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Short Communication

Contribution of Hair Care Products in Heavy Metals Exposure in Pakistan

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Abstract

Products used for hair care by humans are essential for cleaning, protection, perfuming, and beautification. These are applied directly on the skin and can be a potential factor for dermal exposure to toxic metals. The present research deals with the assessment of heavy metals in the hair care products available in the local markets of Karachi, Pakistan. A total of 20 brands of shampoo and 05 brands of conditioners were collected in triplicate and analyzed for 10 heavy metals (Fe, Mn, Cr, Ni, Cu, Co, Pb, Cd, Zn, and Hg) by atomic absorption spectrophotometer. Toxic metals were found to be higher in conditioner than in shampoo of respective color and brand. Ni and Zn concentrations have exceeded the maximum permissible limits. Consumers belonging to the lower class are more vulnerable to heavy metals exposure because of the high metal content in low-cost products. These results suggested that hair care products should also be considered as one of the sources of heavy metals exposure.

Keywords: Shampoo, Conditioner, Hair, Heavy metals, Karachi

Introduction

The use of branded cosmetics for routine body care is part of civilization mostly by the upper and middle strata of the society but the availability of cheap cosmetics has also attracted the lower strata. Advancement in cosmetics industries has occurred in the last few decades through the production of cosmetics needed for the beautification and care of hair, teeth, skin, body, and nails [1].

Hair care products are used to clean, protect, perfume, and change in appearance or beautification purposes by humans. These applied directly on the skin can be a potential factor for dermal exposure to toxic metals through absorption and sweating [2]. Insufficient attention in Karachi has been paid to personal care goods, especially hair care

products as the source of heavy metals exposure to the consumers [3].

Commercially manufactured shampoo and conditioners became available for common people only from the turn of the 20th century. It is a highly competitive market in which new products are constantly being released with celebrity endorsement and advertising campaigns, due to which some people spend a great deal of money on their hair care. The fundamental properties of a good shampoo are: (a) It must clean the hair and scalp; (b) It must result in shiny and soft hair rather than dull and dry hair; (c) It must be washed off easily and completely; (d) It must not produce inflammation; and (f) It must contain pleasant odor and physical state.

To achieve these properties, many popular brands of shampoos contain mixtures of synthetic detergents and soaps. While, conditioner facilitates the manageability of the hair by making them shinier, smoother, and easier to be combed. It also maintains hair's moisture content to reduce flyaway hair [4].

As the demand for cosmetics in the market is increasing progressively among beauty-conscious people, issues about cosmetics containing heavy metals as ingredients and their toxic effects also attained the attention of clinicians and researchers [5].

Information about dermal contact with toxic heavy metals through hair care products is very scanty [6] and even unavailable in several places around the world. The present research deals with the assessment of 10 heavy metals in the hair care products (shampoos and conditioners) available in the local markets of Karachi, Pakistan.

Materials and Methods

Samples Collection

Samples of the most popular brands of shampoos and conditioners were collected randomly from local markets in Karachi. A total of twenty (20) brands of shampoo and five (05) brands of conditioners were considered; triplicate samples of each brand were collected. The products used by both upper-class and lower-class people were selected; on the other hand, those made for only a particular gender were selected as well. Codes were assigned to each sample and information about the ingredients on the product label was noted.

Samples Preparation

Shampoo and conditioner samples were prepared for heavy metal analysis according to Chauhan et al. [1]. Digestion of 1

g sample was done by a 5 mL mixture of concentrated nitric acid (HNO₃) and perchloric acid (HClO₄) in 3:1 ratio. The sample was heated on a hot plate for 2-3 hrs then the clear solution was filtered and made up to 10 mL in triple de-ionized water.

Analysis of Heavy Metals

The qualitative and quantitative analysis of heavy metals including iron (Fe), manganese (Mn), chromium (Cr), nickel (Ni), copper (Cu), cobalt (Co), lead (Pb), cadmium (Cd), zinc (Zn), and mercury (Hg) in the collected samples of shampoos and conditioners were performed by using Atomic Absorption Spectrophotometer (AAS) Perkin Elmer model A Analyst 700 using both air-acetylene flame (i-e FAAS) and graphite furnace (i-e GFAAS). Table 1 shows the analytical conditions of AAS. Concentrations of mercury in the samples were determined by the cold vapor (CVAAS) technique in which NaBH₄ was used as a reducing agent.

