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Health Risk Assessment of some Cosmetic Products sold in Keffi Markets, Nasarawa State Nigeria

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Abstract
This study assesses the health risk associated with exposure to heavy metals in various brands of cosmetics sold in Nigeria market using the x-ray fluorescence spectroscopy Analyzer. Eight heavy metals were measured in thirty two cosmetics samples (ten talcum powder, ten pressed powder, six dental powder, four eye shadow, four eye liner, and two hair dye) commonly used in local market and super markets in keffi, Nasarawa state. The concentration of heavy metals such as Cd, Pd, Cr, Zn, Mn, Fe, Cu, Ni was determined. The Systemic exposure dose, Margin of safety, Hazard quotients and Hazardous indices were determined. Results shows that, the range of mean concentrations of metals in the cosmetics sample are Cd (0.216 -1.46 µg/g), Pd (53.628- 267.962 µg/g), Cr (18.571- 30.631 µg/g), Zn (10.443 -315.746 µg/g), Mn (77.693 - 256.319 µg/g), Fe (123.081 - 632.828 µg/g), Cu (9.285 - 36.126 µg/g), and Ni (8.603 – 48.887 µg/g). The hazard quotients were found to be greater than 1,which indicates the risk of carcinogenesis. The systemic exposure dosage (SED) values for these metals acquired from the personal care products were below the WHO limit of 100. The margin of safety values obtained were greater than 100, indicating that the concentrations of metals investigated in these facial cosmetics exert no risk associated with their occurrence in these products. The maximum value of oral cancer risk was detected in Hair dye and the minimum value in eye Liner. Conclusively heavy metal content within the studied cosmetic were ordered as Fe>Pb>Mn> Zn > Cr > Ni > Cu> Cd at all cosmetics. Eye linerhas the highest MOS values which indicate that there is little risk associated with the concentration of metals in eyeliner. HQ value was higher than 1 indicated that the overall risks in both exposure pathways are not within safe level. HI value washigher than 1.

Keywords: Heavy metals, cosmetics products, XRF spectrometry analyzer, Skin disease and Hazard parameters.

INTRODUCTION
The cosmetics industry has grown by average 4.5% per year in the past 20 years. This industry was able to be one of the most stable industries despite the economic downturn is because of the demand that keeps increasing all over the world (Lopaciuk & Loboda, 2013). Despite the high global demand for cosmetic products, the safety of these products is of great concern and has attracted the attention of researchers, toxicologists and regulators, with the common objective of ensuring the safety levels of ingredients in products (Nnorom *et al*., 2005).

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Safety of the cosmetics has become a major concern (Draelos, 2012). Group of fragrances, preservatives, antioxidants, vehicles, ultraviolet absorbers, humectants, emollients, emulsifiers, acrylates, hair dyes, and nail polish components are the most common ingredients in cosmetics. These additive chemicals are sometimes hazardous and prohibited due to the health risk it possesses (Amasa *et al*., 2012; Adepoju2012).
There are variable types of personal care products, PCP, between lip stick and lip gloss (used to color the lips); Mascara, eyes and eye shadows (used to color the eyelids); blusher and powder (used to color your face, reduce and eliminate defects); nail polish (used to color nails and feet) and different types of moisturizing and lightening / toning creams. Heavy metals are widely used in dyed makeup products. Cosmetics are one of the most severe reasons to release heavy metals (Abdel & Pingitor, 2009). This research work is aimed at assessing the health risk associated with heavy metal present in cosmetics products sold in Keffi markets, Nasarawa State Nigeria.

MATERIALS AND METHOD

Sample Collection

Thirty two samples in all; twenty face powder (Talcum and Presses), four eye liner, two hair dye and six dental powder, of different brands were bought from different cosmeticsshops from Taal modelmarket in keffi, Nasarawa state based on commonly used cosmetics and cost implication wasalso taken into consideration. These categories of cosmetics wasthe most commonly used andfrom eachcategory representative sample from various brands willbe selected. The samples that will be useare of different qualities and popular brands withdifferent price ranges from expensive products and cheap products (that is higher and lower prices).

