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Concentrations and exposure risks of some metals in facial cosmetics in Nigeria

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ABSTRACT

The concentrations of nine metals (Cd, Pb, Ni, Cr, Co, Cu, Fe, Mn and Zn) were determined in lip sticks, lip glosses, lip balms, eye pencils, eyeliners, eye shadows, blushes, mascaras and face powders. The study was aimed at providing information on the risk associated with human exposure to metals in these facial cosmetic products. The concentrations of metals in the samples were measured by atomic absorption spectrometry after digestion with a mixture of nitric acid, hydrochloric acid and hydrogen peroxide. The mean concentrations of metals in these facial cosmetics ranged from 3.1 to 8.4 $\mu g\,g^{-1}$ Cd, 12–240 $\mu g\,g^{-1}$ Pb, 9.1–44 $\mu g\,g^{-1}$ Cr, 18–288 $\mu g\,g^{-1}$ Ni, 1.6–80 $\mu g\,g^{-1}$ Cu, 7.9–17 $\mu g\,g^{-1}$ Co, 2.3–28 $mg\,g^{-1}$ Fe, 12–230 $\mu g\,g^{-1}$ Mn, and from 18 to 320 $\mu g\,g^{-1}$ Zn. The concentrations of Ni, Cr and Co were above the suggested safe limit of 1 $\mu g\,g^{-1}$ for skin protection, while Cd and Pb were above the Canadian specified limits. The systemic exposure dosage (SED) values for these metals obtained from the use of these facial cosmetic products were below their respective provisional tolerable daily intake (PTDI)/or recommended daily intake (RDI) values. The margin of safety values obtained were greater than 100 which indicated that the concentrations of the metals investigated in these facial cosmetics do not present considerable risk to the users except in the case of face powders.

1. Introduction

Cosmetics are used by all strata of society as a part of routine body care. In the past metals were used as ingredients of cosmetics, for example, the addition of the preservative thimerosal (mercury), lead acetate in progressive hair dye and red cinnabar (mercuric sulfide) in a number of tattoo pigments [1]. The deliberate use of metals as active ingredients in cosmetic products is prohibited by legislation in most countries, but metal impurities do exist in such products due to their persistence and ubiquitous natures. Metals such as Cd, Pb, Ni, Cr and Co are retained as impurities in the pigments of eye shadows or released by the metallic devices used during the manufacturing of these products. The continuous use of these cosmetic products could lead to the absorption of metals through skin. Facial cosmetics are used daily and applied to the thinnest area of the facial skin, such as the peri-occular areas, and lips, where absorption may be very high [2]. Although, lipstick as a product is intended for topical use, it can be unconsciously ingested and therefore presents an obvious oral route of exposure to metal contaminants in cosmetics [3]. Metals are of environmental and human health significance because they exhibit a wide range of toxic and chronic health effects, such as cancer; reproductive, developmental and neurological disorders; cardiovascular, kidney and renal problems; lung damage; contact dermatitis; brittle hair and hair loss. Many are implicated as endocrine disruptors and respiratory toxins [4]. The use of cosmetics has been known to cause sensitization, dermatitis, allergic reactions and to be an important route of exposure to metals in humans as exemplified by the use of eye cosmetics such as kohl and surma.

Studies on the concentrations of metals in facial cosmetic products in Nigeria have been documented in the literature [1,5,6–8]. However, although most of the studies established the levels of metals in these facial cosmetic products, they paid little attention to systemic exposure dosages and risk evaluation of the elements

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investigated. The objectives of this study were to determine the concentrations and exposure risks of Cd, Pb, Ni, Cr, Cu, Co, Zn, Fe and Mn in some facial cosmetics in the Nigerian market.

2. Materials and methods

2.1. Sample collection

Samples of different brands of facial cosmetics (n = 160) were collected from cosmetics shops in Abraka, Warri, and Benin City in the southern part of Nigeria. The cosmetic samples were popular brands, some of which were produced locally and others imported. Most of the imported products examined were from the USA, China, Korea, India, France, Italy, Taiwan and the United Kingdom. The choice of brands was carefully made to reflect the types used by different income classes. The facial cosmetics were classified into eight broad groups, namely, (1) lipsticks, (2) lip glosses and balms, (3) eye shadows, (4) eye pencils, (5) eyeliners, (6) mascaras, (7) blushes and (8) face powders. The samples were stored under conditions similar to those of the retail shops until the analysis was completed.

2.2. Reagents

All reagents, nitric acid (HNO_3 69% v/v), hydrochloric acid (HCl 37% v/v) and hydrogen peroxide (H_2O_2 30% v/v) were Suprapur® (Merck, Darmstadt, Germany). The calibration standards were prepared by diluting 1000 mg L^{-1} commercial standards of Cd, Pb, Ni, Cr, Cu, Co, Zn, Fe and Mn (Merck, Darmstadt, Germany) with 0.25 mol L^{-1} HNO_3.

2.3. Sample preparation

A mass of 1.0 g of each sample was placed into a Teflon vessel and treated with 20 mL of concentrated nitric acid, 10 mL of hydrochloric acid and 5 mL of hydrogen peroxide. The samples were covered and left to stand overnight. The following day, the samples were heated to 125 °C for 2 h. The clear supernatant solutions were allowed to cool, filtered and made up to 25 mL with 0.25 mol L^{-1} HNO_3. Four blanks were prepared in a similar way, but omitting the samples.

