Toxicology Reports 3 (2016) 796–803

Contents lists available at ScienceDirect

Toxicology Reports

journal homepage: www.elsevier.com/locate/toxrep

Evaluation of human exposure to metals from some commonly used hair care products in Nigeria

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ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form
20 September 2016
Accepted 5 October 2016
Available online 6 October 2016

Keywords:
Metals
Systemic exposure dosage
Margin of safety
Risk assessment
Hair care products
Nigeria

ABSTRACT

The concentrations of nine metals, namely, cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), cobalt (Co), nickel (Ni), manganese (Mn), zinc (Zn), and iron (Fe), were determined in 26 brands of hair care products including hair relaxers, conditioners and shampoos. The study was aimed at providing information on the possible risks arising from heavy metals associated with the use of these products. The concentrations of the metals were determined by means of atomic absorption spectrophotometry after digestion of the samples with a mixture of acids. The concentrations of the respective metals in hair relaxers, shampoos and conditioners were found to be 0.8–2.5, 0.6–3.0, <LOQ-2.8 $\mu g\,g^{-1}$ Cd; 4.5–26.0, <LOQ-28.0, <LOQ-425 $\mu g\,g^{-1}$ Pb; <LOQ-0.6, <LOQ-3.4, <LOQ-4.2 $\mu g\,g^{-1}$ Cr; <LOQ-3.5, <LOQ-6.0, <LOQ-3.5 $\mu g\,g^{-1}$ Cu; <LOQ-7.0, <LOQ-7.0, 0.5–4.5 $\mu g\,g^{-1}$ Co; 1.0-5.5, <LOQ-10.5, 1.5–6.0 $\mu g\,g^{-1}$ Ni; <LOQ-9.0, 2.0–25.5, <LOQ-15 $\mu g\,g^{-1}$ Mn; 36.5–48.0, 35.5–1080 $\mu g\,g^{-1}$, 30.0–69.0 $\mu g\,g^{-1}$ Zn; and 84.5–123, 66.7–284, 57.6–153 $\mu g\,g^{-1}$ Fe respectively. The systemic exposure dosage (SED) values of the studied metals were below their respective provisional tolerable daily intakes (PTDI)/recommended daily intakes (RDI), while the margins of safety were greater than 100 which indicate that these products are safe to use.

1. Introduction

The use of cosmetics to beautify the human body is a worldwide tradition spanning thousands of years. Despite challenging economic conditions, the demand for cosmetic products has increased worldwide because of human's consciousness of the need to beautify their bodies [1,2] and the sharp rise in advertisements of products both in the print and electronic media [2,3]. The use of cosmetics as routine body care cuts across all income classes in society [4].

The sources of metallic impurities in cosmetic products include their use as ingredients as exemplified by the use of zinc oxide in sunscreen creams, inorganic mercury compounds in skin-lightening creams, lead acetate in progressive hair dyes, and aluminium and zirconium salts in antiperspirants [2], and/or as contaminants arising from the manufacturing processes. The intentional use of compounds of antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), and nickel (Ni) as ingredients of cosmetic products is prohibited by Annex II of directive 76/768/EEC of the European Union because they are considered unsafe as a result of toxicity problems, but these compounds still persist in today's cosmetic products owing to their ubiquitous nature and from contamination from production processes.

The occurrence of metals in cosmetic products is of concern for three principal reasons: (i) the use of cosmetic products could represent a possible source of population-wide exposure daily, and often long-term exposure to metals in cosmetic products [6,7], (ii) metals can accumulate in the body over time, and (iii) a number of them are known to exhibit different chronic health effects, such as cancer, contact dermatitis, developmental, neurological and reproductive disorders, brittle hair and hair loss. Some metals are potent endocrine disruptors and respiratory toxins. Moreover, some metals, such as Cd, As, Pb, Hg and Sb, are exceptionally toxic with a wide variety of chronic health effects, whereas Cr, Ni and Co are well known skin sensitizers [4,7,8]. For these reasons, the cosmetic industries have become a target for increased regulatory scrutiny

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http://dx.doi.org/10.1016/j.toxrep.2016.10.001

Table 1
Information on the hair care products.

Brand name	Colour	Country of Origin
Hair Relaxers		
Care times	Milky	Nigeria
Relax regular	White	Nigeria
BEVA	White	USA
Ozone	Milky	Nigeria
TCb No base	White	South Africa
No Lye	White	Nigeria
Hair Shampoos		
Our choice	Pink	Nigeria
Petals	Pink	Nigeria
Olive oil	Lemon	UK
BEVA	Milky	USA
Mega growth	Milky	USA
Neutralizing	Milky	Nigeria
Anti-dandruff Hair Shampoos		
Vinoz	Green	Nigeria
Viola	Orange	Nigeria
Nizoral	White	USA
Selsium	Orange	USA
Head & Shoulders	White	France
Hair Conditioners		
Soul mate	Brown	Nigeria
Petals hair food	Orange	Nigeria
Blue magic	Blue	USA
Milky way hair darkey	White	Nigeria
Petals	White	Nigeria
Dark & Lovely	Pink	South Africa
Ultra reconstructor	White	South Africa
Dark & Lovely corrective	White	South Africa
Liquid activator	White	South Africa

worldwide with a common goal of ensuring safe levels of the ingredients in these products.

A survey of the literature indicates that there are a limited number of studies on the concentrations of metals in hair care products in Nigeria and other parts of the world [1,9–11]. This study evaluates the concentrations and risks of metals (Cd, Pb, Cr, Cu, Co, Ni, Mn, Zn and Fe) in some hair care products in Nigeria.

2. Materials and methods

2.1. Samples and sample collection

A total of 26 brands of commonly used hair care products were purchased from markets in Abraka, Warri, Benin-City and Lagos, Nigeria. Within a given brand, a total of three samples with different batch numbers and dates of manufacture were collected in order to study the variations in elemental concentrations within a particular brand. The brands collected included those manufactured in Nigeria as well as those imported from other countries. The brands studied were carefully selected to reflect the popular brands used by different income classes. The samples collected for this study were within their specified usage periods (shelf-life). Information regarding brand names and the country of origin of these products is shown in Table 1.

