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Assessment of cadmium, lead, and nickel levels in hair care products marketed in Turkey

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Synopsis

This study evaluated the content of cadmium (Cd), lead (Pb), and nickel (Ni) in 105 hair care products commercially available in Turkey. Cd, Pb, and Ni were detected in 40%, 21.91%, and 94.29% of the samples, respectively. Maximum Cd concentrations were detected in two shampoo samples, and the highest Pb level was found in a hair conditioner, all of them were herbal-based formulations. The highest mean levels of Ni were detected in hairstyling agents. The overall results were lower than the Canadian and German regulatory limits; however, according to the European Council Directive and Turkish Cosmetic Legislation, Cd, Pb, and Ni are listed as the substances that are prohibited in any amounts in cosmetics. Moreover, Ni content of 17.14% of the samples was above the limit of allergic contact dermatitis. It is known that these toxic metals tend to accumulate in body and prolonged use of them may potentially pose threat to human health. Thus, regular market monitoring and safer limits should be seriously considered especially for susceptible groups of the population like the pediatric group.

INTRODUCTION

Cosmetic products are commonly used by millions of consumers on a daily basis. Within the last few decades, there has been a great increase in the number of cosmetic industries producing various types of cosmetic products, which are needed for the care and good appearance of skin, hair, nails, teeth, and body (1,2). Cosmetics however were shown to be possibly contaminated by unwanted impurities such as toxic metallic powders of nickel (Ni), lead (Pb), and cadmium (Cd), which are unintentionally introduced to the cosmetics during their preparation. The metallic impurities in cosmetics have been disputable due to the biological accumulation of the metals and their possible dermal and systemic health problems in humans (3,4). There have been a number of studies about the presence of heavy metals in cosmetic products. In a study conducted by Nnorom *et al*., the

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trace metals content of facial cosmetics commonly used in Nigeria were examined. Results indicated that the concentration of Pb in the candy lipstick product is 2.8 times higher than the limit value regulated by American Food and Drug Administration (FDA) (5). In another study, it was found that more than half of the 33 tested lipsticks from top local brands contained detectable Pb (6). In a similar study, Al-Saleh *et al*. assessed the levels of Pb, Cd, Ni, chromium (Cr), mercury (Hg), arsenic (As), and antimony (Sb) in 28 samples of 14 lipstick brands in Saudi Arabia (7). While this study found that the levels of all metals were lower than the FDA limits, As level (3 μg/g) was higher than the limit value in one brand of lipstick. Also, the levels of Ni in 10 and Cr in 4 of the 28 lipsticks were found to be above the trigger limit of 1 μg/g for allergic contact dermatitis. Ayenimo *et al*. demonstrated that personal care products, including soaps, cosmetic, and hair creams, are notable sources of Cd and Cr in the human body (8). In another study, Sin *et al*. revealed high levels of Hg in cosmetic creams (9).

Although some information have been reported on the metal content of different cosmetic products, few data exist on the hair care products in literature. There is also a limited amount of information on this field in Turkey. This study examined the levels of Cd, Pb, and Ni in commonly used hair care products commercially sold in Turkey. Data generated through this study will procreate awareness about risks associated with the use of these products and also provide baseline information for further studies.

MATERIALS AND METHODS

All chemicals and metal stock standard solutions were obtained from Sigma-Aldrich (St. Louis, MO) and Merck (Darmstadt, Germany).

One hundred and five samples from 51 different brands commonly sold in Turkey were randomly purchased from different markets in Istanbul and classified as shampoos, hair conditioners, hairstyling agents (hair sprays, setting lotions and setting mousses, hair creams and hair gels), and pediatric bath cleaning products.

Samples (0.5 g) were first transferred to Teflon acid digestion cups. Three milliliters of 65% nitric acid (HNO_3) and 1 ml of 44% hydrofluoric acid were then added to samples and digested in a microwave acid digestion unit (Milestone Mega 1200, Bergamo, Italy) according to the manufacturer's application notes. The digested samples were then quantitatively transferred and diluted to 5.0 ml with triply distilled water (Simplicity Water Purification System, Millipore, Molsheim, France).

Cd, Pb, and Ni determination in digested samples were done by using graphite furnace atomic absorption spectrometry (AAS) with Zeeman background correction (Analytic Jena, Zeenit 700, Jena, Germany). The calibration curve was plotted with standard solutions of Cd (0.2–1 μg/l), Pb (6–34 μg/l), and Ni (6–30 μg/l). All standards were prepared in 0.05% HNO_3. Suitable dilutions were prepared from digested samples with triply distilled water. Peak Signal area mode was used for quantifications and the manufacturer's application notes were used for metal measurements checking validation parameters. Table I shows AAS furnace parameters.