Sample Preparation

Samples already bought from the Keffi main market where it was first crushed in agate mortar before air dried for about 6 hours in a clean plastic container under ambient temperature. After air drying, the sample were allowed to pass through 2.00 mm sieve. The 0.5g sample were placed in polytene bag and labelled accordantly and was sent to Centre for Solid Minerals Research and Development (CSMRD), Kaduna Polytechnic, Kaduna, Nigeria where they were analyze for heavy metals using XRF spectrometry analysis.
The spectrometer brand name is ECLIPSE III supplied by AMTEK INC. MA; USA with Model number: XR-100CR which is a high performance X-ray Detector with preamplifier and a cooler system which uses a thermoelectrically cooled Si-PIN photodiode as an X-ray detector. The samples to be irradiated are placed in the sample chamber. The sample chamber has connections to it, which are at angle 45o to it respectively, the source X-ray tube and the SiPIN photodiode detector. The source X-ray tube is maintained at a voltage of 25kV and a current of 50μA and each of the samples is irradiated for 1000sec.

Safety and Risk Assessment of Cosmetics Products

Systemic Exposure Dosage (SED)

The systemic availability of a cosmetic substance is estimated by taking into consideration the amount of the finished product applied to the skin per day, the concentration of metals in the cosmetic product under study, the dermal absorption of the metal and a human body weight value. The systemic exposure dosage (SED) is given by the formula:

$$SED = \frac{CSxAAxSSAxFxRFxBF}{BW} x10^{-3} \quad (1)$$

Where; Cs is the concentration of metal in the facial cosmetic product, SSA is the skin surface area onto which the products are applied, AA is the amount of facial cosmetic product applied per day, RF is the retention factor, F is the frequency of application per day, BF is the bio accessibility factor, and BW is the body weight(AbdEl-Aziz *et al*., 2017).

Lowest No Observed Adverse Effect Level (NOAEL)

The NOAEL values were calculated from the oral reference doses (RFDs). NOAEL is calculated using the relationship;

$$NOAEL = RFDxUFxMF \quad (2)$$

where UF and MF are the uncertainty factor (reflecting the overall confidence in the various data sets) and the modifying factor (based on the scientific judgment used) respectively. In this case the default values of UF and MF were 100 and 1. The RFDs (in mg $kg^{-1}day^{-1}$) used were Pb (4×10^{-3}), Cd (1×10^{-3}), Cr (3×10^{-3}), Co (3×10^{-4}), (Zn (3.0×10^{-1}), Fe (7.0×10^{-1}), Cu(4.0×10^{-2}), Mn (1.4×10^{-1}),Ni (2×10^{-2}) and Hg(3×10^{4}) (AbdEl-Aziz *et al*., 2017; USEPA, 2011).

Margin of Safety

The Margin of Safety (MOS) is the ratio of the lowest no observed adverse effect level (NOAEL) value of the cosmetic substance under study to its estimated systemic exposure dosage (SED).

$$MOS = \frac{NOAEL}{SED} \quad (3)$$

World Health Organization, WHO, recommends a minimum value of 100 and it is generally accepted that the value should not exceed 100 in other to conclude that a substance is safe for use(AbdEl-Aziz *et al*., 2017; USEPA, 1989).

Hazard Quotients

Hazardous Quotient (HQ) associated with the use cosmetics was determined by the ratio of Systemic Daily Exposure Dose (SED) to the oral reference dose (RfD) for each metal. Where, RfD is the oral reference doses(AbdEl-Aziz *et al*., 2017). RfD is an estimate of a daily dermal exposure of the human population, which does not cause deleterious effects during a lifetime.

$$HQ = \frac{SED}{RfD} \quad (4)$$

Where, SED is the Systemic Exposure Dosage, RfD is the oral reference dose (AbdEl-Aziz *et al*., 2017; USEPA, 1989).

Hazardous Index (HI)

Hazardous Index (HI) is used to estimate the risk to human health due to the exposure to the nine heavy metals. Hazard index is the sum of the hazard quotients for all heavy metals, which was calculated by:

$$HI = \sum HQ = HQ_{Cr} + HQ_{Cu} + HQ_{Fe} + HQ_{Pb} + HQ_{Zn} + HQ_{mg} + HQ_{Mn} + HQ_{Nl}. \quad (5)$$

where HQ is the hazardous quotients calculated for Cr, Cu, Fe, Pb, Zn, Mn, and Ni respectively.