2.4. Chemical analysis

All digested samples were analysed in triplicate for Cd, Pb, Ni, Cr, Cu, Co, Fe, Mn and Zn by means of flame atomic absorption spectrometry (PerkinElmer, Analyst 200, Norwalk CT, USA). Blank and calibration standard solutions were analysed in a similar way as the samples. In each batch of analyses, at least 3–4 blanks were analysed. 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 and sample vials were soaked in a solution of 10% nitric acid followed by thorough rising with distilled deionized water. The instrument was calibrated after every ten runs. In the absence of a certified reference material, a spike recovery method and an independent inter-laboratory comparison were used to validate the analytical procedure. The spike recoveries for the metals examined were Cd (97.6%), Pb (96.4%), Ni (93.2%), Cr (101%), Cu (92.4%), Co (98.2%), Fe (103%), Mn (96.7%) and Zn (97.2%). The relative standard deviations for replicate analyses ranged between 2.3–12.5% for all the elements quantified. The inter-laboratory study was carried out at the University of Ibadan, Multidisciplinary Central Laboratory, on 10% of the total samples. The results from the inter-laboratory analysis showed strong agreement. The limits of detection and quantification (LODs and LOQs respectively) were evaluated on the basis of the noise obtained for the analysis of the blank samples (n = 3). The LOD and LOQ were defined as the concentration of analyte that produced a signal-to-noise ratio of 3 and 10 respectively. The limits of detection for the examined metals ($\mu g\, g^{-1}$) were Cd (0.23), Pb (0.1), Cr (0.6), Ni (0.8), Cu (0.08), Co (0.05), Fe (1.7), Mn (0.1) and Zn (0.8), and the limits of quantification ($\mu g\, g^{-1}$) were Cd (0.7), Pb (0.3), Cr (1.8), Ni (2.3), Cu (0.24), Co (0.15), Fe (5), Mn (0.3) and Zn (2.4). Analysis of variance and a Tukey multiple comparison test were used to determine whether the concentrations of metals varied significantly within the same group and between the different facial cosmetics respectively. All statistical analyses was carried by using SPSS software version 15.0 (SPSS Inc, Chicago, IL, USA).

2.6. Safety evaluation of facial cosmetic products

The risk of human exposure to metallic impurities in these facial cosmetic products can be assessed by making use of the uncertainty factor called the Margin of Safety (MoS). The 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) [9].

$$MoS = \frac{NOAEL}{SED} \quad (1)$$

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 [9].

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

$$SED(\mu g\ kg^{-1}\, bw\, day^{-1}) = \frac{C_s \times AA \times SSA \times F \times RF \times BF}{BW} \times 10^{-3} \quad (2)$$

where C_s is the concentration of metal in the facial cosmetic product (mg kg^{-1}) and AA is the amount of facial cosmetic product applied per day. The estimated daily amounts (in g) applied were 0.057, 0.51, 0.02, 0.005, 0.02 and 0.025 for lipstick/lip gloss/lip balm, face powder, eye shadow, eyeliner/eye pencil, blush and mascara respectively [9]. SSA is the skin surface area onto which the products are applied. The applied surface areas (in cm^2) for the different facial cosmetic products were 4.8, 4.8, 563, 24, 3.2, 3.2, 24 and 1.6 for lipsticks, lip gloss/lip balm, face powder, eye shadow, eyeliner, eye pencil, blush and mascara respectively [9]. RF is the retention factor (1.0 for leave-on cosmetic products); F is the frequency of application per day; BF is the bioaccessibility factor; 10^{-3} is the unit conversion factor; and BW is the body weight (kg). A default body weight of 60 kg was used in this study. The values of AA, SSA, and RF used in this study were the standard values established by the Scientific Committee on Consumer Safety (SCCS) [9].

The NOAEL values were obtained from the oral reference doses (RFDs). The latter are "an estimate of the daily exposure to the human population (including sensitive sub-groups) that is likely to be without an appreciable risk of deleterious effects during life time" [9]. For the studied metals the NOAEL values were calculated by using the relationship, NOAEL = RFD × UF × MF, 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})[10], 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})[11,12].

The World Health Organization (WHO) proposed a minimum value for the MoS of 100 and it is generally accepted that it should at least be 100 to conclude that a substance is safe for use [9]. The SCCS also noted the fact that in many conventional computations of MoS, the oral bioavailability of the substance is assumed to be 100% if oral absorption data are not available. However, it is considered appropriate to assume that not more than 50% of an orally administered dose is systemically available [9]. For the purpose of this study, the computation of MoS was based on the median concentrations of the metals since the data were highly skewed and two scenarios were considered, i.e. oral bioavailability of the investigated metals at 50%, and 100% of the measured concentrations of metals in the facial cosmetic products, for the purpose of comparison with reference exposure dosage values.

3. Results and discussion

The mean concentrations of nine metals quantified in specific classes of some brands of popular facial cosmetics are presented in Table 3 while Table 2 presents a comparison of data obtained in this study, along with the levels reported for facial cosmetics in the literature. The bolded values in parentheses represent the median concentrations while the concentration ranges of the metals are shown in parentheses below the mean values in Table 1. The working rule is that any value greater than three standard deviations from the mean should be treated as an outlier [5]. In this study, some data points yielded extremely high concentrations of Cd, Pb, Cr, Ni, Cu, Fe, Mn and Zn in some brands of facial cosmetic products. The analysis of samples with exceptionally high concentrations of metals was repeated three times following all the analytical steps from digestion to atomic absorption analysis and the results were consistent. As for possible matrix effects, our recovery results indicate that the analytical steps were efficient. Since we do not have any special reason to account for these deviations and it is not advisable to delete these data points because they might represent the true concentrations of these metals in these samples, the suspected outliers were retained. However, the median values are provided alongside the mean values in Table 1. The median value is less sensitive to outliers and is a better measure than the mean for highly skewed distributions. The concentrations of metals observed in our samples are compared with those of metals in some facial cosmetic products reported in the literature in Table 2. The concentrations of the metals studied here fall within the ranges reported for facial cosmetics in the literature. The facial cosmetic samples produced in Asian countries had higher concentrations of the studied metals than those from Nigeria, Europe and the USA, except for Cd in Nigerian-produced eyeliners.