2.2. Reagents

All the reagents used in this study were of analytical grade, namely, nitric acid (HNO_3, 69%), hydrochloric acid (HCl, 37%), and perchloric acid ($HClO_4$, 69%) (British Drug House, Poole, UK). The calibration standards were prepared by diluting 1000 mg L^{-1} commercial standards of Cd, Pb, Cr, Cu, Co, Ni, Mn, Zn and Fe (Merck, Darmstadt, Germany) with 0.25 mol L^{-1} HNO_3.

2.3. Sample preparation

For each sample a mass of 0.5 g was placed in a Teflon vessel; then 10 mL of concentrated hydrochloric acid, 5 mL of concentrated nitric acid and 5 mL of perchloric acid were added and the mixture was predigested for at least 4–5 h. The vessel was covered and the sample was heated on regulated hotplate to 120 °C for 1 h. The sample solution was allowed to cool to room temperature, filtered and made up to 25 mL with 0.25 mol L^{-1} HNO_3. Three blanks were prepared in a similar way, but omitting the samples.

2.4. Chemical analysis

The concentrations of metals (Cd, Pb, Cr, Cu, Co, Ni, Mn, Zn and Fe) in the filtrates were analyzed in triplicate by using flame atomic absorption spectrophotometry (Perkin Elmer, Analyst 200, Norwalk, CT, USA). Calibration standards and blank solutions were analyzed in a similar way as the samples. For each analysis at least three blanks were analyzed. The average blank signal was subtracted from the analytical signal of the sample before statistical analysis.

2.5. Quality control and statistical analysis

All glassware used in this study was previously soaked in 10% nitric acid solution for 24 h and rinsed with deionized water. The instrument was calibrated after every ten runs. In the absence of a certified reference material, the accuracy of the analytical procedure was validated by using spike recovery methods. A known amount of the test elements at three concentration levels was introduced into fresh parts of already analyzed samples, and all the analytical steps from digestion to atomic absorption analysis were repeated. The percent spike recoveries for the metals were between 83.4 and 105% while the intra-day and inter-day calibration precisions were less than 13% (Table 2). The working conditions of the atomic absorption spectrophotometer, and the limits of detection and quantification for the studied metals are also provided in Table 2. Analysis of variance (ANOVA) and Tukey post hoc tests were used to determine whether the concentrations of metals varied significantly within the same brand and between different categories of hair care products respectively.

2.6. Evaluation of systemic exposure dosage and margin of safety

The risk of human exposure to the metals contained in these hair care products can be evaluated by using the uncertainty factor called the Margin of Safety (MoS). This is the ratio of the lowest no observed adverse effect level (NOAEL) value of the metal under investigation to its estimated systemic exposure dosage (SED) [12].

$$MoS = \frac{NO(A)EL}{SED}$$

Information on the systemic dosage of metals in cosmetics can be obtained by taking into account the amount of the cosmetic product applied to the body per day, the applied surface area, the concentration of the metal in the cosmetic product under investigation, the dermal absorption of that particular contaminant and a human body weight value [12].

The systemic exposure dosage (SED) is given by the expression:

$$SED\left(\mu g kg^{-1} bw day^{-1}\right) = \frac{Cs \times AA \times SSA \times F \times RF \times BF}{BW} \times 10^{-3}$$

where Cs is the concentration of the particular metal in the product (mg kg^{-1}); AA is the amount of the cosmetic product used per day (16.67 g per day); SSA is the surface area of skin (17500 cm^2); F is

Table 2
Atomic absorption spectrophotometer settings and validation data for metals analyzed.

	Instrument Settings				Flame composition		Percent recovery			Linearity	Precision[b]			
	Wavelength (nm)	Slit width (nm)	Relative noise	Lamp curren (mA)	Air (L/min)	Acetylene (L/min)	[a]0.05 μg g^{-1}	[a]2.0 μg g^{-1}	[a]10 μg g^{-1}	R^2	Intra-day	Inter-day	LOD (μg g^{-1})	LOQ (μg g^{-1})
Cd	228.8	0.7	1.0	10	9.5	2.3	84.5	88.4	92.4	0.9994	5.3	6.2	0.02	0.06
Pb	283.3	0.7	0.43	8	9.5	2.3	96.7	92.4	93.8	0.9999	6.2	7.8	0.03	0.09
Cr	357.9	0.7	1.0	12	9.5	2.3	94.9	96.4	90.2	0.9998	8.2	9.2	0.04	0.12
Ni	232.0	0.2	1.0	30	9.5	2.3	88.5	92.3	93.2	0.9992	6.4	4.2	0.02	0.06
Cu	324.8	0.7	1.0	25	9.5	2.3	84.6	93.5	99.6	0.9998	10.5	11.3	0.02	0.06
Co	240.7	0.2	1.0	15	9.5	2.3	99.7	101	83.6	0.9997	12.2	12.3	0.04	0.12
Mn	279.5	0.2	1.0	12	9.5	2.3	92.5	93.6	98.4	0.9998	5.8	8.6	0.03	0.09
Zn	213.9	0.7	1.0	15	9.5	2.3	96.4	93.2	98.6	0.9998	10.2	7.2	0.04	0.12
Fe	248.3	0.2	1.0	15	9.5	2.3	92.3	105	83.4	0.9996	6.3	7.8	0.03	0.09

[a] amount added.
[b] average of three concentration levels.

the frequency of application (1.43/day); RF is the retention factor (0.01 for non-leave-on cosmetic products); BF is the oral bioaccessibility factor; BW is the body weight (kg) and 10^{-3} is a unit conversion factor. The AA, SSA, F and RF values used in the estimation of SED and MoS in the present study were the standard values established by the Scientific Committee on Consumer Safety (SCCS) [12] and a default body weight value of 60 kg was used. The NOAELs of the metals were obtained from their oral reference doses (RfD) by multiplying the latter by the uncertainty factor (UF) and the modifying factor (MF). The oral reference dose is an estimate of the daily exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during one's life time. The UF represents the uncertainty factor (reflecting the overall confidence in the various data sets) while MF represents the modifying factor (based on the scientific judgment used). In this case the default values of UF and MF were 100 and 1 respectively. The RfDs (in mg kg^{-1} day^{-1}) for the metals were Pb (4×10^{-3}) [13], 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}) and Ni (2×10^{-2}) [14]. The World Health Organization (WHO) has proposed a minimum MoS value of 100 as acceptably safe for the product to be used on the human body [12]. The SCCS acknowledged the fact that in many conventional calculations of MoS, the oral bioavailability of the substance is assumed to be 100% if oral absorption data are available. However, it is considered appropriate to assume that not more than 50% of an orally administered dose is systemically available [12].