Table 1. Parameters used for the estimation of different elements by FAAS and GFAAS.

Elements	Wavelength (nm)	Slit Width (nm)	Gas used	Detection Limit (µg/L)
Cr	357.9	0.7	Ar	0.004
Mn	279.5	0.2	Ar	0.005
Fe	248.3	0.2	A-Ac	5
Co	240.7	0.2	Ar	0.15
Ni	232.0	0.2	Ar	0.07
Cu	324.8	0.7	Ar	0.014
Zn	213.9	0.7	A-Ac	1.5
Cd	228.8	0.7	Ar	0.002
Pb	283.3	0.7	Ar	0.05

A-Ac: Air-Acetylene, Ar: Argon

The instrument was calibrated with standard solutions prepared from commercially available stock standard solutions (1000 mg/L) of metals. The calibration curve was obtained prior to each analysis with a calibration blank and three working standards. Three replicates were obtained for each analysis and their mean was

taken to interpret the results. Quality control samples were run before each batch of analysis while matrix spike samples were analyzed after every 20 samples with 85% recovery.

Results and Discussion

Table 2 presented concentrations of heavy metals obtained in shampoos and conditioners considered in this study. On comparing the means of each metal in shampoos with conditioners, it was revealed that certain metals were found higher in shampoos than in conditioners; these metals include Mn, Cr, Ni, Zn, and Hg. While, mean concentrations of Fe, Cu, Co, Pb, and Cd were higher in conditioners than in shampoos. The shampoos were classified according to their function, color, cost, and gender-specific properties to better understand their contribution to metal exposure to consumers.

All brands were classified according to their specific function into five groups. Function-wise comparison of shampoos gave clarity about different metal content present. Mean Ni concentration was found to be highest in anti-hair fall shampoos. Although no international standards are available for Ni, Co, and Cr in cosmetics products. Basketter et al. [7] suggested $5 \mu\text{g.g}^{-1}$ as the maximum limit for skin protection. The mean Ni concentration in anti-hair fall shampoos has exceeded this maximum limit (i.e., $5 \mu\text{g.g}^{-1}$). Ni exposed to the skin can get oxidized easily by sweat, resulting in diffusible and soluble compounds that can penetrate the skin. Although this penetration is limited (<1%), it may be enhanced by time of exposure, dosage, sweat oxidizing capacity, presence of counter ions (Cl^- , CH_3COO^- , SO_4^{2-} , NO_3^-), and gender (male or female). The complexing ability of Ni to form Ni-complexed proteins could also be attributed to skin irritation or contact allergy [8-11].

Mean Zn concentrations in anti-dandruff and black shine shampoos have surpassed the permissible limit (i.e., $100 \mu\text{g.g}^{-1}$) for Zn set by the World Health Organization (WHO) [12]. Several other studies had also investigated the presence of Zn in antidandruff shampoos [13-14] and in other shampoos [15], that had also exceeded the permissible limit set by WHO. Dandruff is the most common disorder of the scalp in which dead skin cells are shed from the scalp. It mostly occurs after pubertal age in both genders. Persons experience itching, irritation, and redness in the scalp accompanied by flaking of dead cells either normal or high [16].

Zinc pyrithione is commonly used as an effective ingredient in antidandruff shampoos. It is widely used because of its antimicrobial potency, greater depositing ability into hair follicles, and high efficiency against dandruff [17]. High exposure to Zn may cause its enrichment which may result in certain health hazards, such as gastric ailment, allergy, or even neurological disorder [13].