The mean concentrations of Cd ranged from 3.1 to 8.4 $\mu g\,g^{-1}$. In this study, exceptionally high concentrations of Cd were found in a local eyeliner (Tiro 13.5 $\mu g\,g^{-1}$) and a brand of lipstick (37.3 $\mu g\,g^{-1}$). Apart from these two samples, all other samples had Cd concentrations less than 6 $\mu g\,g^{-1}$. However, the median concentration of Cd in lip sticks was 4.3 $\mu g\,g^{-1}$. Lip glosses had the lowest mean level of Cd. The concentrations of Cd varied significantly ($p > 0.05$) within the same group of facial cosmetics. However, no significant difference ($p > 0.05$) was observed in the mean concentration of Cd in facial powders and eye pencils, and between that of rouge and mascara. Canada has set the maximum amount allowed for Cd as an impurity in cosmetics at 3 $\mu g\,g^{-1}$ while in Germany this value is set at 5 $\mu g\,g^{-1}$ [32,33]. The mean concentrations of Cd in these facial cosmetics were above the limit specified by the Canadian Authority. The use of Cd in cosmetics products is due to its ability to produce different colours in combination with other elements and it has been used as a colour pigment in many industries [34]. Cadmium sulfide is used for its yellow colour and it can produce a wide range of colours from orange to practically black (the colour of cadmium selenide) by adding increasing amounts of selenium. Cadmium yellow is sometimes combined with viridian (Cr(III) oxide) to produce a light green mixture known as cadmium green [4].

The concentrations of Pb in the facial cosmetics showed remarkable intra- and inter-group differences ($p > 0.05$). An exceptionally high concentration of Pb was observed in one brand of face powder (3400 $\mu g\,g^{-1}$). Also, higher concentrations of Pb were observed in some brands of blush (rouge) and eyeliner relative to other types within the groups. Among the eyeliners, the local eyeliner (Tiro) had the maximum concentration of Pb. The median values of Pb in face powder, rouge and eyeliner were 18.7, 15.7 and 15.9 $\mu g\,g^{-1}$ respectively. Health Canada's National Health Products Directorate (NHPD) set the limit for Pb in cosmetic products applied to skin as 10 $\mu g\,g^{-1}$ [33] while the US FDA's limit for Pb as an impurity in colour additives used as ingredients in cosmetics is 20 $\mu g\,g^{-1}$ [35]. Apart from a few high Pb values in the data set, the concentrations of Pb in other samples examined varied between 10 and 20 $\mu g\,g^{-1}$. Tsankov et al. found that the concentrations of Pb in various cosmetics products (such as creams, cleansing milk, shampoo, hair dyes, eye shadow, rouge, lipsticks, powder, fond de tient, toothpastes) were approximately 2.08 $\mu g\,g^{-1}$, and higher concentrations of Pb were found in some decorative cosmetics (41.1 $\mu g\,g^{-1}$) [14]. The authors attributed the high concentrations of Pb in these products to inadequate purification of the initial raw materials and suggested that the maximum permissible limit of Pb in cosmetics should be 10 $\mu g\,g^{-1}$ based on sub-acute dermal toxicity studies in albino rats [14]. It is worthy to note that a high concentration of Pb was observed in a local eyeliner (Tiro, 323 $\mu g\,g^{-1}$). Apart from lipsticks, lip glosses and lip balms which can be ingested, the other facial cosmetics including eye shadows, eyeliners, eye pencils, rouge, mascara and face powders are applied externally, however, cosmetics products with high concentrations of Pb whether applied once or a number of times per day could lead to human exposure to Pb.

The mean concentrations of Cr in these facial cosmetic products ranged from 9.1 to 44.4 $\mu g\,g^{-1}$. Higher concentrations of Cr were observed in two samples of eye shadow (128 and 146 $\mu g\,g^{-1}$) and a brand of face powder (232 $\mu g\,g^{-1}$). Apart from these exceptionally high values, the concentrations of Cr in the other samples examined were less than 50 $\mu g\,g^{-1}$. The higher concentrations of Cr found in eye shadows could be due to the use of Cr-containing colouring agents. For example, chromium hydroxide green ($Cr(OH)_3$) and chromium oxide green ($Cr_2O_3.2H_2O$) are colouring agents used in cosmetic products. These colourants contain chromium(III) which causes skin allergies through percutaneous absorption through the skin. Eye shadow is an example of a cosmetic product in which significant amounts of colourants are used [36]. Chromium in the +III and +VI oxidation states is a potential hapten in the development of contact allergy [37,38]. Exposure to Cr can cause skin ulcers, and severe redness and swelling of the skin [39]. There are no international guidelines or limits for Cr, Ni and Co in cosmetic products, however, several studies have shown that the presence of irritants, and/or following repeated exposures to Ni, Cr and Co, subjects rarely react to levels below 10 $\mu g\,g^{-1}$ [40–43]. For this reason, Basketter et al. [43] recommended that consumer products should not contain more than 5 $\mu g\,g^{-1}$ of Cr, Ni or Co, or for better health protection levels should not exceed 1 $\mu g\,g^{-1}$.

The mean concentrations of Ni in the cosmetic products investigated varied from 17.5 to 76.5 $\mu g\,g^{-1}$. Samples of mascara contained higher mean concentrations of Ni than other categories of facial cosmetics. In this study, the highest sample concentration of Ni (589 $\mu g\,g^{-1}$) was observed in a brand of mascara. The mean concentrations of Ni in lipsticks and eye shadows, and those of eyeliners and eye pencils, were similar ($p > 0.05$). The concentrations

Table 1
Concentrations of metals ($\mu g\,g^{-1}$ wet weight) in facial cosmetic products in Nigeria (n = 20).

