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Assessment of the Exposure to Elements from Silver Jewelry by Hair Mineral Analysis

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Abstract The aim of the present article was to assess the effect of wearing silver jewelry on mineral composition of human scalp hair. To investigate the possible effect of gender, a group of females and males was distinguished. Subjects, who declared in the questionnaire wearing silver jewelry, constituted 55% of the whole population. It was found that individuals wearing jewelry had increased levels of Ag ($\sim$ 3 times), Ba (30%), Ca (33%), La (40%), Li (25%), and Zn (27%) in hair and lowered level of: Al (34%), K (79%), and Na (32.5%) in comparison with the group that did not wear jewelry. Those differences were statistically significant. Lower levels of K and Na in hair of subjects wearing jewelry was probably related with an antagonism between Ag-K and Ag-Na found in the present work. Analyzing the effect of two grouping variables—gender and wearing silver jewelry—on hair composition, it was observed that statistically significant differences were determined for the following elements: As, Ba, Ca, and Se. Female hair contained two times more Ca, four times Ba, 36% less As, and five times less Se. It was found that 34% of the population wearing silver jewelry had higher Ag content in hair than the upper value of the reference range (0.567 mg/kg) determined for subjects who did not wear jewelry. Ag and other metals (especially Cu and Zn) from jewelry could be absorbed through the skin and therefore hair mineral analysis is useful in the assessment of this exposure. The study was carried out on Poles, among which silver jewelry is particularly popular. The population can be thus considered as exposed.

Jewelry signifies items of personal adornment, such as necklaces, rings, brooches, earrings, and bracelets. Wearing jewelry has a very ancient origin. The first signs of established jewelry-making in Ancient Egypt were around 3000–5000 years ago. The Egyptians preferred the luxury, rarity, and workability of gold over other metals (Reader's Digest 1986). Nowadays, wearing jewelry expresses not only one's own style but also societal aspects. Very often, jewelry is perceived as a symbol of power, beauty, and wealth.

Jewelry is made of many materials. In the manufacture of jewelry, several metals are used: silver (Ag), gold (Au), platinum (Pt), palladium (Pd), or titanium (Ti). The model composition of silver alloy is as follows: 2.5–19.5% copper (Cu), 0.02–2.0% silicon (Si), 0.01–3.3% gemanium (Ge), and Ag to 100% (Eccles 1996). Another silver alloy—a quinary Ag-Cu-Zn-Sn-Si—consists of about 35–48% Ag, 25–35% zinc (Zn), 0.5–3.5% tin (Sn), 0.01–0.4% of Si, 0–1% nickel (Ni), 0–1% of Pd, and 0–0.5% phosphorous (P)and Cu (Steine et al. 1977).

Through lifetime, an organism of human has contact with various metal alloys, either from jewelry, orthodontic appliances, or dental amalgams. Those alloys frequently contain toxic and sensitizing metals [e.g. Ni, Cr (chromium), Mo (molybdenum), Co (cobalt), Ag, Ti, In (indium)] (Jurado-López and Luque de Castro 2003; Mikulewicz and Szymkowski 2006; Milošev and Kosec 2007). These components of alloys, if present in/on human organism, undergo deterioration through the action of sweat (Milošev and Kosec 2007) or saliva (Mikulewicz and Szymkowski 2006). It is important to emphasize that ions released from alloys, which can cause an allergic reaction, depend on the chemical composition of the applied alloy's pH and temperature of sweat or saliva (Mikulewicz and

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Szymkowski 2006). One of the most common constituents of alloys is Ni, which can cause an allergic reaction in ~5–10% of the population (Bales 1983). Women are more prone to Ni allergy than men due to ear piercing and costume jewelry (Afridi et al. 2006). So far, in the literature, it has not been explicitly stated if using alloys for such purposes can be related to the exposure to metals in toxic doses.

This topic has not been discussed yet by the investigation of the effect of skin route exposure to metals by hair mineral analysis, a technique that is widely used in human biomonitoring studies, whereby chronic exposure occurs. Hair analysis is in fact potentially useful for an estimation of ongoing intoxication phenomena caused by trace elements, to diagnose diseases and to assess the nutritional status of an individual. This is a widely accepted biomarker of chronic exposure to toxic elements (Barbosa et al. 2001; Senofonte et al. 2000).