All of the results are expressed as the mean ± S.D. The differences between the groups were evaluated with Kruskal–Wallis analysis of variance and comparisons between two

Table I
Atomic Absorption Spectrometer and Graphite Furnace Parameters for Metal Analysis

Element	Wavelength (nm)	Maximum ash temperature (°C)	Atomization temperature (°C)	Modifier	Zeeman mode[a]
Cd	228.8	300	950	-	2-field[b]
Ni	232	1100	2350	-	2-field
Pb	283.3	500	1650	5 µl Pd $(NO_3)_2$ (0.1 %)	3-field dynamic[c]

[a]The measurement mode for the background correction.
[b]The measurement with magnetic field strength 0 and maximum field strength.
[c]The measurement of the absorbance values at various magnetic field strengths.

independent groups were made with the Mann–Whitney *U*-test. $p < 0.05$ was considered statistically significant.

RESULTS AND DISCUSSION

The mean Cd, Pb, and Ni levels of our samples were found to be 6.09 ± 4.26 ng/ml, 0.20 ± 0.09 µg/ml, and 1.08 ± 2.78 µg/ml, respectively (Tables II—IV). The samples with the concentrations below the limit of detection (LOD) were excluded from mean, median, and range calculations. LOD of Cd, Pb, and Ni were 0.03, 2.25, and 1.40 ng/ml, respectively.

Cd was detected in 40% of the total samples. The results with detectable Cd levels varied from 1.01 to 25.08 (ng/g). Maximum levels of Cd were detected in two shampoo samples (25.08 and 17.14 ng/g). Both of them were herbal-based formulations. The order of content of Cd in the hair care products was determined as shampoos > hairstyling agents > pediatric products > hair conditioners. No significant differences were found between different classes of hair care products.

Pb was determined in 23 of the 105 total samples (21.91%). The highest Pb level (0.42 µg/g) was observed in hair conditioner followed by hairstyling samples (0.37 µg/g), while the lowest Pb value was detected in shampoo samples (0.07 µg/g). The highest values were found in coconut and wheat protein-based formulations. The mean amount of Pb in

Table II
Cd Content (ng/g) in Hair Care Products

Classes of analyzed hair care product	Tested samples (n)	Mean	S.D.	C.V. (%)	Range	Median	Samples with detectable Cd levels	
							n	%
Shampoos	30	6.89	5.73	83.16	1.01–25.08	6.51	20	66.67
Hair conditioners	39	4.05	2.62	64.69	1.26–9.23	3.53	9	23.08
Hairstyling agents	21	6.38	0.79	12.38	5.23–7.72	6.24	7	33.33
Pediatric	15	6.17	1.47	23.82	4.47–8.70	6.00	6	40
Total	105	6.09	4.26	69.95	1.01–25.08	6.05	42	40

Table III
Pb Content (μg/g) in Hair Care Products

Classes of analyzed hair care product	Tested samples (n)	Mean	SD	CV (%)	Range	Median	Samples with detectable Pb levels	
							n	%
Shampoos	30	0.11	0.05	45.45	0.07–0.15	0.11	4	13.33
Hair conditioners	39	0.24[a]	0.09	37.5	0.12–0.42	0.2	9	23.08
Hairstyling agents	21	0.25[a]	0.08	32	0.16–0.37	0.26	7	33.33
Pediatric	15	0.13	0.04	30.77	0.11–0.18	0.11	3	20
Total	105	0.20	0.09	45	0.07–0.42	0.18	23	21.91

[a]$p < 0.05$ versus shampoos.

samples was in the order of hairstyling agents > hair conditioners > pediatric products > shampoos. Pb content in hair conditioners and hairstyling agents was statistically higher than shampoo samples ($p < 0.05$).

With the presence of Cd and Pb at the highest level in herbal-based hair care formulations, it is considered that natural products are not always inherently safer for public use. Because of unwanted contaminations, herbal products can cause some health problems to the public.

Approximately 94% of the total samples contained Ni at detectable values. These values were in the range of 0.1 μg/g in shampoo to 20.98 μg/g in hair conditioners, followed by hairstyling with 12.46 μg/g. The lowest values were determined in pediatric products. There was a statistically significant difference between the Ni levels of the hairstyling agents and pediatric products ($p < 0.05$).