(AbdEl-Aziz *et al*., 2017; USEPA, 1989).

RESULTS AND DISCUSSION

The variation of heavy metal concentrations (μg/g) among different types of cosmetics are presented in Figure 1-7. The mean concentration of the various brands of cosmetics samples are presented in Table 1.

The variations of heavy metal concentrations (µg/g) in cosmetics sample collected were sorted in the following order Fe>Zn>Mn>Pd>Ni>Cr>Cu>Cd, as illustrated in Figure 1-6. The mean values of Cd was lowest in eye liner with concentration of 0.216 µg/g while,highest value was found in talcum powder with concentration of 1.46 µg/g. In eye shadow, the concentration Cd ranged from 0.411 µg/g to 2.785 µg/g, where in talcum powder was 0.034 µg/g to 5.897 µg/g and in pressed powder was ND to 5.897 µg/g which were below the international permissible limits 5 µg/g for FDA, Italy and Germany and 3 µg/g for Health Canada. Only one sample PP5 was above the limits and may cause harm. The result is in agreement with other studies (Al-Saleh *et al*., 2011; Sani*et al*., 2016). The order of cadmium concentrations in the samples were talcum powder > pressed powder > dental powder > eye shadow > hair dye and eye liner.

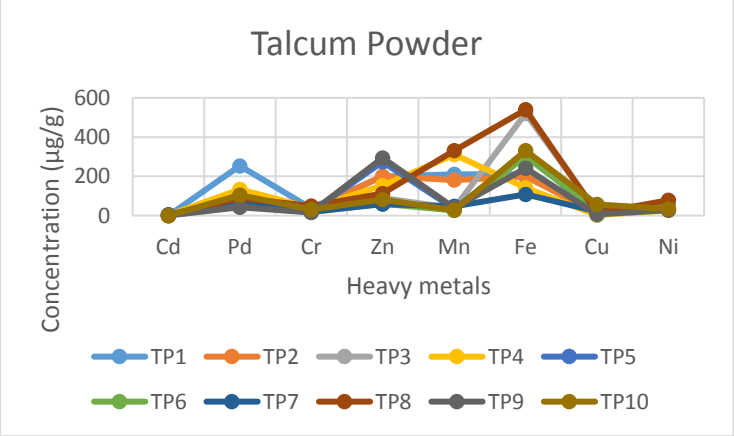

Figure 1: Chart of Heavy metal in Talcum Powder

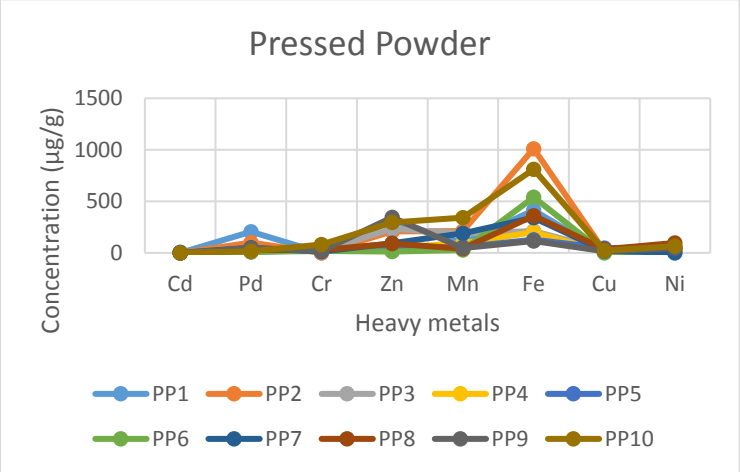

Figure 2: Chart of Heavy metal in Pressed Powder

Chromium concentrations ranged from 16.904 to 49.003 µg/g in talcum powder, 0.008 to 81.903 µg/g in pressed powder samples, 8.211 to 42.113 µg/g in dental powder samples, 8.003 to 29.004 µg/g in eye shadow, 22.021 to 41.012 µg/g in eye liner samples.
High concentrations of chromium were found in PP10, pressed powder. Comparing with results reported by Abd El-Aziz et al. (2017) and Iwegbue *et al*. (2016), the obtained results are almost similar. The concentration of Chromiun is due to its application in Cr-