3. Results and discussion

The results for the determination of the metal concentrations in these brands of hair care products are presented in Table 3. The concentrations of the metals varied significantly ($p < 0.05$) from one brand to another and also between the different categories of hair products. These differences may be associated with the difference in raw material types and sources, and branding and manufacturing processes. There are currently no established regulatory control limits for metals in cosmetics in most countries of the world including Nigeria. However, the results obtained in this study shall be compared with the few available international regulatory control limits.

The concentration of Cd varied from <LOQ to 3.0 μg g^{-1}. Hair conditioners had higher concentrations of Cd than hair relaxers and shampoos. The maximum allowable limit for Cd as an impurity in cosmetic products is set at 3.0 μg g^{-1} by the Canadian authority [15] while in Germany, the maximum allowable limit for Cd in cosmetics is set at 5.0 μg g^{-1} [16]. The concentrations in these samples of hair care products were below the Canadian and German regulatory control limits. Cd concentrations in the range of 2.58–6.95 μg g^{-1} in hair care products in Nigeria were reported [11]. Lavilla et al. [9] found <0.002 μg g^{-1} in hair conditioners and shampoos [9]. Chauhan et al. reported Cd concentrations of 0.033–0.042 μg g^{-1}. Amartey et al. [10] found Cd concentrations of 4.2–6.8 μg g^{-1} in hair creams. The concentrations of Cd in our samples were lower than some of the Cd levels previously reported [10,11]. However, other studies on hair care products indicated lower levels than those found in our samples [9,17].

Lead concentrations in these products varied from <LOQ to 425 μg g^{-1}. In this study HCP-21 had an exceptionally higher concentration than the other products. Apart from HCP-21, the other products had Pb concentrations less than 28 μg g^{-1}. If we remove the exceptionally high data point associated with a sample of hair conditioner, the relaxers had higher concentrations of Pb than the other hair care products. The maximum allowable limit for Pb as an impurity in cosmetic products is set at 10 μg g^{-1} by the Canadian authority [15] while the US FDA limit for Pb as an impurity in colour additives used as ingredients of cosmetics is 20 μg g^{-1} [18]. In this study, 12 out the 26 brands investigated exceeded the Canadian limit while six out of the 26 brands exceeded the US FDA limit. Pb concentrations of 0.43–1.30 μg g^{-1} were reported in some hair care products in Nigeria [11]. Pb concentrations in the range of 10.667–25.350 μg g^{-1} in hair cream were reported in Ghana [10]. Apart from HCP-21, the concentrations of Pb in these samples are comparable with those reported by Amartey et al. [10].

The concentrations of Cr in the majority of these samples were below the limit of quantification. Chromium was detected in 27% of the brands investigated at concentrations ranging from 0.2 to 4.2 μg g^{-1}. A wide concentration range of Cr in cosmetic products has been reported in the literature. For instance, the mean concentrations of Cr in hair conditioners, hair gels and shampoos were reported as 0.058–0.17 μg g^{-1} [9]. Cr concentrations of <0.001 μg g^{-1} in hair creams in Ghana were reported [10] while Umar and Caleb [11] found Cr concentrations in the range of 0.34–0.49 μg g^{-1} in hair care products in Nigeria. The concentrations of Cr in the majority of our samples are comparable with Cr levels reported for hair care products in the literature [9–11]. Chromium compounds can cause skin ulcers and allergenic reactions, including severe redness and swelling of the skin [19]. Chromium in the +VI oxidation state permeates the skin more than Cr(III) due to its high solubility [20–22], however, both Cr(III) and Cr(VI) are potential haptens in the development of contact allergies [4,8,23]. The rate of permeation of Cr through the skin is related to the contact time, synthetic sweat at low pH and the use of cleansers [24].

The concentrations of Ni in our samples ranged from <LOQ to 10.5 μg g^{-1}. The brand with the highest concentration was

Table 3
Concentrations ($\mu g\,g^{-1}$) of metals in hair care products in Nigeria.

