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Full Length Research Paper

Concentrations of heavy metals in some pharmaceutical effluents in Lagos, Nigeria

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The concentrations of some heavy metals in the effluents of nine pharmaceutical companies operating in Lagos, Nigeria were determined using atomic absorption spectrophotometer. The heavy metals analyzed in this study included Cadmium, Chromium, Lead, Nickel, Zinc and Copper. Most of the samples were found to contain the metals in varying concentrations. The highest concentration of heavy metal detected was Zinc with concentration of 1.437 mg/L. Mostly, the concentrations were above the WHO recommended maximum contaminant concentration level. The highest concentrations were found to be 0.132 mg/L for Nickel, 0.644 mg/L for Lead, 0.337 mg/L for Copper, 0.280 mg/L for Cadmium, 1.437 mg/L for Zinc, and 0.491 mg/L for Chromium. This study reveals the need for enforcing adequate effluent treatment methods before their discharge to surface water to reduce their potential environmental hazards.

Key words: Heavy metals, pharmaceutical effluents, ecotoxicity, surface water.

INTRODUCTION

Various devastating ecological effects and human disasters in the last 40 years have arisen majorly from industrial wastes causing environmental degradation (Abdel-Shafy and Abdel-Basir, 1991; Sridhar et al., 2000). The discharges from these industries constitute biohazard to man and other living organisms in the environment because they contain toxic substances detrimental to health (Adebisi et al., 2007; Adriano, 2001; Bakare et al., 2003). Recently, there has been an alarming and worrisome increase in organic pollutants (Nadal et al., 2004). Since many effluents are not treated properly, these products are discharged on the ground or in the water bodies (Odiete, 1999), and most of these discharges to water bodies accumulate in the system through food chain (Odiete, 1999).

Pharmaceutical effluents are wastes generated by pharmaceutical industries during the process of drugs manufacturing. Their risk to human health and environmental species cannot be overemphasized. In Nigeria, the increase in demand for pharmaceuticals has resulted in a consequent increase in pharmaceutical manufacturing companies in the country and hence increased pharmaceutical waste which most times contain substantial amount of heavy metals. These effluents are usually discharged into the environment and when improperly handled and disposed, they affect both human health and the environment (Osaigbovo and Orhue, 2006; Ayodele et al., 1996; Anetor et al., 1999).The uncontrollable growing use of pharmaceutical products now constitutes a new challenge. Most pharmaceutical effluents are known to contain varying concentrations of organic compounds and total solids including heavy metals. Heavy metals such as Lead, Mercury, Cadmium, Nickel, Chromium and other toxic organic chemicals or phenolic compounds discharged from pharmaceutical industries are known to affect the surface and ground waters (Foess and Ericson, 1980). Due to mutagenic and carcinogenic properties of heavy metals, much attention has been paid to them since they have direct exposures to humans and other organisms

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(Momodu and Anyakora, 2010).

Heavy metals are natural components of the earth crust. These metals enter into living organisms through food or proximity to emission sources. They tend to bioaccumulate and are stored faster than excreted (Lenntech, 2006; Daniel et al., 1997;Davies et al.,2006). Industrial exposure accounts for a common route of contact in adults and ingestion for children (Roberts, 1999).

This study was aimed at determining the presence of six heavy metals, namely Lead, Chromium, Cadmium, Zinc, Copper and Nickel in the effluents of nine selected pharmaceutical companies in Lagos, Nigeria. The results obtained may form the basis for intervention by encouraging the pharmaceutical companies to effectively treat their effluent before being discharged into the environment.

MATERIALS AND METHODS

Chemicals and reagents

All chemicals and reagents were of analytical grade and were obtained from BDH Chemicals Ltd, UK. Conc. HNO_3 was used for the digestion of the samples while corresponding metal salts [namely: $CdCl_2.H_20$, Cu(SO4)$_2$, $Zn(SO_4)_2$, $Pb(NO_3)_2$, $NiCl_2.6H_2O$ and $Cr(NO_3)_3$,] were used as standards.