containing colouring agents. The chromium concentrations is ordered in the samples as eye liner> hair dye > dental powder > talcum powder > pressed powder and eye shadows. Chromium exposurecan cause skin ulcers,and severe redness and swelling of the skin. Several studies indicated that thepresence of irritants following repeated exposuresto Cr and Ni rarely react to levels below 10 µg/g. For this reason, Basketter *et al*. (2003)recommended that cosmetics products should have concentration not more than 5 µg/g for Ni and Cr, and for better health protection levels should not exceed 1 µg/g.

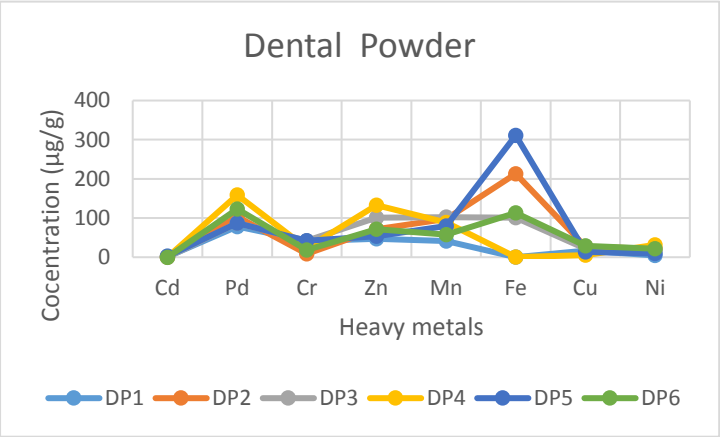

Figure 3: Chart of Heavy metal in Dental Powder

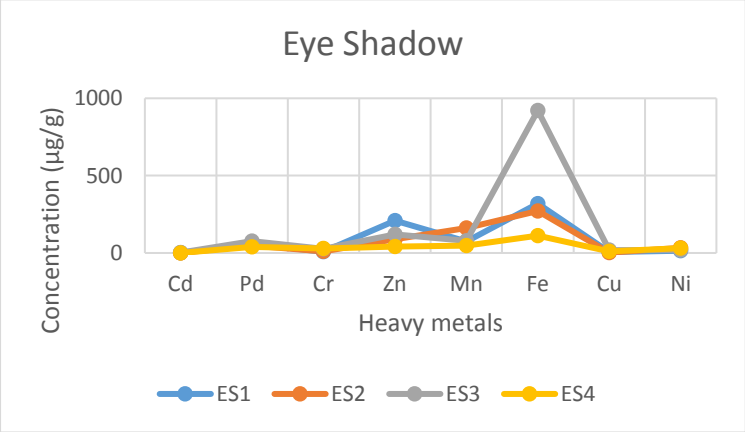

Figure 4: Chart of Heavy metal in Eye Shadow

The maximum values Copper in talcum powder, pressed powder, dental powder, eye liner, and hair dye were 57.989, 46.781, 29.187, 10.016, 12.902 and 47.139 µg/g, respectively, while the minimum values were 2.001, 2.113, 5.141, 2.005, 4.983 and 25.112, respectively. The highest mean concentration of copper was observed in in hair dye. Order of Cu concentration in samples was hair dye > pressed powder > dental powder > talcum powder > eye liner and eye shadow. Mean concentrations of Mnwere 124.8255 µg/g, 129.340 µg/g, 77.693 µg/g, 90.729 µg/g, 67.394 µg/g and 256.319 in talcum powder, pressed powder, dental powder, eye shadow, eye liner, and hair dye respectively. Order of Mn concentration in cosmetic samples was hair dye >talcum powder > pressed powder > eye shadow > dental powder and eye liner.