	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Hair Relaxers									
HCP1	1.5 ± 0.25	19.0 ± 3.0	<LOQ	<LOQ	2.0 ± 0.05	4.5 ± 0.6	7.0 ± 0.9	44.5 ± 4.6	102 ± 0.5
HCP2	0.8 ± 0.05	15.0 ± 0.5	<LOQ	<LOQ	2.5 ± 0.1	4.0 ± 0.9	9.0 ± 0.6	42.0 ± 1.0	108 ± 1.1
HCP3	1.3 ± 0.3	26.0 ± 4.5	<LOQ	3.5 ± 0.3	<LOQ	1.0 ± 0.3	<LOQ	36.5 ± 1.4	84.5 ± 5.7
HCP4	1.0 ± 0.05	24.0 ± 0.0	<LOQ	1.0 ± 0.7	0.5 ± 0.7	4.5 ± 0.2	2.0 ± 0.2	43.0 ± 0.5	111 ± 2.6
HCP5	1.4 ± 0.05	20.0 ± 1.5	0.6 ± 0.8	0.5 ± 0.4	0.5 ± 0.4	5.5 ± 0.05	3.0 ± 0.3	37.0 ± 1.3	116 ± 0.9
HCP6	2.5 ± 0.1	4.5 ± 0.5	0.2 ± 0.9	<LOQ	7.0 ± 0.15	4.0 ± 1.4	7.5 ± 0.2	48.0 ± 3.7	123 ± 3.9
Hair Shampoos									
HCP7	2.3 ± 0.3	28.0 ± 0.5	<LOQ	<LOQ	0.5 ± 0.3	4.5 ± 0.3	3.0 ± 0.7	42.5 ± 2.9	68.9 ± 3.4
HCP8	1.7 ± 0.05	0.5 ± 0.5	<LOQ	0.5 ± 0.1	<LOQ	6.0 ± 0.9	2.5 ± 0.6	56.0 ± 1.2	111 ± 2.7
HCP9	0.9 ± 0.1	<LOQ	<LOQ	<LOQ	<LOQ	7.5 ± 0.3	2.0 ± 0.2	44.5 ± 5.0	127 ± 2.9
HCP10	1.2 ± 0.05	6.0 ± 1.5	3.4 ± 0.35	<LOQ	2.0 ± 0.05	6.5 ± 0.4	7.0 ± 2.3	35.5 ± 2.1	66.7 ± 1.2
HCP11	1.8 ± 0.05	<LOQ	2.0 ± 0.25	1.0 ± 0.15	7.0 ± 0.25	1.5 ± 1.0	11.5 ± 1.5	60.5 ± 2.3	110 ± 1.8
HCP12	3.0 ± 0.15	3.0 ± 1.0	<LOQ	<LOQ	4.5 ± 0.1	3.0 ± 0.1	6.0 ± 0.3	40.5 ± 4.0	82.3 ± 5.65
Anti-dandruff Hair Shampoos									
HCP13	1.5 ± 0.1	22.0 ± 0.0	<LOQ	<LOQ	1.0 ± 0.25	5.0 ± 1.5	2.5 ± 1.7	37.0 ± 0.6	68.3 ± 3.1
HCP14	2.7 ± 0.05	10.0 ± 0.5	3.3 ± 0.15	5.0 ± 0.15	1.5 ± 0.4	<LOQ	11.0 ± 1.8	46.5 ± 3.1	90.6 ± 2.4
HCP15	0.6 ± 0.20	6.5 ± 0.5	<LOQ	<LOQ	3.5 ± 0.8	7.5 ± 1.7	15.5 ± 1.0	1075 ± 0.6	196 ± 1.1
HCP16	1.3 ± 0.0	9.5 ± 0.5	<LOQ	<LOQ	3.0 ± 0.05	6.5 ± 0.8	11.0 ± 0.3	45.5 ± 1.8	195 ± 0.8
HCP17	1.4 ± 0.2	8.5 ± 0.5	<LOQ	6.0 ± 0.2	5.5 ± 0.3	10.5 ± 0.055	25.5 ± 1.8	44.0 ± 2.0	284 ± 0.9
Hair Conditioners									
HCP18	1.2 ± 0.05	10.5 ± 2.0	<LOQ	3.5 ± 0.0	1.5 ± 0.1	5.0 ± 0.9	<LOQ	69.0 ± 1.5	140 ± 3.2
HCP19	<LOQ	14.5 ± 1.0	<LOQ	0.5 ± 0.4	1.5 ± 0.2	3.5 ± 0.05	<LOQ	39.0 ± 0.2	153 ± 4.6
HCP20	0.7 ± 0.2	15.5 ± 1.5	<LOQ	<LOQ	1.0 ± 0.1	1.5 ± 0.2	<LOQ	41.0 ± 0.8	75 ± 3.5
HCP21	1.3 ± 0.0	425 ± 4.0	<LOQ	<LOQ	2.5 ± 0.5	3.0 ± 0.3	9.0 ± 0.8	48.5 ± 2.4	137 ± 1.2
HCP22	2.1 ± 0.05	<LOQ	<LOQ	<LOQ	1.0 ± 0.4	6.0 ± 0.3	2.0 ± 0.05	50.0 ± 4.6	149 ± 1.8
HCP23	2.1 ± 0.0	7.5 ± 0.5	4.2 ± 0.75	0.5 ± 0.05	2.0 ± 0.3	1.5 ± 1.0	15.0 ± 0.8	61.0 ± 4.5	119 ± 0.2
HCP24	2.8 ± 0.05	1.5 ± 2.0	<LOQ	<LOQ	4.0 ± 0.5	4.0 ± 0.2	10.0 ± 0.8	57.0 ± 0.6	148 ± 1.6
HCP25	0.9 ± 0.1	<LOQ	3.0 ± 0.2	2.0 ± 0.05	0.5 ± 0.2	2.5 ± 0.0	5.5 ± 0.7	30.0 ± 1.5	57.6 ± 3.6
HCP26	1.7 ± 0.1	<LOQ	<LOQ	<LOQ	4.5 ± 0.3	3.0 ± 0.8	3.5 ± 1.7	30.5 ± 1.9	80.5 ± 2.2

HCP-17. On average, hair shampoos had higher concentrations of Ni than hair relaxers and conditioners. Ni concentrations of 0.83–3.11 $\mu g\,g^{-1}$ were found in some hair products in Nigeria [11]. Ni concentrations in hair pomades in Ghana were reported as 13–72 $\mu g\,g^{-1}$ [10]. Lavilla et al. found Ni concentrations of <0.009–12 $\mu g\,g^{-1}$ in hair care products including hair gels, hair conditioners and shampoos [9]. Ullah et al. found Ni concentrations of 0.095–0.386 $\mu g\,g^{-1}$ in shampoos from the Pakistan market [1]. The concentrations of Ni in our samples were higher than those reported by Ullah et al. and Umar and Caleb [1,11]. Nickel in contact with human skin can be easily oxidized by sweat to form soluble and diffusible compounds that penetrate the stratum corneum through appendageal, transcellular or intracellular routes [25]. The rate of diffusion of Ni across the stratum corneum is usually limited to <1% and it is influenced by many factors including the counter ions (acetate, chloride, nitrate, sulfate), oxidizing capacity of sweat, sex (male or female), exposure time and the amount applied (dosage) [22,25,26]. The ability of Ni to bind with amino acid residues to form Ni-complexed proteins has been suggested as the main factor responsible for contact allergy and irritations caused by exposure to Ni [27].