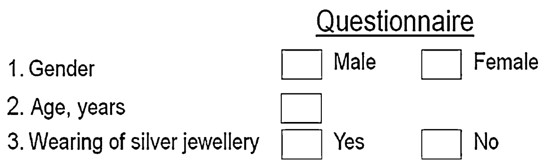
In the literature, dermal exposure from Ag jewelry has not been studied so far. The preliminary research, which signaled the problem, has appeared recently. Qureshi et al. (1982) indicated a higher content of Ag in hair of the female group possibly due to the extensive use of Ag jewelry in a society living in Pakistan (Islamabad). The content of Ag in hair of males ranged from 0.02 to 1.78 mg/kg and in hair of females from 0.01 to 3.93 mg/kg. Rodushkin and Axelsson (2000) also suggested that the higher content of Ag in hair was due to extensive use of jewelry by the inhabitants of northern Sweden.

The aim of the present article was to investigate dermal exposure to metals, as the effect of wearing Ag jewelry, using hair mineral analysis as a noninvasive biomarker of chronic exposure to metals. The examined population was divided into two groups: wearing and not wearing jewelry. Additionally, the effect of gender, as the second grouping variable, was analyzed.

Materials and Methods

Sampling and Preparation

Hair for mineral analysis was provided by volunteers, who previously filled out a questionnaire (Fig. 1) that included questions on their individual characteristics: gender and wearing or not wearing Ag jewelry. The subjects were not exposed to toxic substances and were not kept under special conditions. The present research was carried out on hair sampled from 155 individuals (58 males and 97 females) who lived in Wrocław and in the surroundings. The participants underwent similar environmental and occupational exposure because they were students of the same university and specialization.


Questionnaire

1. Gender ☐ Male ☐ Female
2. Age, years ☐
3. Wearing of silver jewellery ☐ Yes ☐ No

Fig. 1 The questionnaire administered to the subjects

The participants cut hair (5 cm long) from the nape of the neck directly after four consecutive washings of their hair with Johnson's Baby shampoo and drying (for cutting hair, surgical scissors made from stainless steel were used [Hilbro International (Pvt) Ltd]. The selection of the shampoo was determined by its composition; among the metal cations, only Na was present. Hair was stored in a paper envelope and underwent digestion without additional washing steps. The goal was to elaborate an easier analytical procedure without steps of extraction from hair with acids, organic solvents, and so forth, which, on one hand, are presented in the literature as the method—which removes exogenous contamination—but, on the other hand, as the source of contamination.

Analytical Methods

The content of 39 elements (Ag, Al, As, B, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pt, Rb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, W, Y, Zn, and Zr) in hair was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (macroelements) and inductively coupled plasma mass spectrometry (ICP-MS) (microelements and toxic elements), as described previously. The samples of hair (0.5 g) were solubilized with 5 mL of the concentrated nitric acid (69% m/m) Suprapur grade (from Merck) and digested in a microwave oven (Milestone, USA). After mineralization, the samples were diluted with ultrapure water deionized by Aquadem 50 l (WilhelmWerner GmbH, Germany) and Millipore Simplicity UV (France) systems to 50 g. The samples were then analyzed directly by ICP-OES Vista MPX (Australia) with a pneumatic nebulizer for the content of macroelements and, after 10 times dilution, by ICP-MS Thermo Scientific (Germany) for the content of microelements, toxic elements, and other trace elements. The samples were analyzed in triplicate (the relative standard deviation of the measurement did not exceed 5%). The presented data are the arithmetic average from three measurements. Uncertainty was also reported. For the preparation of standard solutions (1.0, 10, 50, and 100 mg/L), the multielemental standard (100 mg/L Astasol$^{®}$; Prague, Czech Republic) was used (Chojnacka et al. 2010a).

The analytical process was controlled by NCS Reference Material–Human Hair NCS ZC81002 from the China

National Analysis Center. The analyses were carried out in the laboratory certified by ILAC-MRA and the Polish Centre of Accreditation (No. AB 696) according to ISO/IEC 17025.

Statistical Methods

The results were elaborated statistically by Statistica (version 9.0). The differences between the two groups were investigated with a *t*-test and between several groups with one-way analysis of variance (ANOVA) using the Tukey multiple comparison test. Results were considered significantly different when $p < 0.05$ and $p < 0.1$, respectively.