Although Mn and Cu are rare skin sensitizers, there were cases reported with increased menstrual pain and blood loss as a result of exposure to Cu from widely used intra-uterine

devices (IUDs) or immune reactions due to exposure to Cu from handling of euro coins, while the risk of sensitization for both Cu and Mn has been reported from the use of prosthetic materials in dentistry (AbdEl-Aziz *et al*., 2017; Iwegbue *et al*., 2016).

Iron was relatively high in all cosmetics samples. Ranges of mean concentrations were 290.5065 µg/g in talcum powder, 413.279 µg/g in pressed powder, 123.081 µg/g in dental powder, 406.053 µg/g in eye shadow, 267.702 µg/g in eye liner, and 632.828 µg/g in hair dye. Fe concentrations in these samples were higher than any element studied. Exposure to small amounts of Fe from cosmetic products may cause cellular death or colorectal cancer as a result of cumulative effects (AbdEl-Aziz *et al*., 2017; Iwegbue *et al*., 2016).

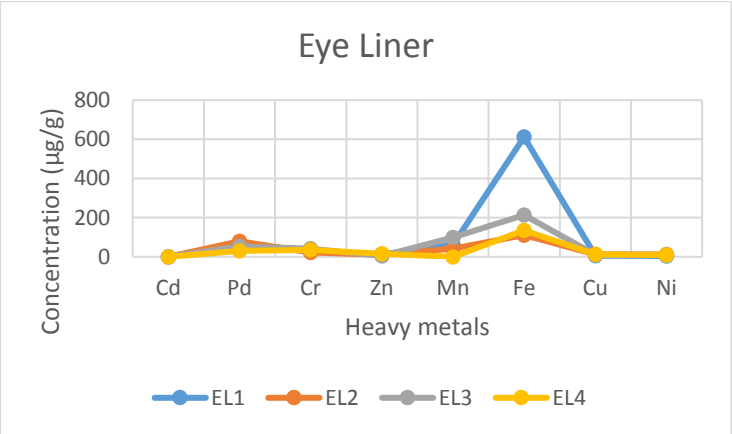

Figure 5: Chart of Heavy metal in Eye Liner

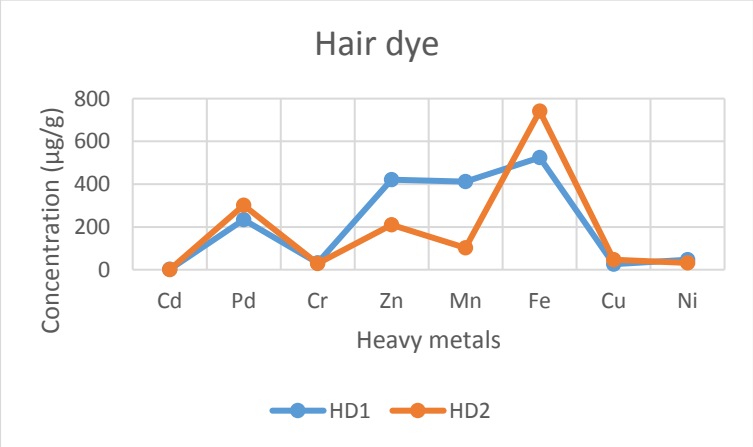

Figure 6: Chart of Heavy metal in Hair Dye

The concentration of Pb in this study were relatively high. The mean concentration range was 103.07 µg/g in talcum powder, 53.628 µg/g in pressed powder, 106.372 µg/g in dental powder, 55.354 µg/g in eye shadow, 57.528 µg/g, and 267.962 µg/g. A high concentration of Pb was observed in all samples when compared with international guidelines of FDA, Italy and Germany (20 µg/g) and Health Canada (10 µg/g).The results agrees with those reported by Iwegbue *et al.*(2016). High levels of Pb were observed in Kohl that is ordinary composed of galena (PbS) and silver galena (Pb_2SO_4) (Al-Ashban *et al*., 2004).