The concentrations of Co in these hair care products ranged from <LOQ to 7.0 $\mu g\,g^{-1}$. The highest concentrations of Co were found in HCP-6 and HCP-11. On average, shampoos had higher concentrations of Co than relaxers and conditioners. Cobalt concentrations of 0.183–0.373 $\mu g\,g^{-1}$ were found in shampoos in Pakistan [1] and hair pomades marketed in Ghana contained as much as 10.66–25.35 $\mu g\,g^{-1}$ Co [10]. The concentrations of Co in our samples were lower than those found in hair care products in Ghana. Cobalt is a skin allergen responsible for allergic contact dermatitis (ACD) as confirmed by the positive response observed in 7.9% of cases on 25,000 European subjects patch tested in 2008 [28]. The flux of Co ions through the skin is closely related to the oxidation capacity of the sweat [29,30]. Exposure to Co is known to cause itching, and eczematous periungal and palmar lesions [31]. There are no international guidelines and standards for Cr, Ni and Co in cosmetic products. Piela and Kirć-Swierczyńska [32] have identified the elicitation concentration as 50 $\mu g\,g^{-1}$ based on a dose response study with 72 Co allergic patients, while Fischer and Rystedt [33] found that Co allergic reactions could occur at a concentration of 19 $\mu g\,g^{-1}$, however, Basketter et al. [34] have shown that presensitized subjects rarely react to concentrations of Cr, Ni and Co below 10 $\mu g\,g^{-1}$. On the basis of these findings, it was recommended that cosmetic products to be used on the skin should not contain Cr, Ni and Co at levels above 5 $\mu g\,g^{-1}$ or for greater skin protection these metals should be present at concentrations less than 1 $\mu g\,g^{-1}$ [34]. In this study, only three brands in the case of Co and ten brands of the products investigated in the case of Ni surpassed the limit of 5 $\mu g\,g^{-1}$ suggested by Basketter et al. [34]. However, the majority of our samples had Co and Ni concentrations above 1 $\mu g\,g^{-1}$ suggested for greater skin protection. From the foregoing, the concentrations of Ni and Co in these products may be of concern to presensitized subjects.

Copper was only detected in 42% of the brands of hair products investigated at concentrations in the range of 0.5–6.0 $\mu g\,g^{-1}$. The highest concentration of Cu was observed in HCP-17. Relatively few studies have reported the concentrations of Cu in hair care products. For instance, Ullah et al. reported Cu concentrations of 0.071–2.387 $\mu g\,g^{-1}$ in shampoos marketed in Pakistan [1] while Cu concentrations in the range of 0.70–12.80 $\mu g\,g^{-1}$ were found in hair care products in Ghana [10]. The concentrations of Mn in these samples ranged from <LOQ to 25.5 $\mu g\,g^{-1}$. Hair shampoos had higher concentrations of Mn than hair relaxers and conditioners. Amartey et al. [10] reported an average Mn concentration of 9.8 $\mu g\,g^{-1}$ in hair pomades in Ghana while Mn concentrations in the range of <0.05–31.8 $\mu g\,g^{-1}$ have been found in body creams and underarm cosmetics in Nigeria [2,5]. Copper is an essential element in both human and animal nutrition, however, Cu has been implicated as

Table 4
Systemic Exposure Dosage and Margin of Safety values of metals in hair care products for a 50% oral bioaccesibility factor.