Product	Cd	Pb	Cr	Ni	Cu	Co	Fe	Mn	Zn
Lipstick	8.40 ± 11.7	14.9 ± 2.6	24.7 ± 36.9	25.8 ± 7.4	21.0 ± 43.6	11.6 ± 4.7	13000 ± 17000	38.4 ± 49.7	18.2 ± 7.90
	(**4.3**)	(**14.5**)**	(**11.9**)	(**23.6**)	(**2.70**)	(**11.8**)	(**2650**)	(**15.7**)	(**17.7**)
	(3.00–37.3)	(11.6–18.0)	(17.1–116)	(17.0–37.9)	(1.10–135)	(4.5–19.9)	(422–44000)	(2.10–151)	(9.20–33.0)
Lip gloss/Lip balm	3.10 ± 1.3	11.9 ± 5.0	9.10 ± 3.80	17.5 ± 6.90	1.60 ± 1.20	7.9 ± 3.9	2330 ± 6270	12.2 ± 29.8	17.5 ± 6.90
	(**3.5**)	(**12.7**)	(**9.4**)	(**18.9**)	(**9.40**)	(**1.1**)	(**321**)	(**3.80**)	(**8.80**)
	(0.70–4.70)	(1.9–18.3)	(1.80–15.2)	(1.70–25.5)	(0.30–4.10)	(1.3–15.0)	(26.9–23100)	(0.28–107)	(5.40–40.4)
Face Powder	4.0 ± 0.80	325.6 ± 1020	33.0 ± 66.4	21.8 ± 6.5	6.70 ± 6.40	11.1 ± 3.4	2110 ± 13800	68.8 ± 46.0	325 ± 987
	(**4.1**)[a]	(**18.7**)	(**10.9**)	(**23.7**)	(5.50)	(**10.8**)	(**23700**)	(**54.9**)	(**30.9**)
	(2.10–5.00)	(5.9–3400)	(4.60–233)	(5.30–27.7)	(1.4–23.4)	(5.2–15.2)	(157–47100)	(18.0–154.5)	(8.0–3300)
Eye Shadow	4.70 ± 0.50	15.3 ± 7.30	44.4 ± 57.5	25.1 ± 3.3	79.5 ± 119	13.4 ± 2.5	18900 ± 17900	53.4 ± 44.7	75.7 ± 132
	(**4.5**)**	(**17.7**)	(**16.5**)	(**23.9**)	(**10.5**)	(**12.9**)**	(**18700**)	(**54.6**)	(**28.5**)
	(3.70–5.10)	(0.30–21.6)	(7.30–146)	(20.9–30.8)	(2.00–194.)	(9.2–17.1)	(143–52036)	(2.40–159.1)	(8.60–415)
Eyeliner	5.10 ± 3.00	49.9 ± 102	9.40 ± 4.10	26.8 ± 15.9	2.50 ± 2.9	9.9 ± 4.2	8750 ± 26600	230 ± 626	26.4 ± 25.4
	(**4.30**)	(**15.9**)	(**10.0**)	(**21.9**)	(**1.50**)	(**8.8**)	(**369**)	(**4.20**)	(**20.1**)
	(2.80–13.5)	(9.60–323)	(4.00–19.1)	(18.4–68.8)	(1.30–10.8)	(5.2–103)	(422–44070)	(2.6–2100)	(9.2–33.0)
Eye Pencil	3.90 ± 1.60	20.4 ± 11.1	22.4 ± 12.1	27.8 ± 14.8	25.5 ± 23.8	17.4 ± 11.1	27900 ± 27200	164 ± 329	122.8 ± 145
	(**4.20**)[a]	(**19.9**)	(**20.5**)	(**24.5**)	(**17.8**)	(**15.3**)	(**17600**)	(**42.4**)	(**42.4**)
	(0.70–5.20)	(3.30–33.8)	(10.5–45.1)	(2.20–55.7)	(1.50–67.2)	(1.4–43.6)	(71.6–86500)	(107–456)	(107–456)
Blush (Rouge)	3.50 ± 1.00	55.6 ± 121	17.4 ± 10.3	18.3 ± 6.3	2.90 ± 1.40	9.3 ± 2.7	15553 ± 2290	69.0 ± 114	33.3 ± 22.2
	(**3.70**)[ab]	(**15.7**)	(**12.7**)	(**19.7**)	(**3.10**)	(**9.7**)	(**9880**)	(**32.7**)	(**30.1**)
	(1.30–4.80)	(12.1–378)	(9.90–41.1)	(3.30–25.3)	(0.7–5.2)	(2.5–12.0)	(115–77500)	(4.20–386)	(12.1–89.8)
Mascara	3.60 ± 0.80	11.9–4.20	11.4 ± 5.30	76.5 ± 180	6.20 ± 5.90	10.6 ± 6.0	9860 ± 21600	56.6 ± 151	48.8 ± 85.7
	(**3.70**)[ab]	(**11.0**)	(**9.40**)	(**21.6**)	(**3.40**)	(**8.7**)	(**383**)	(**3.30**)	(**21.6**)
	(1.80–5.10)	(5.40–18.5)	(5.00–21.3)	(10.3–589)	(1.60–16.9)	(4.6–16.6)	(143–68800)	(2.40–462)	(8.20–276)

**,[a], [ab] Not significant at ($p < 0.05$), the bolded values represent median concentrations.

of Ni observed in our samples fall within the concentration ranges reported in the literature (Table 2). A Ni concentration of about 0.5 $\mu g\,g^{-1}$ is sufficient to cause contact dermatitis in an already irritated skin [43]. The levels of Ni found in these cosmetic products can trigger contact dermatitis in presensitized subjects. The transport of Ni across the stratum corneum is slow, and is limited to < 1%, but it depends on a number of factors including the counter ion (e.g. acetate, chloride, nitrate, sulfate), the oxidizing capacity of sweat, the anatomical site, gender of the skin, dosage and exposure time [44,45,46]. Contact allergies associated with Ni exposure arise due to the ability of nickel to bind to amino acid residues to form Ni-complexed proteins [47].