Instrumentation

AAS instrument (PERKIN ELMER A. Analyst 200; Germany) consisting of a hollow cathode lamp, slit width of 0.7 nm and an air-acetylene flame was used for this work. The samples were analyzed for six heavy metals namely, Chromium which was analyzed at wavelength of 357.87 nm, Nickel at 232.00 nm, Cadmium at 228.80 nm, Zinc at 213.86 nm, Lead at 283.31 nm and Copper at 324.75 nm.

Sampling

Nine companies were identified due to their intense production; these companies are represented here with the letters A to I. Samples was taken at three different times between March and September, 2008. The pharmaceutical effluent samples were collected using thoroughly cleaned 250 ml Pyrex bottles each at the point where the effluents leaves the companies to the environment and stored in a refrigerator at 2 - 8℃ before analysis. A total of 27 samples were collected at various peak production periods.

Sample preparation

To ensure removal of organic impurities and prevent interference during analysis, each of 50 ml volume sample was digested using 10 ml conc. HNO_3 in a 250-ml conical flask placed on a fume cupboard (Momodu and Anyakora, 2010). The samples were covered properly with aluminum foil to avoid spillage and heated on a hot plate until the solution reduced to 10 ml. This was allowed to cool and made up to mark with distilled water before filtering into a 50-ml standard flask, labeled and ready for analysis. The blank constituted 5% HNO_3.

Standard preparation

This served as the stock solution equivalent to 1000 ppm. Subsequently lower concentrations of 2 ppm, 4 ppm and 6 ppm were prepared from the stock by serial dilution. The same method was adopted for Cr, Ni, Pb, Cu and Zn.

RESULTS AND DISCUSSION

Calibration curves were obtained using a series of varying concentrations of the standards for all six metals. Calibration curve for all the metals were linear with a correlation coefficient of approximately one. The effluents analyzed contain some heavy metals in varying concentrations. Tables 1 to 3 give the summary of the results obtained in this study while Table 4 summarizes guidelines by different international agencies.

Nickel concentrations appear to be higher than the normal acceptable contaminant level according to WHO standard of 0.02 mg/L with company E showing the highest value of 0.132 mg/L. Companies A, C, B and D follow in a decreasing order of above normal concentration. However, companies G, H and I have no detectable Nickel concentration in their effluents, which could be as a result of the absence of the metal from the raw material in use at the time of sample collection. Nickel toxicity can cause a devastating histological change on plants and animal tissues (Moore, 1991).

Lead on the other hand gave an alarming result of 0.644 mg/L in company E followed by A with 0.241 mg/L. The WHO maximum contamination level is 0.01 mg/L. Only companies C and D gave a non-detectable result for lead. This may be due to its absence from the raw materials used at the time of sample collection. Lead poisoning could cause abdominal pain, loss of appetite, insomnia and constipation. Severe kidney as well as brain damage has been reported on long term exposure (Momodu and Anyakora, 2010). It is much more worrisome as it can substitute for calcium in bone causing skeletal anomalies especially in children (Bottcher and Hamman, 1986). Lead toxicity has been reported in some plant parts such as root and leaf most of which are either used as food or as medicine (Hrsak et al., 2000). The presence of lead in the air as a result of incomplete combustion from vehicles and generating sets in Nigeria especially at urban centers also contribute to the build-up of the metal. This is more worrisome as 80% of 140 million estimated populations of Nigerians live or migrate to the urban cities either for a short or long stay. Out of this population, over 15 million people reside in Lagos State - south west of Nigeria, where these effluents are discharged. The heavy metals in the effluents may end up in drinking water and food chain.

The Copper concentrations in batch 1 are all within the maximum acceptable concentration of 2.0 mg/L but companies H and I had no detectable copper in the effluents. Zinc concentrations in all samples fall below

Table 1. Heavy Metal concentration in the first batch effluent samples.

Company	Ni^{2+} (mg/L)	Pb^{2+} (mg/L)	Cu^{2+} (mg/L)	Cd^{2+} (mg/L)	Zn^{2+} (mg/L)	Cr^{2+} (mg/L)
A	0.044	0.241	0.070	0.015	ND	ND
B	0.029	0.079	0.097	0.007	ND	ND
C	0.030	ND	0.046	0.028	ND	ND
D	0.002	ND	0.003	0.023	ND	ND
E	0.132	0.644	0.337	0.280	0.206	ND
F	0.014	0.031	0.072	0.054	1.437	ND
G	ND	0.068	0.040	0.020	0.858	ND
H	ND	0.043	ND	0.006	ND	ND
I	ND	0.038	ND	0.016	ND	ND

Table 2. Heavy metal concentration in the second batch effluent samples.