Fe and Mn were detected in all samples. While, Hg concentration was within the permissible limit set by WHO i.e., $1 \mu\text{g.g}^{-1}$ [18]. Conditioners contained higher Pb and Cd concentrations than shampoos. Canadian authority set the maximum allowable limit for lead in cosmetics at $10 \mu\text{g.g}^{-1}$, while that for Cd is $3 \mu\text{g.g}^{-1}$, as an impurity [13]. Both metals were found within the limits. The presence of Cd in other cosmetics like lipsticks was reported numerously. Pb and Cd were found to be higher in hair care products in some other regions of the world as well like Ghana, Nigeria, and Gwalior [1, 3, 5]. Attention should be paid to the fact that hypertension may be caused due to even a minor amount of Cd exposure because of increased blood pressure. Other than that, it may also target the liver, kidney, brain,

immune system, and lungs [19]. While, Pb exposure may result in renal diseases, decreased intelligence, and a weakened nervous system [20].

Table 2. Concentrations (mean \pm SD) of heavy metals in different hair care products.

Category	Fe	Mn	Cr	Ni	Co	Zn	Pb	Cd	Cu	Hg
Product-wise classification ($\mu\text{g}\cdot\text{g}^{-1}$)										
Shampoo	6.286 ± 0.116	1.719 ± 0.090	0.553 ± 0.102	2.695 ± 0.210	0.208 ± 0.135	180.706 ± 15.612	0.127 ± 0.231	0.386 ± 0.038	0.196 ± 0.076	0.021 ± 0.008
Conditioner	6.616 ± 0.361	0.812 ± 0.072	0.499 ± 0.051	2.247 ± 0.827	0.285 ± 0.161	0.935 ± 0.033	0.643 ± 0.311	0.555 ± 0.050	0.478 ± 0.022	0.010 ± 0.001
Function-wise shampoo classification ($\mu\text{g}\cdot\text{g}^{-1}$)										
Anti hair fall	7.847 ± 1.030	1.120 ± 0.995	0.489 ± 0.081	6.026 ± 0.033	0.062 ± 0.008	85.668 ± 6.639	0.183 ± 0.033	0.330 ± 0.043	0.170 ± 0.012	0.030 ± 0.011
Anti lice	3.576 ± 0.992	1.412 ± 1.310	0.633 ± 0.021	2.405 ± 1.170	0.112 ± 0.061	1.941 ± 0.191	0.283 ± 0.037	0.258 ± 0.051	0.039 ± 0.007	0.013 ± 0.009
Anti dandruff	6.917 ± 2.110	1.980 ± 1.261	0.500 ± 0.318	1.217 ± 1.001	0.180 ± 0.004	451.312 ± 17.838	0.010 ± 0.003	0.443 ± 0.019	0.220 ± 0.131	0.001 ± 0.011
For Silky softness	4.883 ± 0.931	2.526 ± 1.559	0.512 ± 0.619	2.226 ± 0.991	0.497 ± 0.203	3.081 ± 0.741	0.162 ± 0.035	0.422 ± 0.031	0.212 ± 0.113	BDL
For Black shine	9.081 ± 1.002	1.562 ± 0.172	0.583 ± 0.318	1.481 ± 1.020	0.062 ± 0.010	290.393 ± 13.315	0.147 ± 0.017	0.329 ± 0.021	0.240 ± 0.099	0.011 ± 0.071
Color-wise shampoo classification ($\mu\text{g}\cdot\text{g}^{-1}$)										