The mean concentrations of Co ranged from 7.9 to 17.4 $\mu g\,g^{-1}$. The highest mean level of Co was observed in an eye pencil. There were no significant differences between the mean concentrations of Co observed in eyeliners and blushes, and those of face powders, mascaras and lipsticks. The results of the present study indicated that these samples of facial cosmetic products contained Cr, Ni, and Co at concentrations above the suggested safe limit for greater health protection.

The mean concentrations of Cu in these facial cosmetics ranged from 1.6 to 79.5 $\mu g\,g^{-1}$. The highest mean concentration observed was in an eye shadow while the lowest mean concentration was observed in a lip gloss. Within the eye shadows, three samples had exceptionally high concentrations of Cu (87.7, 194 and 322 $\mu g\,g^{-1}$). Apart from these samples with higher concentrations of Cu, other samples of facial cosmetics analysed had Cu concentrations less than 25 $\mu g\,g^{-1}$. Higher concentrations of Cu in eye shadows could be due to the fact that copper-containing compounds might have been used as pigments in these types of facial cosmetics.

The mean concentrations of manganese in these facial cosmetics varied from 12.2 $\mu g\,g^{-1}$ in lip glosses to 230 $\mu g\,g^{-1}$ in eyeliners. In each group of facial cosmetics, one or two samples had exceptionally high concentrations of Mn, more so than the other samples within the same type. For instance, the highest sample concentration of Mn was observed in a brand of eyeliner (2100 $\mu g\,g^{-1}$). Although Cu and Mn are rare skin sensitizers, there are reported cases of increased menstrual blood loss and pain as a result of exposure to Cu from widely used intra-uterine devices (IUDs) [48] 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 [49,50].

The highest mean concentration of Zn was observed in a face powder (355 $\mu g\,g^{-1}$) while the lowest mean concentration was observed in an eyeliner (29.9 $\mu g\,g^{-1}$). The maximum sample concentration of Zn was observed in a brand of face powder (3300 $\mu g\,g^{-1}$). Zinc used in anti-dandruff shampoos has been shown to cause allergic contact dermatitis [51]. The high concentrations of Cu, Fe, Mn and Zn in some of the products are due to the use of some natural or inorganic pigments such iron oxides, carmine, mica, titanium dioxide, aluminium powder and manganese violet [15,52].

The concentrations of Fe varied significantly within the same class of face powders and among other classes of facial cosmetics. The mean concentration of Fe ranged from 2.33 $mg\,g^{-1}$ in lip glosses to 27.9 $mg\,g^{-1}$ in eye pencils. The concentrations of Fe in these cosmetic products were higher than the other elements studied. Ajayi et al. [5] reported high concentrations of Fe in graphite-based Kwali (> 4300 $\mu g\,g^{-1}$) and Pb-based Kwali (0.98–1.2%) which reflects the natural sources of these materials. Higher concentrations of Zn (35.8%) and Fe (6.15%) have been reported in ornamental Pb which is used to adorn eyelashes in Nigeria [6]. Dalmazio and Menezes [21] reported Fe concentrations of 11.63–103.4 $mg\,g^{-1}$, 4.259–24.26 $mg\,g^{-1}$ and 13.77–36.0 $mg\,g^{-1}$ for Brazilian eye shadow, facial concealer/lipstick and compact face powder respectively. Exposure to small amounts of Fe from cosmetic products may cause cellular death [53] or colorectal cancer [54] as a result of cumulative effects.

3.1. Estimation of systemic exposure dosage and margin of safety

The estimated SED ($\mu g\,kg^{-1}$ bw day^{-1}) and MoS of metals from the use of these facial cosmetic products are displayed in Table 3. The SED of Cd from the use of these facial cosmetic products ranged from 1.12×10^{-6} to 3.92×10^{-2} $\mu g\,kg^{-1}$ bw day^{-1} for both 50 and 100% bioaccessibility scenarios. The provisional tolerable daily intake (PTDI) of Cd is set at 1 $\mu g\,kg^{-1}$ bw day^{-1}; however, the European Food Safety Authority (EFSA) set the provisional tolerable weekly intake (PTWI) of Cd as 2.5 $\mu g\,kg^{-1}$ bw $week^{-1}$ [55]. The SED values of Cd from the use of these facial cosmetic products consti-

Table 2
A comparison of metal concentrations ($\mu g\, g^{-1}$) in facial cosmetics in this study with some published data on concentrations of metals in facial cosmetics in the literature.