Company	Ni^{2+} (mg/L)	Pb^{2+} (mg/L)	Cu^{2+} (mg/L)	Cd^{2+} (mg/L)	Zn^{2+} (mg/L)	Cr^{2+} (mg/L)
A	ND	0.278	0.056	0.065	0.190	0.174
B	ND	0.089	0.069	ND	0.294	0.343
C	ND	ND	0.038	0.206	0.241	ND
D	ND	0.090	0.102	0.098	0.248	0.206
E	ND	0.152	0.054	ND	0.217	0.278
F	ND	ND	0.028	ND	0.055	0.513
G	ND	0.304	0.150	0.040	0.050	ND
H	ND	ND	0.162	ND	0.356	0.491
I	ND	0.094	0.071	ND	0.198	0.381

Table 3. Heavy metal concentration in the third batch effluent samples.

Company	Ni^{2+} (mg/L)	Pb^{2+} (mg/L)	Cu^{2+} (mg/L)	Cd^{2+} (mg/L)	Zn^{2+} (mg/L)	Cr^{2+} (mg/L)
A	ND	ND	0.162	ND	0.693	0.461
B	ND	ND	0.102	ND	0.345	0 0.489
C	ND	ND	0.281	0.050	0.306	0.171
D	ND	ND	0.100	ND	0.820	0.387
E	ND	ND	0.145	ND	1.227	0.479
F	ND	ND	0.206	0.129	1.245	0.294
G	0.058	0.0368	0.102	0.064	0.084	ND
H	ND	ND	ND	ND	ND	0.415
I	ND	ND	0.175	ND	0.874	0.457

Table 4. Comparison between International drinking water and FDA bottled water guidelines for the parameters analyzed in the study.

Parameter	USEPA MAC (mg/L)	Canada MAC (mg/L)	EU MAC (mg/L)	Japan MAC (mg/L)	WHO guideline (mg/L)	Bottled water US Federal drug administration level (mg/L)
Chromium	0.1	0.05	0.05	0.05	0.05	0.1
Cadmium	0.005	0.005	0.005	0.1	0.003	0.005
Copper	1.3	1.0	2.0	1.0	1-2	1.0
Lead	0.015	0.01	0.01	0.05	0.01	0.005
Nickel	0.1	-	0.02	0.01	0.02	-
Zinc	5.0	5.0	NS	1.0	3-5	-

USEPA – United State Environmental Protection Agency; MAC – Maximum Allowable Concentration; EU – European Union; WHO – World Health Organization.

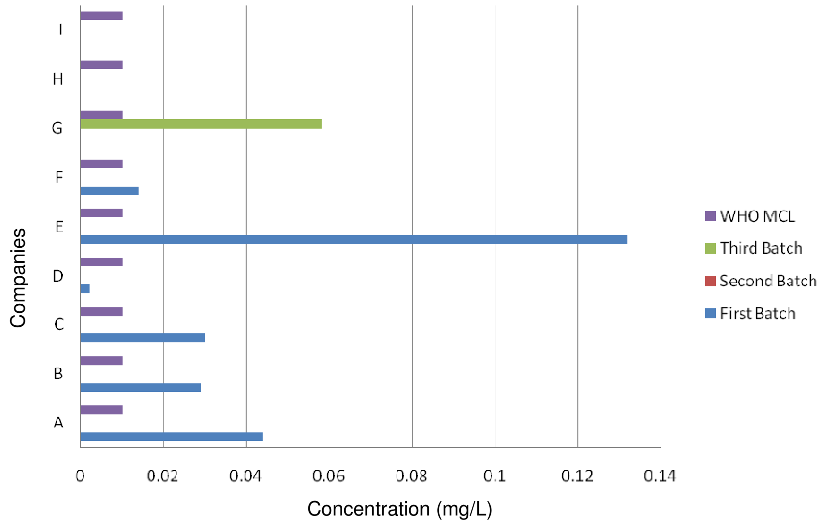

Figure 1. Nickel concentration in the samples.

