of this effluent could increase the concentration of heavy metals in the topsoil. The modified degree of contamination (mCd = 24.65) revealed extremely high degree of contamination by the studied metals. The soil in the study area would therefore require remediation before it can be recommended for agricultural use.

4. CONCLUSIONS

Concentrations of some heavy metals contained in effluents from a pharmaceutical company in Minna have been assessed. It was discovered that all the heavy metals studied are present in the effluent at a concentration beyond the recommended limits by FAO (2000) and WHO (2003). It was also observed from the research that the treatment being carried out on the effluent is not good enough to reduce the heavy metals concentration to allowable level. Continuous discharge of this effluent on Minna soil is very dangerous as it may have a long time health effect, cleaning up of what may be difficult years after the production and effluents discharge have been stopped.

Consequent upon our findings, it is recommended that measures such as phytoremediation and other remedial measures should be taking promptly to reduce heavy metal concentration on the receiving soil. Legislative measures should bind the individual industries to forbid discharge of untreated or poorly treated industrial effluents, also, continuous monitoring and further studies on the level of these heavy metals should be carried out in the near future to ascertain long-term effects of anthropogenic impact.

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