Product type	Origin/Market site	Cd	Pb	Cr	Ni	Cu	Co	Fe	Mn	Zn	Reference
Lip stick		3.0–37.3	11.6–18.0	17.1–115.8	17.0–37.9	1.1–135.4	4.5–19.9	421.6–44070	2.1–151.0	9.2–33.0	This study
Lip gloss/Lip balm		0.7–4.7	1.9–18.3	1.8–15.2	1.7–25.5	0.3–4.1	1.3–15.0	26.9–23072	0.28–106.7	5.4–40.4	This study
Face Powder		2.1–5.0	5.9–3399.9	4.6–232.5	5.3–27.7	1.4–23.4	5.2–15.2	157.3–47098	18.0–154.5	8.0–3300	This study
Eye Shadow		3.7–5.1	0.3–21.6	7.3–146.4	20.9–30.8	2.0–194.3	9.2–17.1	142.8–52036	2.4–159.1	8.6–414.8	This study
Eyeliner		2.8–13.5	9.6–322.5	4.0–19.1	18.4–68.8	1.3–10.8	5.2–103	421.6–44070	2.60–2102.58	9.2–33.0	This study
Eye Pencil		0.7–5.2	3.3–33.8	10.5–45.1	2.2–55.7	1.5–67.2	1.4–43.6	71.6–86466	107–456.2	107–456.2	This study
Blush (Rouge)		1.3–4.8	12.1–378.0	9.9–41.1	3.3–25.3	0.7–5.2	2.5–12.0	115.4–77517	4.2–385.8	12.1–89.8	This study
Mascara		1.8–5.1	5.4–18.5	5.0–21.3	10.3–588.5	1.6–16.9	4.6–16.6	142.8–68782	2.4–461.5	8.2–276.2	This study
Lipstick	Pakistan/China	0.2–0.430	2.58–11.33	<LOD-0.77	0.696–1.610	0.026–6.036	0.3–0.872	258–1164		0.437–5.99	[13]
Surma (Kohl)	Pakistan/Unknown	0.229–0.942	2.774–1071	<LOD-0.078	0.290–1.014	0.228–302.2	0.342–0.72	116.9–1272		1.362–508.8	
Eye shadow, Lipstick	Bulgaria		<LOD-41.1								[14]
Lipstick	China/Taiwan/Thailand/ Germany/USA/Japan/ Belgium/France		0.27–3760								[15]
Eye shadow	China/France/USA	0.004−0.08	0.42–58.7	0.17–16.54	0.09–4.24						[16]
Lipstick	France/Italy/USA/ Canada/China/Korea		0.30–2.44								
Eye shadow, Lipstick	Bulgaria		<20		1.0–49						[17]
Lip gloss	Europe/USA/ Japan/Canada		0.04–2.12								[18]
Lipstick			0.04–3.75								
Eye shadow	China/Nigeria	<LOD-8.89	<LOD-55.0	<LOD-150	77.22–359.44	1.67–465.0	122.78–258.33		15.0–270.56	28.33–342.22	[1]
Eye shadow	China/Italy/USA	0.0006–0.033	0.0007–0.304	0.015–0.287	0.022–4.148						[19]
Lipstick	Iran	13.3–27.2	1.07–2.21								
Eye shadow	Iran	21.23–33.72	1.15–5.0								[20]
Lipstick		12.99–37.96	0.58–3.36								
Eye shadow	Brazil			4.3–3085			2.6–8.4	11630–104300	36–5380	11.0–7283	[21]
Facial concealer	Brazil			4.2			<0.09	4259	5.9	718	
Lipstick	Brazil			4.1			0.23	9455	11	648	
Liquid base	Brazil			5.2			2.4	24260	25	945	
Compact face powder	Brazil			5.0–18.4			2.5–2.8	13770–36700	36–75	50–11690	
Lipstick	Jordan			1.47–31.2	<LOD-3.30	0.13–1.89	<LOD	13000–32600		8.17–32.2	[22]

Eye shadow	Jordan			0.44–258	1.56–9.02	900–2150	<LOD-0.11	2260–55300		<LOD-33514	
Eye shadow	Saudi Arabia	0.014–0.266		8.99–7000	3.26–112.0	14.3–37.3	1.28–31.3	7360–300000	55.2–837.0	54.7–20000	[23]
Mascara	Saudi Arabia	0.002–0.035			5.07–468.0	0.141–1.04	1.73–20.4	30000–100000	72.8–536.0	0.744–151.0	
Eyeliner	Nigeria	0.3–1.8	60.4–213.6	33.5–43.1	4.4–14.5			78–325.2		72.0–128.5	[7]
Eye pencil	Nigeria	0.5–1.1	66.0–187.1	25.8–64.3	4.9–21.5			17.0–288.3		36.5–198.7	
Lipstick	Nigeria	0.5–2.4	28.7–252.4	20.5–58.8	7.0–22.8			92.2–632.0		43.2–174.8	
Lipstick	Palestine	<LOD-0.14	<LOD-15.92	<LOD-81.6	<LOD-4.94	<LOD-118.6			0.89–48.89	<LOD-118.6	[24]
Facial powder	Palestine	<LOD-0.93	<LOD-9.38	4.45–18.12	3.232–214.54	1.05–9.690	<LOD-13.02		1.31–18.12	1.676–25398	
Kohl	Palestine	<LOD-0.958	<LOD-10.3	2.16–8.57	<LOD-6.014	<LOD-2.464			<LOD-1.31	5.39–284634	
Eye shade	Palestine				18.45	18.95				54.91	
Foundation cream	Palestine	<LOD-0.82	<LOD-5.78	6.22–15.75	4.24–10.53	1.05–4.84	<LOD-5.33		3.0–13.54	9.64–25398	
Lipstick/lipgloss	Not reported	<0.002–3.48	0.025–1.32	<0.005–9.7	<0.012–9.73		<0.005–1.30		0.35–38.5		[25]
Lipstick	Japan, China, France, Nertherlands, England, Germany			0.52–3.07			0.055–0.105	139–620	<0.2%	1.94–2.38	[26]
Eye shadow	Japan, China, France, Nertherlands, England, Germany			3.24–15.3			1.05–2.45	8800–11900	1020–1020	10–1820	
Facial cream	Japan, China, France, Nertherlands, England, Germany			0.72–2.16			0.589–2.20	9100–21900	<15%	15.9–15.9	
Bronzing powder	Japan, China, France, Nertherlands, England, Germany			<3.0–46.1			3.21–5.64	12200–12900		<4.0–26.3	
Lipstick	China/India	4.9–10.4	5.7–9.9	9.3–40.8						7.7–14.7	[27]
Foundation/concealer/ powder/blushes/ bronzers/mascara	Canada, Europe, Korea, USA	<LOD-0.29	<LOD-110		0.3–230						[28]
Kohl	India/Madina/ Makkah/Pakistan		0.004–52.370								[29]
Eye shadow, eyeliner, facial powder, facial cream, lipgloss	Nigeria	<LOD-29.05	0.27–61.86	0.23–1.47	0.55–12.85						[30]
Lipstick		0.00595–0.144	0.321–1.38	0.226–93.3							[31]

Table 3
Systemic exposure dosage and margin of safety of metals in facial cosmetics obtained by using 50% bioaccessibility.