	Systemic Exposure Dosage									Margin of Safety								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Hair Relaxers																		
HCP1	0.0005	0.0067	0.0000	0.0000	0.0007	0.0016	0.0025	0.0156	0.0360	1.90×10^5	5.99×10^4	0.00	0.00	4.27×10^4	1.26×10^6	5.69×10^6	1.92×10^6	1.95×10^6
HCP2	0.0003	0.0053	0.0000	0.0000	0.0009	0.0014	0.0032	0.0148	0.0379	3.56×10^5	7.59×10^4	0.00	0.00	3.41×10^4	1.42×10^6	4.43×10^6	2.03×10^6	1.85×10^6
HCP3	0.0004	0.0091	0.0000	0.0012	0.0000	0.0004	0.0000	0.0128	0.0297	2.28×10^5	4.38×10^4	0.00	3.25×10^6	0.00	5.69×10^6	0.00	2.34×10^6	2.36×10^6
HCP4	0.0004	0.0084	0.0000	0.0004	0.0002	0.0016	0.0007	0.0151	0.0391	2.85×10^5	4.74×10^4	0.00	1.14×10^7	1.71×10^5	1.26×10^6	1.99×10^7	1.99×10^6	1.79×10^6
HCP5	0.0005	0.0070	0.0002	0.0002	0.0002	0.0019	0.0011	0.0130	0.0408	2.03×10^5	5.69×10^4	1.42×10^6	2.28×10^7	1.71×10^5	1.03×10^6	1.33×10^7	2.31×10^6	1.72×10^6
HCP6	0.0009	0.0016	0.0001	0.0000	0.0025	0.0014	0.0026	0.0169	0.0433	1.14×10^5	2.53×10^5	4.27×10^6	0.00	1.22×10^4	1.42×10^6	5.31×10^6	1.78×10^6	1.62×10^6
Hair Shampoos																		
HCP7	0.0029	0.0351	0.0000	0.0000	0.0006	0.0056	0.0038	0.0533	0.0864	3.46×10^4	1.14×10^4	0.00	0.00	4.78×10^4	3.54×10^5	3.72×10^6	5.62×10^5	8.10×10^5
HCP8	0.0021	0.0006	0.0000	0.0006	0.0000	0.0075	0.0031	0.0703	0.1399	4.83×10^4	6.37×10^5	0.00	6.37×10^6	0.00	2.66×10^5	4.46×10^6	4.27×10^5	5.00×10^5
HCP9	0.0011	0.0000	0.0000	0.0000	0.0000	0.0094	0.0025	0.0559	0.1596	9.37×10^4	0.00	0.00	0.00	0.00	2.12×10^5	5.58×10^6	5.37×10^5	4.39×10^5
HCP10	0.0014	0.0075	0.0043	0.0000	0.0025	0.0082	0.0088	0.0446	0.0837	6.93×10^4	5.31×10^4	7.03×10^4	0.00	1.20×10^4	2.45×10^5	1.59×10^6	6.73×10^5	8.37×10^5
HCP11	0.0022	0.0000	0.0024	0.0013	0.0088	0.0019	0.0144	0.0759	0.1376	4.55×10^4	0.00	1.23×10^5	3.19×10^6	3.41×10^3	1.06×10^6	9.70×10^5	3.95×10^5	5.09×10^5
HCP12	0.0038	0.0038	0.0000	0.0000	0.0056	0.0038	0.0075	0.0508	0.1032	2.66×10^4	1.06×10^5	0.00	0.00	5.31×10^3	5.31×10^5	1.86×10^6	5.90×10^5	6.78×10^5
Anti-dandruff Hair Shampoos																		
HCP13	0.0019	0.0276	0.0000	0.0000	0.0013	0.0063	0.0031	0.0464	0.0857	5.31×10^4	1.45×10^4	0.00	0.00	2.39×10^4	3.19×10^5	4.46×10^6	6.46×10^5	8.17×10^5
HCP14	0.0033	0.0126	0.0041	0.0063	0.0019	0.0000	0.0138	0.0584	0.1137	3.01×10^4	3.19×10^4	7.24×10^4	6.37×10^5	1.59×10^4	0.00	1.01×10^6	5.14×10^5	6.16×10^5
HCP15	0.0008	0.0082	0.0000	0.0000	0.0044	0.0094	0.0195	1.3493	0.2458	1.33×10^5	4.90×10^4	0.00	0.00	6.83×10^3	2.12×10^5	7.20×10^5	2.22×10^4	2.85×10^5
HCP16	0.0016	0.0119	0.0000	0.0000	0.0038	0.0082	0.0138	0.0571	0.2447	6.37×10^4	3.35×10^4	0.00	0.00	7.97×10^3	2.45×10^5	1.01×10^6	5.25×10^5	2.86×10^5
HCP17	0.0017	0.0107	0.0000	0.0075	0.0069	0.0132	0.0320	0.0552	0.3562	5.90×10^4	3.75×10^4	0.00	5.31×10^5	4.35×10^3	1.52×10^5	4.37×10^5	5.43×10^5	1.97×10^5
Hair Conditioners																		
HCP18	0.0002	0.0014	0.0000	0.0005	0.0002	0.0007	0.0000	0.0091	0.0184	6.33×10^5	2.89×10^5	0.00	8.68×10^6	1.52×10^5	3.04×10^6	0.00	3.30×10^6	3.80×10^6
HCP19	0.0000	0.0019	0.0000	0.0001	0.0002	0.0005	0.0000	0.0051	0.0202	0.00	2.09×10^5	0.00	6.07×10^7	1.52×10^5	4.34×10^6	0.00	5.84×10^6	3.47×10^6
HCP20	0.0001	0.0020	0.0000	0.0000	0.0001	0.0002	0.0000	0.0054	0.0099	1.08×10^6	1.96×10^5	0.00	0.00	2.28×10^5	1.01×10^7	0.00	5.56×10^6	7.05×10^6
HCP21	0.0002	0.0559	0.0000	0.0000	0.0003	0.0004	0.0012	0.0064	0.0180	5.84×10^5	7.15×10^3	0.00	0.00	9.11×10^4	5.06×10^6	1.18×10^7	4.70×10^6	3.89×10^6
HCP22	0.0003	0.0000	0.0000	0.0000	0.0001	0.0008	0.0003	0.0066	0.0196	3.62×10^5	0.00	0.00	0.00	2.28×10^5	2.53×10^6	5.31×10^7	4.56×10^6	3.57×10^6
HCP23	0.0003	0.0010	0.0006	0.0001	0.0003	0.0002	0.0020	0.0080	0.0156	3.70×10^5	4.05×10^5	5.42×10^5	6.07×10^7	1.14×10^5	1.01×10^7	7.09×10^6	3.73×10^6	4.48×10^6
HCP24	0.0004	0.0002	0.0000	0.0000	0.0005	0.0005	0.0013	0.0075	0.0195	2.76×10^5	2.02×10^6	0.00	0.00	5.69×10^4	3.80×10^6	1.06×10^7	4.00×10^6	3.58×10^6
HCP25	0.0001	0.0000	0.0004	0.0003	0.0001	0.0003	0.0007	0.0040	0.0076	8.93×10^5	0.00	7.72×10^5	1.52×10^7	4.56×10^5	6.07×10^6	1.93×10^7	7.59×10^6	9.23×10^6
HCP26	0.0002	0.0000	0.0000	0.0000	0.0006	0.0004	0.0005	0.0040	0.0106	4.47×10^5	0.00	0.00	0.00	5.06×10^4	5.06×10^6	3.04×10^7	7.47×10^6	6.61×10^6

Table 5
Systemic Exposure Dosage and Margin of Safety values of metals in hair care products for a 100% oral bioaccesibility factor.