Results and Discussion

In the present article, the effect of Ag jewelry on the mineral composition of hair is presented. It is important to emphasize that jewelry is not the only source of the exposure to Ag and that Ag is not the only element to which individuals are exposed from silver alloys. A wide variety of Ag uses allows exposure through various routes of entry into the body (e.g., ingestion is the primary route of exposure to Ag compounds and colloidal Ag proteins). It is worth mentioning that Ag compounds have been used in the medical field to treat burns and a variety of infections and also as preservatives (Morones et al. 2005). Inhalation of dust or fumes containing Ag occurs primarily in occupational settings. Skin contact takes place at the workplace, from the application of burn creams. Ag can also access the body through the use of acupuncture needles, catheters, dental amalgams, or accidental puncture wounds (Agency for Toxic Substances and Disease Registry 1990; Drake and Hazelwood 2005). The most common health effect associated with prolonged exposure to Ag is the development of a characteristic, irreversible pigmentation of the skin (argyria) and/or the eyes. Localized argyria is caused by direct, local contact with Ag, such as through jewelry, and involves the formation of gray-blue patches on the skin (Goyer and Clarkson 2001). Chronic bronchitis has also been reported from the medicinal use of colloidal Ag. Large oral doses of silver nitrate may cause severe gastrointestinal irritation due to its caustic action. Lesions of the kidneys and lungs and arteriosclerosis have been attributed to both industrial and medicinal exposure (Agency for Toxic Substances and Disease Registry 1990).

Table 1 The content of elements in hair of subjects (mean ± SD; mg/kg) wearing ($N = 86$) or not wearing ($N = 69$) Ag jewelry

Element	Ag jewelry		*p*-Value
	No	Yes	
Ag	0.225 ± 0.196^{a}	0.659 ± 1.447^{a}	*0.0197*
Al	14.6 ± 13.7^{a}	9.70 ± 11.19^{a}	*0.0160*
As	0.743 ± 0.315	0.769 ± 0.477	0.695
B	1.21 ± 1.84	1.27 ± 2.37	0.878
Ba	2.46 ± 2.63^{A}	3.20 ± 2.83^{A}	*0.0945*
Bi	0.256 ± 0.600	0.190 ± 0.421	0.425
Ca	1958 ± 1271^{a}	2600 ± 1544^{a}	*0.00606*
Cd	0.0797 ± 0.0416	0.0826 ± 0.069	0.762
Ce	0.197 ± 0.306	0.206 ± 0.333	0.871
Co	0.619 ± 0.401	0.688 ± 0.322	0.240
Cr	1.05 ± 1.09	0.983 ± 0.431	0.581
Cu	20.4 ± 31.6	22.6 ± 22.7	0.609
Fe	23.3 ± 7.0	23.1 ± 8.8	0.869
Hg	0.208 ± 0.171	0.210 ± 0.148	0.922
K	283 ± 617^{a}	60.0 ± 46.9^{a}	*0.00101*
La	0.469 ± 0.348^{a}	0.664 ± 0.380^{a}	*0.00127*
Li	0.0754 ± 0.074^{A}	0.0961 ± 0.079^{A}	*0.0985*
Mg	113 ± 107	131 ± 110	0.309
Mn	1.08 ± 0.83	1.08 ± 0.89	0.963
Mo	0.384 ± 1.62	0.430 ± 1.432	0.852
Na	486 ± 375^{a}	328 ± 211^{a}	*0.00114*
Ni	0.975 ± 1.004	0.910 ± 0.888	0.670
P	148 ± 43	150 ± 49	0.792
Pb	2.99 ± 2.24	2.55 ± 1.54	0.146
Pt	0.241 ± 0.595	0.365 ± 0.795	0.287
Rb	1.83 ± 2.22	2.01 ± 2.47	0.650
S	40606 ± 2152	40372 ± 1707	0.450
Sb	0.393 ± 0.811	0.433 ± 0.749	0.750
Se	3.10 ± 3.11	6.61 ± 18.88	0.128
Si	131 ± 183	114 ± 162	0.532
Sn	3.60 ± 3.96	3.28 ± 3.26	0.585
Sr	6.12 ± 6.29	7.34 ± 8.80	0.334
Ti	2.37 ± 3.01	2.15 ± 2.99	0.647
Tl	0.308 ± 0.815	0.492 ± 1.022	0.225
V	1.09 ± 0.83	1.22 ± 0.95	0.376
W	2.00 ± 1.78	2.37 ± 2.34	0.272
Y	0.0480 ± 0.045	0.0463 ± 0.034	0.795
Zn	221 ± 106^{a}	280 ± 207^{a}	*0.0316*
Zr	0.578 ± 1.014	0.422 ± 0.652	0.249

Note: Italics indicate statistically significant differences: ^{a} $p < 0.05$; ^{A} $p < 0.1$