	Cd	Pb	Cr	Ni	Cu	Co	Fe	Mn	Zn
Systemic Exposure Dosage									
Lipstick	1.96×10^{-5}	6.61×10^{-5}	5.43×10^{-5}	1.08×10^{-4}	1.23×10^{-5}	5.38×10^{-5}	1.21×10^{-2}	7.16×10^{-5}	8.07×10^{-5}
Lip gloss/Lip balm	1.60×10^{-5}	5.79×10^{-5}	4.29×10^{-5}	8.62×10^{-5}	4.29×10^{-5}	5.02×10^{-6}	1.46×10^{-3}	1.73×10^{-5}	4.01×10^{-5}
Face powder	1.96×10^{-2}	8.95×10^{-2}	5.22×10^{-2}	1.13×10^{-1}	2.63×10^{-2}	5.17×10^{-2}	1.13×10^{2}	2.63×10^{-1}	1.48E-01
Eye shadow	3.60×10^{-5}	1.42×10^{-4}	1.32×10^{-4}	1.91×10^{-4}	8.40×10^{-5}	1.03×10^{-4}	1.50×10^{-1}	4.37×10^{-4}	2.28×10^{-4}
Eyeliner	1.15×10^{-6}	4.24×10^{-6}	2.67×10^{-6}	5.84×10^{-6}	4.00×10^{-7}	2.35×10^{-6}	9.85×10^{-5}	1.12×10^{-6}	5.36×10^{-6}
Eye pencil	1.12×10^{-6}	5.31×10^{-6}	5.47×10^{-6}	6.53×10^{-6}	4.75×10^{-6}	4.08×10^{-6}	4.69×10^{-3}	1.13×10^{-5}	1.13×10^{-5}
Blush	2.96×10^{-5}	1.26×10^{-4}	1.02×10^{-4}	1.58×10^{-4}	2.48×10^{-5}	7.76×10^{-5}	7.91×10^{-2}	2.62×10^{-4}	2.41×10^{-4}
Mascara	2.47×10^{-6}	7.33×10^{-6}	6.27×10^{-6}	1.44×10^{-5}	2.27×10^{-6}	5.80×10^{-6}	2.56×10^{-4}	2.20×10^{-6}	1.44×10^{-5}
Margin of Safety									
Lipstick	5.10×10^{6}	6.05×10^{6}	5.53×10^{6}	1.86×10^{7}	3.25×10^{8}	5.58×10^{5}	5.80×10^{6}	1.96×10^{8}	3.72×10^{8}
Lip gloss/Lip balm	6.27×10^{6}	6.91×10^{6}	7.00×10^{6}	2.32×10^{7}	9.33×10^{7}	5.98×10^{6}	4.79×10^{7}	8.08×10^{8}	7.48×10^{8}
Face powder	5.10×10^{3}	4.47×10^{3}	5.75×10^{3}	1.76×10^{4}	1.52×10^{5}	5.80×10^{2}	6.17×10^{2}	5.33×10^{4}	2.03×10^{5}
Eye shadow	2.78×10^{6}	2.82×10^{6}	2.27×10^{6}	1.05×10^{7}	4.76×10^{7}	2.91×10^{5}	4.67×10^{5}	3.21×10^{7}	1.32×10^{8}
Eyeliner	8.72×10^{7}	9.43×10^{7}	1.13×10^{8}	3.42×10^{8}	1.00×10^{10}	1.28×10^{7}	7.11×10^{8}	1.25×10^{10}	5.60×10^{9}
Eye pencil	8.93×10^{7}	7.54×10^{7}	5.49×10^{7}	3.06×10^{8}	8.43×10^{8}	7.35×10^{6}	1.49×10^{7}	1.24×10^{9}	2.65×10^{9}
Blush	3.38×10^{6}	3.18×10^{6}	2.95×10^{6}	1.27×10^{7}	1.61×10^{8}	3.87×10^{5}	8.85×10^{5}	5.35×10^{7}	1.25×10^{8}
Mascara	4.05×10^{7}	5.45×10^{7}	4.79×10^{7}	1.39×10^{8}	1.76×10^{9}	5.17×10^{6}	2.74×10^{8}	6.36×10^{9}	2.08×10^{9}

tuted less than 0.1% of the EFSA provisional tolerable intake. The estimated SED values of Cd from the usage of these lip products were lower than the intake values obtained from the usage of lip products in the USA [25].

The SED of Pb from the use of these facial cosmetic products ranged from 4.24×10^{-6} to 1.79×10^{-1} μg kg^{-1} bw day^{-1}. Despite the fact that the existing PTDI for Pb was withdrawn by the FAO/WHO joint committee as "it could no longer be considered health protective" [56], we nevertheless used the PTDI value of 3.6 μg kg^{-1} bw day^{-1} as an indicator for comparison with the results of the estimated daily intake. The estimated SED of Pb from the use of these facial cosmetic products was below the PTDI value. In the USA, Liu et al. [25] obtained maximum intake values of 0.0015 and 0.008 μg kg^{-1} bw day^{-1} for average and high use scenarios, which is somewhat higher than the SED values obtained from the use of our samples except in the case of face powder. The estimated SED values of Cr obtained from the use of these facial cosmetic products (at 50 and 100% bioaccessibility) ranged between 2.67×10^{-6} and 0.10 μg kg^{-1} bw day^{-1}, while the SED of Ni ranged between 5.84×10^{-6} and 2.27×10^{-1} μg kg^{-1} bw day^{-1}. The tolerable daily intakes of Cr and Ni are 200 μg day^{-1} [57] and 720 μg day^{-1} [58] respectively. The estimated SEDs for Cr and Ni constituted less than 1% of their respective tolerable daily intake values.

The systemic exposure dosage of Cu from the use of these facial cosmetic products ranged from 4.0×10^{-7} to 5.26×10^{-2} μg kg^{-1} bw day^{-1}. The PTDI of Cu is 5000 μg day^{-1} [59]. The intake of Cu from use of these lip products is less than 1% of the tolerable intake value of Cu. The recommended daily intake of Co is set at 100 μg day^{-1} [60,61]. The intake values of Co obtained from the use of our lip products varied from 2.35×10^{-6} to 1.03×10^{-1} μg kg^{-1} bw day^{-1} for both 50 and 100% bioaccessibility scenarios. The intakes of Ni, Cr and Co derived from the use of the studied lip products were lower than those obtained from the use of lip products in the USA [25].