It is difficult to decide if obtained values for Cd and Pb are too high or low since there are no international standards for impurities in cosmetics with only a few regulations at the

Table IV
Ni Content (μg/g) in Hair Care Products

Classes of analyzed hair care product	Tested samples (n)	Mean	SD	CV (%)	Range	Median	Samples with detectable Ni levels	
							n	%
Shampoos	30	1.00	1.66	166	0.10–8.19	0.44	26	86.67
Hair conditioners	39	1.15	3.61	314	0.11–20.98	0.28	39	100
Hairstyling agents	21	1.69[a]	3.21	190	0.13–12.46	0.45	20	95.24
Pediatric	15	0.37	0.37	100	0.12–1.43	0.19	14	93.33
Total	105	1.10	2.80	255	0.10–20.98	0.32	99	94.29

[a]$p < 0.05$ versus pediatric.

national level. For instance, the Canadian regulatory limits for Cd and Pb are 3 and 10 μg/g, respectively (10). Also German Federal Government considers cosmetic products with Cd level above the 5 μg/g and Pb levels above the 20 μg/g as technically avoidable products (11). Cd and Pb levels found in our study were below these limitations. Also Cd and Pb values in this study did not exceed the limitation of 20 μg/g approved by the FDA (12). However, according to the European Council Directive published in 1976 and Cosmetic Legislation in Turkey rearranged in 2006, Cd, Pb, and Ni are listed as the substances that are prohibited in any amounts in cosmetics (13,14).

Systemic toxicity of Ni as well as its association with allergic dermatitis is well known. Some investigations revealed that allergic contact dermatitis is the most common single reason for hospital referrals associated with adverse reactions to cosmetics (15,16). Reports by the contact dermatitis group of North America have consistently ranked Ni as the number one contact allergen on patch testing (17). Ni, in the amounts of over 1.5 μg/g, can cause dermatitis or sensitization of the skin (3). It has been recommended that consumer products should not contain more than 5 μg/g of Ni and preferably this level should be below 1 μg/g to minimize the risk of allergic reactions (1,18). In our study, 94.29% of all the samples analyzed contained detectable levels of Ni. However, 81.82% of them were below the limit of 1 μg/g. In 13 samples with detectable Ni levels, concentrations were between 1 and 5 μg/g, and five samples contained amounts higher than 5 μg/g. The Ni contents of those five samples were 20.98 μg/g (hair conditioner), 12.46 μg/g (hairstyling agent), 9.19 μg/g (hair conditioner), 8.41 μg/g (hairstyling agent), and 8.19 μg/g (shampoo). Considering that only free Ni ions are responsible for induction or exacerbation of sensitization (19), such high concentrations may pose both dermal and systemic threat to human health.

Exposure of infants and children to toxic metals is more concerning owing to the higher vulnerability to this kind of risk. Exposure to these chemicals begins with intrauterine life and continues during lactation period (20,21). In this study, 15 samples from 10 brands of pediatric hair care products were investigated for Cd, Pb, and Ni levels. Cd and Pb were detected in 6 (40%) and 3 (20%) pediatric products, respectively. The maximum levels were 8.70 ng/g for Cd and 0.18 μg/g for Pb. However, Ni was detected in 14 (93.33%) of 15 pediatric hair care products. One sample had the remarkable value of 1.43 μg/g. This sample exceeded the ultimate target level of 1 μg/g (18). Although the amount of investigated toxic metals in pediatric products were found to be below the current regulations, exposure of infants and children to these heavy metals in any amount should be considered as an important risk for their vulnerable bodies.

In conclusion, this study provides new data on toxic metal concentrations of hair care products used in Turkey. To our knowledge, this is the first study to evaluate Cd, Ni, and Pb levels in four different categorized hair care products in Turkey. In all the samples, measurable concentrations of these heavy metals were evident. Despite the concentration of Cd and Pb in all the samples analyzed were lower than the Canadian and German regulatory limits, presence of Cd, Pb, and Ni in cosmetic products are prohibited with no specific limitation in Cosmetic Legislation of Turkey. It is obvious that further studies are required to ascertain the forms of these toxic contaminants in cosmetic products and to assess the absorbed levels and potential risks to humans, especially susceptible groups of the population like the pediatric group. Presence of relatively high levels of Ni in the hair care products also indicates the necessity of routine market surveillance of the cosmetic products in order to decrease the possible side effects on consumers.

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