	Systemic Exposure Dosage									Margin of Safety								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Hair Relaxers																		
HCP1	0.0011	0.0134	0.0000	0.0000	0.0014	0.0032	0.0049	0.0313	0.0720	9.48×10^{4}	3.00×10^{4}	0.00	0.00	2.13×10^{4}	6.32×10^{5}	2.85×10^{6}	9.59×10^{5}	9.73×10^{5}
HCP2	0.0006	0.0105	0.0000	0.0000	0.0018	0.0028	0.0063	0.0295	0.0759	1.78×10^{5}	3.79×10^{4}	0.00	0.00	1.71×10^{4}	7.11×10^{5}	2.21×10^{6}	1.02×10^{6}	9.23×10^{5}
HCP3	0.0009	0.0183	0.0000	0.0025	0.0000	0.0007	0.0000	0.0257	0.0594	1.14×10^{5}	2.19×10^{4}	0.00	1.63×10^{6}	0.00	2.85×10^{6}	0.00	1.17×10^{6}	1.18×10^{6}
HCP4	0.0007	0.0169	0.0000	0.0007	0.0004	0.0032	0.0014	0.0302	0.0782	1.42×10^{5}	2.37×10^{4}	0.00	5.69×10^{6}	8.54×10^{4}	6.32×10^{5}	9.96×10^{6}	9.93×10^{5}	8.95×10^{5}
HCP5	0.0010	0.0141	0.0004	0.0004	0.0004	0.0039	0.0021	0.0260	0.0815	1.02×10^{5}	2.85×10^{4}	7.11×10^{5}	1.14×10^{7}	8.54×10^{4}	5.17×10^{5}	6.64×10^{6}	1.15×10^{6}	8.58×10^{5}
HCP6	0.0018	0.0032	0.0001	0.0000	0.0049	0.0028	0.0053	0.0337	0.0866	5.69×10^{4}	1.26×10^{5}	2.13×10^{6}	0.00	6.10×10^{3}	7.11×10^{5}	2.66×10^{6}	8.89E+05	8.08×10^{5}
Hair Shampoo																		
HCP7	0.0058	0.0703	0.0000	0.0000	0.0013	0.0113	0.0075	0.1067	0.1728	1.73×10^{4}	5.69×10^{3}	0.00	0.00	2.39×10^{4}	1.77×10^{5}	1.86×10^{6}	2.81×10^{5}	4.05×10^{5}
HCP8	0.0041	0.0013	0.0000	0.0013	0.0000	0.0151	0.0063	0.1406	0.2798	2.41×10^{4}	3.19×10^{5}	0.00	3.19×10^{6}	0.00	1.33×10^{5}	2.23×10^{6}	2.13×10^{5}	2.50×10^{5}
HCP9	0.0021	0.0000	0.0000	0.0000	0.0000	0.0188	0.0050	0.1117	0.3192	4.69×10^{4}	0.00	0.00	0.00	0.00	1.06×10^{5}	2.79×10^{6}	2.69×10^{5}	2.19×10^{5}
HCP10	0.0029	0.0151	0.0085	0.0000	0.0050	0.0163	0.0176	0.0891	0.1673	3.46×10^{4}	2.66×10^{4}	3.51×10^{4}	0.00	5.98×10^{3}	1.23×10^{5}	7.97×10^{5}	3.37×10^{5}	4.18×10^{5}
HCP11	0.0044	0.0000	0.0049	0.0025	0.0176	0.0038	0.0289	0.1519	0.2751	2.28×10^{4}	0.00	6.13×10^{4}	1.59×10^{6}	1.71×10^{3}	5.31×10^{5}	4.85×10^{5}	1.98×10^{5}	2.54×10^{5}
HCP12	0.0075	0.0075	0.0000	0.0000	0.0113	0.0075	0.0151	0.1017	0.2065	1.33×10^{4}	5.31×10^{4}	0.00	0.00	2.66×10^{3}	2.66×10^{5}	9.29×10^{5}	2.95×10^{5}	3.39×10^{5}
Hair Shampoo (with Anti dandruff shampoo)																		
HCP13	0.0038	0.0552	0.0000	0.0000	0.0025	0.0126	0.0063	0.0929	0.1713	2.66×10^{4}	7.24×10^{3}	0.00	0.00	1.20×10^{4}	1.59×10^{5}	2.23×10^{6}	3.23×10^{5}	4.09×10^{5}
HCP14	0.0067	0.0251	0.0083	0.0126	0.0038	0.0000	0.0276	0.1167	0.2274	1.50×10^{4}	1.59×10^{4}	3.62×10^{4}	3.19×10^{5}	7.97×10^{3}	0.00	5.07×10^{5}	2.57×10^{5}	3.08×10^{5}
HCP15	0.0015	0.0163	0.0000	0.0000	0.0088	0.0188	0.0389	2.6987	0.4915	6.64×10^{4}	2.45×10^{4}	0.00	0.00	3.41×10^{3}	1.06×10^{5}	3.60×10^{5}	1.11×10^{4}	1.42×10^{5}
HCP16	0.0031	0.0238	0.0000	0.0000	0.0075	0.0163	0.0276	0.1142	0.4894	3.19×10^{4}	1.68×10^{4}	0.00	0.00	3.98×10^{3}	1.23×10^{5}	5.07×10^{5}	2.63×10^{5}	1.43×10^{5}
HCP17	0.0034	0.0213	0.0000	0.0151	0.0138	0.0264	0.0640	0.1105	0.7125	2.95×10^{4}	1.87×10^{4}	0.00	2.66×10^{5}	2.17×10^{3}	7.59×10^{4}	2.19×10^{5}	2.72×10^{5}	9.83×10^{4}
Hair conditioners																		
HCP18	0.0003	0.0028	0.0000	0.0009	0.0004	0.0013	0.0000	0.0182	0.0369	3.16×10^{5}	1.45×10^{5}	0.00	4.34×10^{6}	7.59×10^{4}	1.52×10^{6}	0.00	1.65×10^{6}	1.90×10^{6}
HCP19	0.0000	0.0038	0.0000	0.0001	0.0004	0.0009	0.0000	0.0103	0.0403	0.00	1.05×10^{5}	0.00	3.04×10^{7}	7.59×10^{4}	2.17×10^{6}	0.00	2.92×10^{6}	1.74×10^{6}
HCP20	0.0002	0.0041	0.0000	0.0000	0.0003	0.0004	0.0000	0.0108	0.0198	5.42×10^{5}	9.80×10^{4}	0.00	0.00	1.14×10^{5}	5.06×10^{6}	0.00	2.78×10^{6}	3.53×10^{6}
HCP21	0.0003	0.1118	0.0000	0.0000	0.0007	0.0008	0.0024	0.0128	0.0360	2.92×10^{5}	3.58×10^{3}	0.00	0.00	4.56×10^{4}	2.53×10^{6}	5.91×10^{6}	2.35×10^{6}	1.95×10^{6}
HCP22	0.0006	0.0000	0.0000	0.0000	0.0003	0.0016	0.0005	0.0132	0.0392	1.81×10^{5}	0.00	0.00	0.00	1.14×10^{5}	1.27×10^{6}	2.66×10^{7}	2.28×10^{6}	1.79×10^{6}
HCP23	0.0005	0.0020	0.0011	0.0001	0.0005	0.0004	0.0040	0.0161	0.0313	1.85×10^{5}	2.02×10^{5}	2.71×10^{5}	3.04×10^{7}	5.69×10^{4}	5.06×10^{6}	3.54×10^{6}	1.87×10^{6}	2.24×10^{6}
HCP24	0.0007	0.0004	0.0000	0.0000	0.0011	0.0011	0.0026	0.0150	0.0391	1.38×10^{5}	1.01×10^{6}	0.00	0.00	2.85×10^{4}	1.90×10^{6}	5.31×10^{6}	2.00×10^{6}	1.79×10^{6}
HCP25	0.0002	0.0000	0.0008	0.0005	0.0001	0.0007	0.0014	0.0079	0.0152	4.47×10^{5}	0.00	3.86×10^{5}	7.59×10^{6}	2.28×10^{5}	3.04×10^{6}	9.66×10^{6}	3.80×10^{6}	4.61×10^{6}
HCP26	0.0004	0.0000	0.0000	0.0000	0.0012	0.0008	0.0009	0.0080	0.0212	2.23×10^{5}	0.00	0.00	0.00	2.53×10^{4}	2.53×10^{6}	1.52×10^{7}	3.73×10^{6}	3.30×10^{6}