The recommended daily intakes (RDI) of Fe and Zn are set at 12.5 and 12 mg per day respectively [62], while the recommended dietary allowance value for Mn is 10–18 mg per day. As shown in Table 3, the estimated SEDs of Fe, Mn and Zn from application of these facial cosmetic products are below their respective recommended intake values. The estimated margin of safety for metals in these facial cosmetic products was greater than the proposed value of 100 set by the WHO. Face powders had lower MoS values compared with other facial cosmetic products investigated. The MoS values indicate that there is little risk associated with the concentrations of metals in these products except for face powder (Table 4).

Table 4
Systemic exposure dosage and margin of safety of metals in facial cosmetics obtained by using 100% bioaccessibility.

	Cd	Pb	Cr	Ni	Cu	Co	Fe	Mn	Zn
Systemic Exposure Dosage									
Lipstick	3.92×10^{-5}	1.32×10^{-4}	1.09×10^{-4}	2.15×10^{-4}	2.46×10^{-5}	1.08×10^{-4}	2.41×10^{-2}	1.43×10^{-4}	1.61×10^{-4}
Lip gloss/Lip balm	3.19×10^{-5}	1.16×10^{-4}	8.57×10^{-5}	1.72×10^{-4}	8.57×10^{-5}	1.00×10^{-5}	2.93×10^{-3}	3.47×10^{-5}	8.03×10^{-5}
Face powder	3.92×10^{-2}	1.79×10^{-1}	1.04×10^{-1}	2.27×10^{-1}	5.26×10^{-2}	1.03×10^{-1}	2.27×10^{2}	5.25×10^{-1}	2.96×10^{-1}
Eye shadow	7.20×10^{-5}	2.83×10^{-4}	2.64×10^{-4}	3.82×10^{-4}	1.68×10^{-4}	2.06×10^{-4}	3.00×10^{-1}	8.74×10^{-4}	4.56×10^{-4}
Eyeliner	2.29×10^{-6}	8.48×10^{-6}	5.33×10^{-6}	1.17×10^{-5}	8.00×10^{-7}	4.69×10^{-6}	1.97×10^{-4}	2.24×10^{-6}	1.07×10^{-5}
Eye pencil	2.24×10^{-6}	1.06×10^{-5}	1.09×10^{-5}	1.31×10^{-5}	9.49×10^{-6}	8.16×10^{-6}	9.39×10^{-3}	2.26×10^{-5}	2.26×10^{-5}
Blush	5.92×10^{-5}	2.51×10^{-4}	2.03×10^{-4}	3.15×10^{-4}	4.96×10^{-5}	1.55×10^{-4}	1.58×10^{-1}	5.23×10^{-4}	4.82×10^{-4}
Mascara	4.93×10^{-6}	1.47×10^{-5}	1.25×10^{-5}	2.88×10^{-5}	4.53×10^{-6}	1.16×10^{-5}	5.11×10^{-4}	4.40×10^{-6}	2.88×10^{-5}
Margin of Safety									
Lipstick	2.55×10^{6}	3.02×10^{6}	2.76×10^{6}	9.29×10^{6}	1.62×10^{8}	2.79×10^{5}	2.90×10^{6}	9.78×10^{7}	1.86×10^{8}
Lip gloss/Lip balm	3.13×10^{6}	3.45×10^{6}	3.50×10^{6}	1.16×10^{7}	4.67×10^{7}	2.99×10^{6}	2.39×10^{7}	4.04×10^{8}	3.74×10^{8}
Face powder	2.55×10^{3}	2.23×10^{3}	2.88×10^{3}	8.82×10^{3}	7.60×10^{4}	2.90×10^{2}	3.08×10^{2}	2.66×10^{4}	1.01×10^{5}
Eye shadow	1.39×10^{6}	1.41×10^{6}	1.14×10^{6}	5.23×10^{6}	2.38×10^{7}	1.45×10^{5}	2.34×10^{5}	1.60×10^{7}	6.58×10^{7}
Eyeliner	4.36×10^{7}	4.72×10^{7}	5.63×10^{7}	1.71×10^{8}	5.00×10^{9}	6.39×10^{6}	3.55×10^{8}	6.25×10^{9}	2.80×10^{9}
Eye pencil	4.46×10^{7}	3.77×10^{7}	2.74×10^{7}	1.53×10^{8}	4.21×10^{8}	3.68×10^{6}	7.46×10^{6}	6.19×10^{8}	1.33×10^{9}
Blush	1.69×10^{6}	1.59×10^{6}	1.48×10^{6}	6.35×10^{6}	8.06×10^{7}	1.93×10^{5}	4.43×10^{5}	2.68×10^{7}	6.23×10^{7}
Mascara	2.03×10^{7}	2.73×10^{7}	2.39×10^{7}	6.94×10^{7}	8.82×10^{8}	2.59×10^{6}	1.37×10^{8}	3.18×10^{9}	1.04×10^{9}

4. Conclusions

The present study revealed that Cd and Pb were present in these brands of facial cosmetic products at concentrations above their specified limits by the Canadian authority, while Ni, Cr and Co were above the suggested technically avoidable limits. The estimated margins of safety of metals in these cosmetic products were greater than the minimum value of 100 proposed by the WHO to conclude that a substance is safe for use, although, some metals can build up in the human body over time and cause adverse health effects. In the present circumstance, there is an urgent need to develop guidelines and standards for metals in cosmetics and to establish immediate mandatory regular testing programs to check the contents of metals in facial and other cosmetics imported into Nigeria in order to curtail their excesses and protect the consumer's health.

Transparency document

The Transparency document associated with this article can be found in the online version.

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