Table 1. Mean concentration of heavy metals facial cosmetics products (in µg/g)

Cosmetics brand	Mean Concentration (µg/g)							
	Cd	Pd	Cr	Zn	Mn	Fe	Cu	Ni
Talcum Powder	1.46	103.07	27.581	152.5485	124.8255	290.5065	18.416	39.455
Pressed Powder	1.426	53.628	24.387	167.328	129.340	413.279	21.534	48.887
Dental powder	1.254	106.372	29.197	79.589	77.693	123.081	18.783	17.325
Eye Shadow	1.233	55.354	18.571	115.260	90.729	406.053	9.285	24.411
Eye liner	0.216	57.528	32.256	10.443	67.394	267.702	10.094	8.603
Hair dye	0.829	267.962	30.631	315.746	256.319	632.828	36.126	39.172

Results of margin of safety calculated for dental powder, eye shadow, and eye liner, were found to be greater than 100 which is the minimum value set by the World Health Organization (WHO)(Table 2). Talcum powder, pressed powder, and hair dye were found to have values that is below the proposed limit by WHO. There is a possibility of some substance to buildup in the human body over time and cause adverse health effects. The MOS values agrees with those reported by Abd El-Aziz *et al*. (2017) and Iwegbue *et al*. (2016). These values indicate that there is little risk associated with the use of these facial cosmetic.

Table 2. Calculated Margin of Safety (MoS) for the facial cosmetics sample.

Cosmetics brand	Margin of Safety (MoS)							
	Cd	Pd	Cr	Zn	Mn	Fe	Cu	Ni
Talcum powder	7.80	0.44	1.24	22.40	12.78	27.45	24.74	5.77
Pressed powder	7.98	0.85	1.40	20.42	12.33	19.30	21.16	4.66
Dental powder	51.17	2.41	6.59	241.77	115.57	364.77	136.59	3.70
Eye shadow	5528.00	492.45	1100.822	17737.22	10515.40	11747.86	29356.85	5583.31
Eye liner	947940.89	14214.82	19014.07	5873144.11	424686.97	534576.05	810161.74	475274.33
Hair dye	4.53	0.06	0.37	3.5719	2.05	4.16	4.16	1.92

Table 3. Systemic Exposure Dosage (SED) in (µg kg^{-1}dw day^{-1})

Cosmetics brand	Systemic Exposure Dosage (SED) in (µg kg^{-1}dw day^{-1})							
	Cd	Pd	Cr	Zn	Mn	Fe	Cu	Ni
Talcum powder	0.0128	0.9042	0.2421	1.3391	1.0957	2.5501	0.1617	0.3463
Pressed powder	0.0125	0.4710	0.2140	1.4690	1.1350	3.6280	0.1890	0.4290
Dental powder	0.0020	0.1658	0.0455	0.1240	0.1211	0.1919	0.0293	0.0270
Eye shadow	$1.8x10^{-5}$	$8.0x10^{-4}$	$3.0x10^{-4}$	$1.7x10^{-3}$	$1.3x10^{-3}$	$6.0x10^{-3}$	$1.0x10^{-4}$	$4.0x10^{-4}$
Eye liner	$1.1x10^{-7}$	$2.8x10^{-5}$	$1.6x10^{-5}$	$5.1x10^{-6}$	$3.3x10^{-5}$	$1.0x10^{-4}$	$4.9x10^{-6}$	$4.2x10^{-6}$
Hair dye	0.0221	7.1278	0.8148	8.3989	6.8181	16.8334	0.9609	1.0420

The calculated Systemic Exposure Dosage (SED) (µgkg^{-1}dwday^{-1}) and Margin of Safety (MOS) of heavy metals in cosmetic products under study are displayed in Table 3. The SED of the cosmetic products calculated ranged from $1.1x10^{-7}$ to 0.0221 µg kg^{-1}dw day^{-1} for Cd, $2.8x10^{-5}$ to 7.1278 µg kg^{-1}dw day^{-1} for Pd, $1.6x10^{-5}$ to 0.8148 µg kg^{-1}dw $day^{-1}$for Cr, $5.1x10^{-6}$ to 8.3989 µg kg^{-1}dw day^{-1} for Zn, $3.3x10^{-5}$µgkg^{-1}dwday^{-1} for Fe, $4.9x10^{-6}$ to 0.9609 µg kg^{-1}dw day^{-1} for Cu, and $4.2x10^{-6}$ to 1.0420 µg kg^{-1}dw day^{-1}. The values of SEDs for the cosmetics product are above the recommended intake value.