the main cause of increased menstrual blood and pain in women from its use in intrauterine devices (IUDs) [35]. Sensitization reactions for both Cu and Mn have resulted from the use of prosthetic materials in dentistry [36].

The concentrations of Zn in our samples varied from 30.0 to 1080 $\mu g\,g^{-1}$. The highest Zn concentration was observed in a brand of antidandruff shampoo, HCP-15. The high levels of Zn may be due to its use in hair care products as an antidandruff agent, although its use in this regard has been reported to cause allergic contact dermatitis [37]. Exposure to high levels of Zn is known to cause a wide variety of health effects including brittle hair and nails, and neurological and gastrointestinal disorders [38]. The concentrations of Zn in our samples are comparable with Zn concentrations reported in shampoos in Pakistan [1] and hair pomades in Ghana [10].

Iron is the most abundant metal in these cosmetic products with concentrations ranging from 57.6 to 284 $\mu g\,g^{-1}$. On average, hair relaxers had higher concentrations of iron than hair shampoos and conditioners. The concentrations of Fe found in our samples fall within the range previously reported for hair care products in the literature [1,10]. Although Fe is an essential nutrient to both humans and animals, exposure to Fe from cosmetics has been reported to cause cellular death [39] or colorectal cancer [40] due to cumulative effects.

3.1. Systemic exposure dosage (SED) and margin of safety (MoS)

The estimated systemic exposure dosage and margin of safety values obtained from the use of these hair care products are displayed in Tables 4 and 5 for 50% and 100% bioaccessability, respectively. The SED for Cd from the usage of these cosmetic products ranged from 0.0 to 0.075 $\mu g\,kg^{-1}$ bw day^{-1} for the two scenarios. The European Food Safety Authority (EFSA) set the provisional tolerable daily intake for Cd at 0.35 $\mu g\,kg^{-1}$ bw day^{-1} [41]. The SED of Pb from the use of these hair care products ranged from 0.0 to 0.11 $\mu g\,kg^{-1}$ bw day^{-1}. The shampoos had higher systemic exposure dosages for Cd and Pb than the hair relaxers and conditioners examined. It should be noted that anti-dandruff shampoos had higher SEDs for Pb than other hair products examined. In this study, we used a provisional tolerable daily intake (PTDI) of 3.6 $\mu g\,kg^{-1}$ bw day^{-1} as the indicative value for comparing our results, despite the fact that the existing PTDI for Pb has been withdrawn by the combined FOA/WHO in 2011 as "it could not be considered health protective" [42]. The estimated SEDs for Ni, Cr, Co and Cu were below their respective recommended daily intakes/tolerable intakes of 12, 3.3, 1.7 and 83.3 $\mu g\,kg^{-1}$ bw day^{-1} respectively [43–47]. The recommended daily intake (RDI) for Zn and Fe is set at 12000 and 12500 μg day^{-1} respectively [48]. The SED for Zn ranged from 0.004 to 2.70 $\mu g\,kg^{-1}$ bw day^{-1} while that of Fe ranged from 0.01 to 0.713 $\mu g\,kg^{-1}$ bw day^{-1}. The estimated SEDs for the metals studied were less than 3% of their respective PTDI or RDI values. As shown in Tables 4 and 5, the MoS values for the hair care products examined were greater than the minimum value of 100 proposed by the WHO "to conclude that the substance is safe for use". The MoS values indicate the products are safe to use despite the occurrence of high concentrations of some of the studied metals in these brands of hair care products.

4. Conclusions

The concentrations of toxic metals such as Cd and Pb were below their permissible limits as impurities in cosmetics except for Pb in some of the brands of hair care products studied, while the concentrations of allergenic metals, such as Cr, Ni and Co, were above the 1 $\mu g\,g^{-1}$ limit suggested for greater skin protection, except for Cr. The SEDs of the studied metals were below their respective provisional tolerable daily intakes (PTDI)/recommended daily intakes (RDI) while the MoS values were greater than 100 which indicates that these products are safe to use. This therefore calls for the need to ensure and implement stringent quality control measures during the production of these cosmetics in order to reduce the concentrations of toxic metals to 'near zero' levels and to implement hazard analysis critical control points (HACCPs) in all production processes.

Acknowledgement

BSM is grateful for the award of a South African Medical Research Council Self-initiated Research (SIR) grant.

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