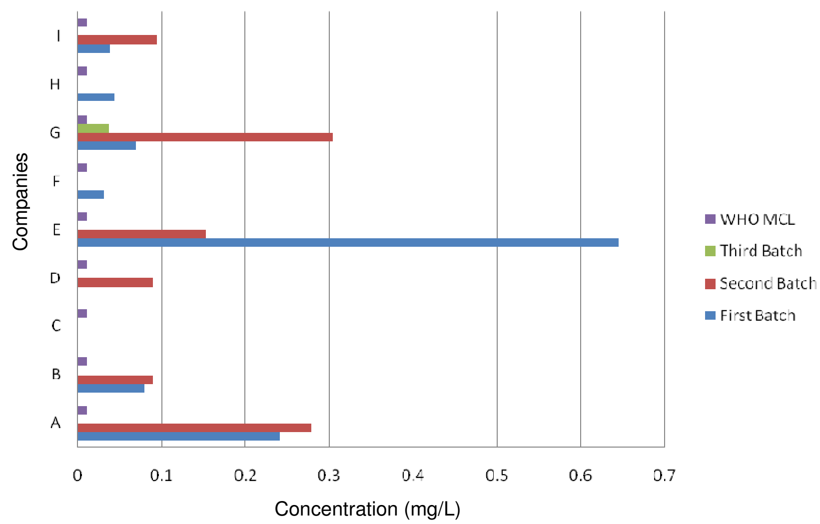

Figure 2. Lead concentration in the samples.

the WHO acceptable maximum of 5.0mg/L. Chromium was not detected in the samples. Cadmium concentrations were found to be higher than the WHO acceptable maximum of 0.003 mg/L. Company E effluent had cadmium concentration of 0.280 mg/L. Cadmium toxicity has been reported to cause food poisoning, mutation, hypertension, and cancer among others (Bottcher and Hamman, 1986). Long term exposure to cadmium has been found to cause serious damage to kidney, liver, bone and blood.

In subsequent batches, the concentrations of the different metals in the effluents fluctuated significantly giving credence to the fact that the metals are due to particular product being manufactured. For instance in the second and third sets of samples, Nickel concentration was only detected in one company's effluent. This variation occurred for all metals. In batch 2, 70% of the samples contain high lead and chromium concentrations and 80% of the samples had detectable chromium concentration in the third batch. In the same batch, 90% of the samples had no detectable lead concentration. Figures 1 to 6 show the distribution of the metals in different samples, and they illustrate these variations well.

Conclusion

The results obtained in this study revealed a high presence of Nickel, Lead, Cadmium and Chromium in the effluents from the pharmaceutical companies analyzed. This may pose adverse consequences on health and