Table 4. Table of Hazardous quotient, HQ, and hazardous index, HI for the measured heavy metals

Cosmetics brand	HQ								HI
	Cd	Pd	Cr	Zn	Mn	Fe	Cu	Ni	
Talcum powder	$7.8x10^{3}$	$1.1x10^{2}$	$4.1x10^{2}$	$7.5x10^{1}$	$9.1x10^{1}$	$3.9x10^{1}$	$6.2x10^{2}$	$2.9x10^{2}$	$9.4x10^{3}$
Pressed powder	$8.0x10^{3}$	$2.1x10^{2}$	$4.7x10^{2}$	$6.8x10^{1}$	$8.8x10^{1}$	$2.8x10^{1}$	$5.2x10^{2}$	$2.3x10^{2}$	$9.6x10^{3}$
Dental powder	$5.1x10^{4}$	$6.0x10^{2}$	$2.2x10^{3}$	$8.1x10^{2}$	$8.3x10^{2}$	$5.2x10^{2}$	$3.4x10^{3}$	$1.9x10^{2}$	$6\text{-}0x10^{4}$
Eye shadow	$5.5x10^{6}$	$1.2x10^{5}$	$3.7x10^{5}$	$5.9x10^{4}$	$7.5x10^{4}$	$1.7x10^{4}$	$7.3x10^{5}$	$2.8x10^{5}$	$7.2x10^{6}$
Eye liner	$9.5x10^{8}$	$3.6x10^{6}$	$6.3x10^{6}$	$2.0x10^{7}$	$3.0x10^{6}$	$7.6x10^{5}$	$2.0x10^{7}$	$2.4x10^{7}$	$1.0x10^{9}$
Hair dye	$4.5x10^{3}$	$1.4x10^{1}$	$1.2x10^{2}$	$1.2x10^{1}$	$1.5x10^{1}$	$5.9x10^{0}$	$1.0x10^{2}$	$9.6x10^{1}$	$4.9x10^{3}$

Table 4 illustrates Hazard Quotients and Hazardous Indices of oral and dermal pathways in the samples of cosmetics in this study. The study reveal that HQ value was greater than 1 which indicate that the overall risks in both exposure pathways are above the safe level. A maximum HQ values to Cd, Pd, Cr, Zn, Mn, Fe, Cu, and Ni, are$9.5x10^{8}$, $3.6x10^{6}$, $6.3x10^{6}$, $2.0x10^{7}$, $3.0x10^{6}$, $7.6x10^{5}$, $2.0x10^{7}$, and $2.4x10^{7}$respectively, indicating that there is high risk of carcinogenic effects.

HI to talcum powder, pressed powder, dental powder, eye shadow, eye liner and hair dye are $9.4x10^{3}$, $9.6x10^{3}$, $6.0x10^{4}$, $7.2x10^{6}$, $1.0x10^{9}$, and $4.9x10^{3}$ respectively. Results are in agreement with those reported by Abd El-Aziz *et al*. (2017) and Iwegbue *et al.*(2016).

CONCLUSION

The present study indicate the present of Fe, Pb, Zn, Mn, Cr, Cu, Ni, and Cd in some cosmetics product sold in Taal model market in Keffi, Nasarawa state. The order of the concentration are Fe>Pb>Mn> Zn> Cr> Ni> Cu> Cd with Cd having the least average concentration. Pb, Cr, and Ni were present in all the cosmetics sample with concentration above the recommended limit. Systemic exposure dosage (SED) of heavy metals in cosmetics sample were found to be less than the recommended daily intake. The estimated margin of safety (SED) calculated for metals in cosmetic products in this study was found to be above the recommended value of 100 set by the WHO. Hazard Quotient (HQ) value appear to be greater than 1 which indicate that the overall risks in both exposure pathways are not within safe level. Hazardous Indices (HI) values were also greater than 1 which indicates the risk in using the cosmetics samples. The study recommends urgent needs for national regulation for manufacturing of cosmetics product.

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