Black	9.581 ± 2.033	0.970 ± 0.022	0.754 ± 0.211	6.489 ± 3.222	0.062 ± 0.036	1.947 ± 0.271	0.183 ± 0.071	0.283 ± 0.057	0.233 ± 0.016	0.011 ± 0.081
Gray	6.812 ± 3.190	2.081 ± 1.313	0.397 ± 0.011	0.628 ± 0.064	0.135 ± 0.012	577.885 ± 15.335	BDL	0.302 ± 0.045	0.150 ± 0.011	0.014 ± 0.001
White	3.991 ± 0.033	1.080 ± 0.999	0.510 ± 0.121	1.860 ± 1.132	0.265 ± 0.031	53.471 ± 2.314	0.153 ± 0.015	0.396 ± 0.034	0.161 ± 0.009	BDL
Pink/Peach	5.485 ± 2.710	2.791 ± 2.100	0.526 ± 0.099	2.397 ± 0.996	0.354 ± 0.042	157.150 ± 10.111	0.118 ± 0.003	0.462 ± 0.023	0.250 ± 0.011	BDL
Blue	9.135 ± 4.912	3.097 ± 1.629	0.612 ± 0.331	0.450 ± 0.031	BDL	629.385 ± 13.580	BDL	0.585 ± 0.050	0.050 ± 0.011	0.012 ± 0.009
Color vs. product-wise classification ($\mu\text{g}\cdot\text{g}^{-1}$)										
Black Shampoo	9.579 ± 1.261	0.971 ± 0.091	0.754 ± 0.691	6.479 ± 2.110	0.063 ± 0.031	1.938 ± 0.201	0.183 ± 0.621	0.283 ± 0.037	0.233 ± 0.099	0.011 ± 0.009
Black Conditioner	6.838 ± 2.001	1.400 ± 0.411	0.363 ± 0.012	3.038 ± 2.131	0.088 ± 0.027	1.850 ± 0.255	1.063 ± 0.691	0.426 ± 0.045	0.375 ± 0.111	0.012 ± 0.011
White Shampoo	3.992 ± 0.182	1.080 ± 0.002	0.511 ± 0.021	1.861 ± 1.208	0.255 ± 0.117	53.472 ± 5.300	0.153 ± 0.118	0.396 ± 0.025	0.162 ± 0.091	BDL
White Conditioner	6.375 ± 3.311	0.225 ± 0.011	0.613 ± 0.083	1.438 ± 0.994	0.463 ± 0.131	BDL	0.225 ± 0.166	0.684 ± 0.083	0.563 ± 0.100	0.006 ± 0.002
Cost-specific shampoo classification ($\mu\text{g}\cdot\text{g}^{-1}$)										
High-cost	5.866 ± 3.591	0.202 ± 0.071	0.302 ± 0.011	1.801 ± 0.518	0.128 ± 0.002	159.795 ± 6.999	0.141 ± 0.016	0.241 ± 0.042	0.178 ± 0.008	0.008 ± 0.001
Low-cost	6.589 ± 1.360	2.235 ± 0.055	0.512 ± 0.381	3.126 ± 0.923	0.336 ± 0.311	157.283 ± 3.472	0.208 ± 0.053	0.386 ± 0.038	0.248 ± 0.041	0.012 ± 0.003
Gender-specific shampoo classification ($\mu\text{g}\cdot\text{g}^{-1}$)										
For Men	9.263 ± 3.598	4.125 ± 1.680	0.550 ± 0.032	BDL	0.250 ± 0.012	484.625 ± 28.002	BDL	0.226 ± 0.019	0.138 ± 0.013	0.002 ± 0.001
For Women	4.863 ± 3.666	0.663 ± 0.028	1.050 ± 0.099	1.350 ± 1.100	BDL	470.250 ± 16.226	BDL	0.201 ± 0.019	0.075 ± 0.009	0.001 ± 0.001
Non specific	6.661 ± 1.184	1.633 ± 0.166	0.489 ± 0.221	3.145 ± 0.917	0.230 ± 0.118	157.099 ± 3.610	0.108 ± 0.097	0.424 ± 0.023	0.234 ± 0.031	0.030 ± 0.011
Permissible Exposure Limit ($\mu\text{g}\cdot\text{g}^{-1}$)										
References	-	-	5 [7]	5 [7]	5 [7]	100 [12]	10 [13]	3 [13]	50 [23]	1 [24]