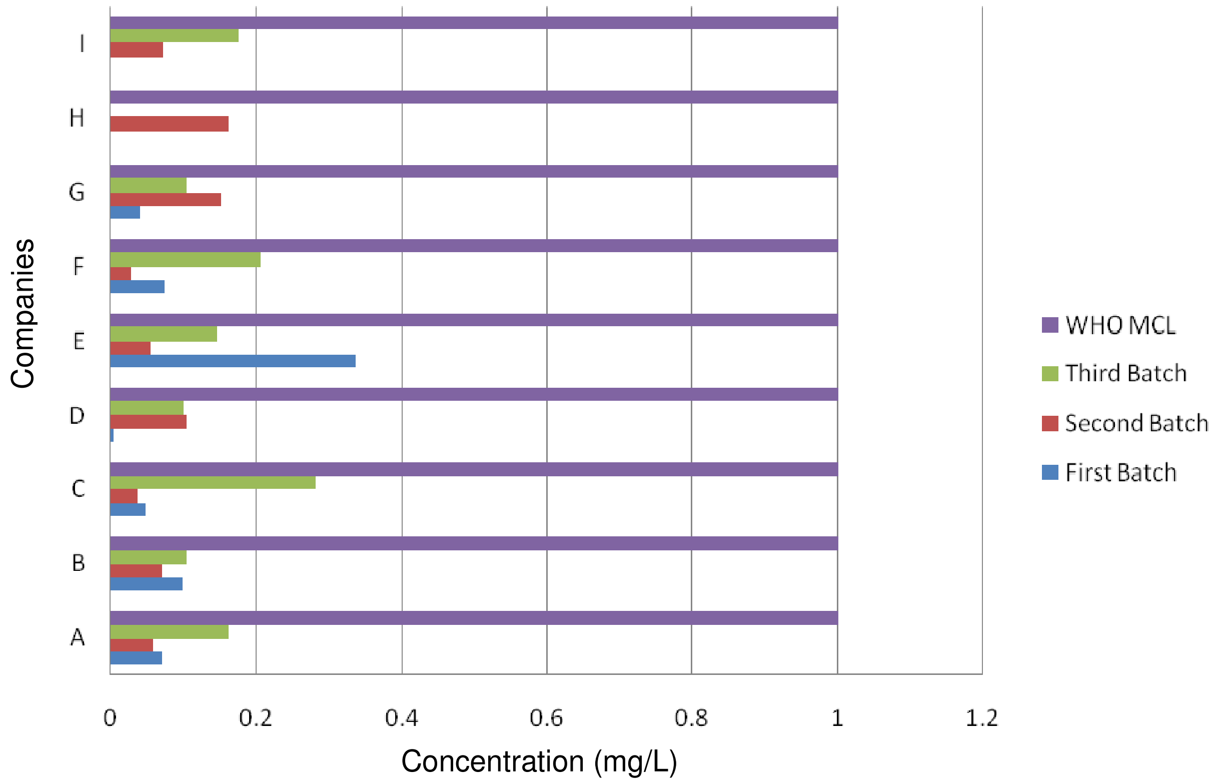

Figure 3. Copper concentration in the samples.

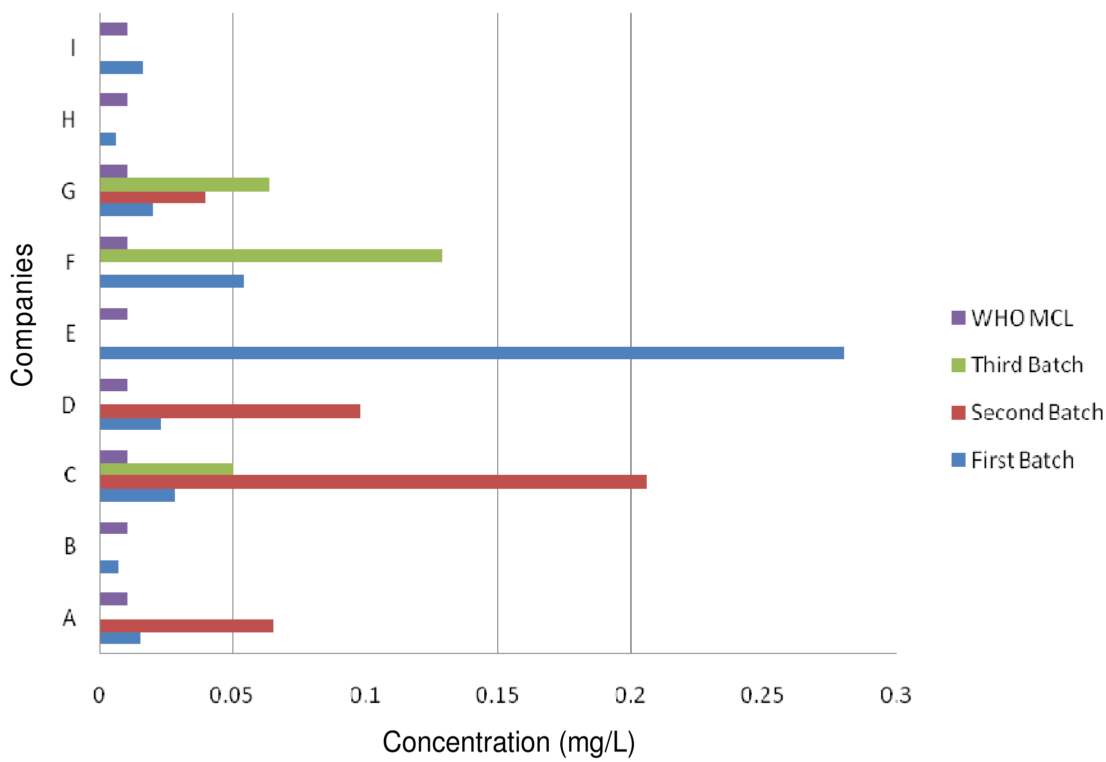

Figure 4. Cadmium concentration in the samples.

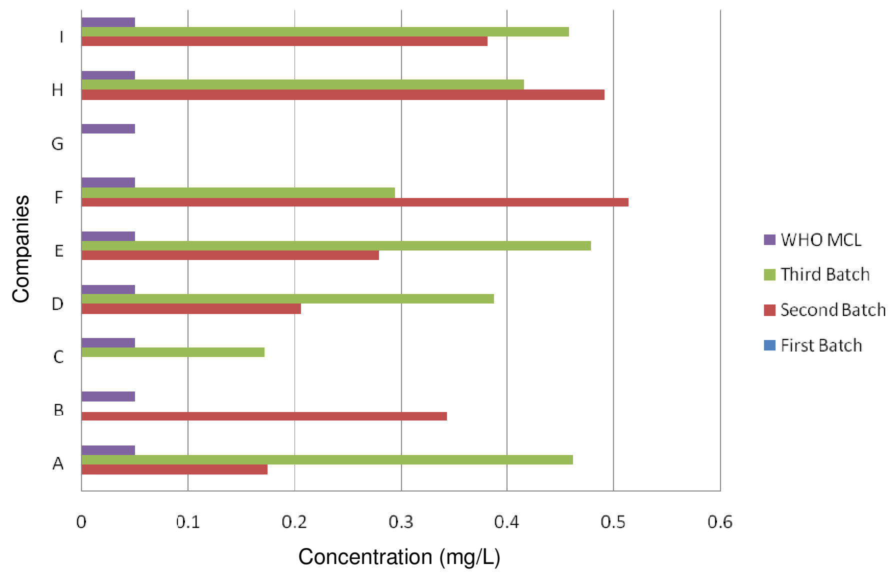

Figure 5. Chromium concentration in the samples.

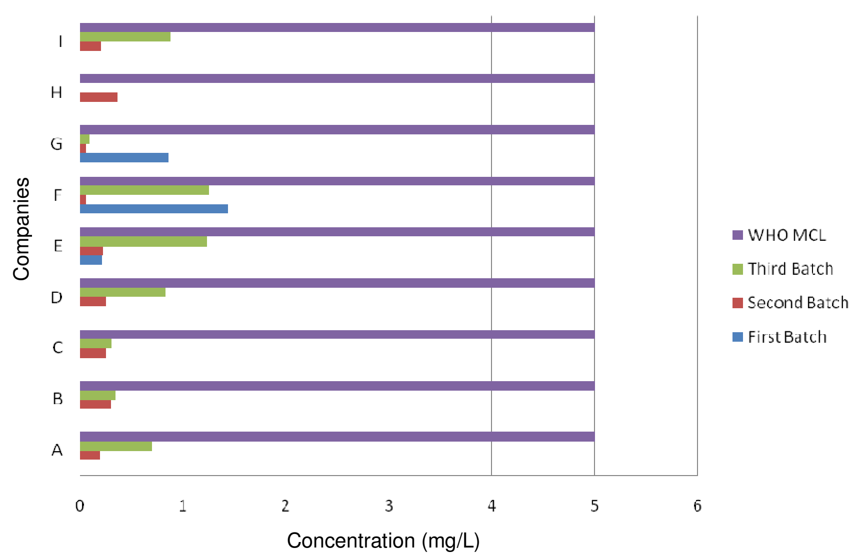

Figure 6. Zinc concentration in the samples.

environment. Therefore, there is an urgent need to enforce effluent treatment to reduce such environmental and health risks.

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