^aBDL = Below detection limit

The data of metals in shampoos were then grouped on the basis of shampoos' colors to evaluate the variation of heavy metal concentrations with respect to the color of the product. Fe, Cr, Ni, and Pb were observed to be highest in black-colored shampoos. Among these, mean Ni concentration has surpassed the permissible limit only in black-colored shampoos. Although other metals are present in low concentrations in these hair care products, toxic metals may cause harmful effects even in low amounts that are being absorbed gradually into the skin. Cr was also found to be associated with eczema and other skin inflammations. In previous studies, positive results of dermal patch tests revealed that Ni is the most common metal responsible for skin diseases such as allergic contact dermatitis (ACD). Ni-induced dermatitis causes lichenification of skin, eczema, and erythema [5]. Other than metals, shampoos contain various detergents, perfumes, solvents, polypeptides, surfactants, and lanolin which may cause contact dermatitis.

Mn, Cd, and Zn were highest in blue-colored shampoos and Cu and Co were present highest in pink/peach-colored

shampoos. On comparing shampoos and conditioners of the same color and same brand, it was revealed that toxic metals (Cd, Hg, and Pb) were found to be more in conditioners than in shampoos of respective color and brands.

Salts of certain metals in cosmetic products are prohibited, such as salts of Sn, As, Cd, Ni, and Pb. The unintentional addition of these metals may have a natural origin in raw materials used like argan oil, essential oils, honey, olive oil, etc. Whereas, salts of other metals are allowed either within the limit or specific salts can be used only, such as Co, Cr, Au, Hg, and Se [21]. In the present study, codes of color additives mentioned on ingredient lists of selected shampoos and conditioners were noted. Table 3 shows the maximum acceptable metal impurities in color additives and other compounds used in cosmetics set by the United States Food and Drug Administration (USFDA), Center for Food Safety and Applied Nutrition (CFSAN), Office of Cosmetics and Colors [22]. All samples contained Pb, Hg, Cr, and Mn concentrations below the maximum acceptable impurity limit.

Table 3. Maximum acceptable metal impurities in color additives and other compounds of shampoo.

Color additives and other compounds in shampoo	Description	Elements ($\mu\text{g.g}^{-1}$)			
		Pb	Hg	Cr	Mn
FD & C Red No. 4	Disodium salt of 3-[(2,4-dimethyl-5-sulfophenyl)azo]-4-hydroxy-1-naphthalenesulfonic acid.	< 10	< 1		
FD&C Yellow No. 6	Disodium salt of 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid	< 10	< 1		
FD&C Yellow No. 5	Trisodium salt of 4,5-dihydro-5-oxo-(1-4-sulfophenyl)-4-[(4-sulfophenyl)azo]-1H-pyrazole-3-carboxylic acid	< 10	< 1		
FD&C Acid Blue No. 9 Ext. D&C Black No. 2	Ethyl - [4 - [[4 - [ethyl -(3 - sulfophenyl) methyl] amino] phenyl] - (2 - sulfophenyl) methylidene] - 1 - cyclohexa - 2, 5 - dienylidene] - [(3 - sulfophenyl) methyl] azanium	< 10		< 50	< 100
Carbazole violet (Pigment Violet 23)	8, 18-Dichloro-5, 15-diethyl-5, 15-dihydrodiindolo(3,2-b:3',2'-m)tri-phenodioxazine				
Ext. D&C Violet No. 2	Monosodium salt of 2-[(9,10-dihydro-4-hydroxy -9,10-dioxo-1-anthracenyl) amino]-5-methyl-benzenesulfonic acid	< 20	< 1		
D&C Black No. 2	Carbon black	< 10	< 1		
Titanium dioxide	TiO ₂	< 10	< 1		
Mica	H ₂ KAl ₃ (SiO ₄) ₃	< 10	< 1		

All metals were found to be higher in low-cost products than in high-cost products. This indicated that lower-class users are more vulnerable to metal exposure by using these products than upper-class consumers. Gender-specific products contained less toxic metals than non-gender-specific products. It indicated that more care is done in the manufacturing of gender-specific and high-cost products which reduces the metal contamination in them.

Conclusion

The results suggested that hair care products could be an overlooked source of metal exposure. Exceeded levels of Ni and Zn in these hair care products are alarming because these metals are making the products susceptible to skin diseases, specifically. The absence of metal content labeled in the formulation list of cosmetics made it evident that all toxic metals were present unintentionally in cosmetics as impurities from the environment, byproducts of the process of manufacturing, or by the decomposition of ingredients. The lack of regulation and testing from manufacturers (especially of low-cost cosmetics) can cause hazardous health effects even at low concentrations from these unintentionally added toxic metals in cosmetics. Local manufacturers should be bound to test toxic metal content in natural raw materials and salts before use in the production of cosmetics so that these can be replaced with alternatives with minimum or no metal contamination. This could be an effective step towards reducing heavy metal exposure via the use of hair care products.

Conflict of Interest

The author declares no conflict of interest.

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