In Table 1, descriptive statistics for element contents in hair, depending on wearing or not wearing Ag jewelry, is presented. Because subjects examined in the present study were of similar age (about 24 years), it was hypothesized that the duration of wearing Ag jewelry was similar (about 10 years). Subjects who declared in the questionnaire that they did wear Ag jewelry ($N = 86$) contained in their hair about a three times higher level of Ag, 40% La, 33% Ca, 30% Ba, 27% Zn, and 25% Li (Ag and Zn are present in Ag alloys) in comparison with the group that did not wear jewelry at all ($N = 69$)—differences that are statistically significant. The first group contained also a lower level of: Al (34%), K (79%), and Na (32.5%)—differences that are statistically significant. It was found that there was an antagonism between Ag-K ($R = -0.0172$) and Ag-Na ($R = -0.0301$). Rodushkin and Axelsson (2000) indicated that the higher content of Ag in hair could be due to extensive use of jewelry. In the literature it is suggested that the presence of Ag in hair is paralleled by the increased concentration of Cu originating, apparently, from the alloys from which jewelry was made (Dybczyński and Boboli 1976). In our research, the content of Cu in hair of subjects wearing jewelry was 11% higher; however, this difference was not statistically significant. The other elements, which are components of Ag alloys—Ni, P, Si, and Sn—were at a similar level in both groups. This means that they were not absorbed through the skin contact and consequently excreted to hair. The decreased level of Na could be caused by the disturbance in its transport through membranes, which is a result of Ag toxicity. The same trend is observed in the case of Cl (chlorine) (Kabata-Pendias and Pendias 1999).

The obtained results were compared with the reference values (RVs) for hair minerals of Polish students, which were as follows: for Ag, 0.036–0.801 mg/kg; for Cu, 8.51–35.0 mg/kg; for Ni, 0.508–1.534 mg/kg; for P, 110–207 mg/kg; for Si, 19.9–132 mg/kg; for Sn, 0.00-7.99 mg/kg; for Zn, 140–371 mg/kg (Chojnacka et al. 2010b). The mean content of Ag in hair of subjects wearing Ag jewelry in the present study was 27% higher than the mean determined in the study of Chojnacka et al. (2010b) (0.518 mg/kg), Cu was 5% higher (21.5 mg/kg), Si was 91% higher (59.7 mg/kg), and Zn was 22% higher (230 mg/kg). The content of the remaining elements was comparable (the RV for Ni was 0.951 mg/kg; for Sn, it was 3.40 mg/kg; for P, it was 154 mg/kg). Additionally, the RVs for Ag for the whole population examined in this article were determined (as the values between the 10th and 90th percentile; it was assumed that the values of the extreme low 10% and high 10% in the population reflected mineral imbalance). For the whole population, the RVs ranged from 0.0364 to 0.733 mg/kg. This corresponds with the literature data (Chojnacka et al. 2010b). RVs for Ag content in hair for subjects wearing or not wearing Ag jewelry were as follows: 0.123–1.01 mg/kg and 0.000–0.567 mg/kg, respectively. The same RVs were also determined for other components of alloys: for Cu: 8.82–42.1 mg/kg (wearing) and 8.92–29.5 mg/kg (not wearing); for Zn: 144–605 mg/kg (wearing) and 133–371 mg/kg (not wearing). Taking into account gender, the RVs for Ag, Cu and Zn were represented as follows: Ag—for males: 0.0109–0.537 mg/kg, for females: 0.0729–0.819 mg/kg; Cu—for males: 8.82–21.5 mg/kg, for females: 8.90–43.7 mg/kg; Zn—for males: 133–376 mg/kg, for females: 146–530 mg/kg.

According to the literature data, Ag is present in the biomass in the range 0.005–0.6 mg/kg. The daily intake of Ag by humans is estimated to be 1.8–80 μg (Kabata-Pendias and Pendias 1999). The obtained results showed that subjects wearing Ag jewelry had an increased level of Ag in hair because in Poland Ag jewelry is very popular and inexpensive.

Although the dose of elements to which individuals are exposed chronically has not been evaluated yet, there is concern that the constituents of jewelry alloys might be absorbed through the skin. Consequently, the composition of alloys is permanently improved by the manufacturers to reduce deterioration of the materials and resulting release of metals. Jurado-López and Luque de Castro (2003) examined the content of Cd in alloys used for jewelry manufacture in order to improve the features of the jewelry as well as to avoid user exposure to potentially hazardous metals. Cd is toxic for most living organisms and is a possible carcinogen. In some types of alloys, Cd could constitute 30%. The content of this element in hair of subjects wearing Ag jewelry was insignificantly higher (3.6%) than in subjects who did not wear Ag jewelry.

In Table 2, the comparison of the content of elements in hair depending on gender is presented. In fact, in the literature many examples of the dependence of the level of minerals in hair are reported. However, in the available literature, only few articles that exemplify the interpretation of the investigation of exposure with respect to gender have been found. Differences statistically significant in the group of females wearing ($N = 74$) or not wearing ($N = 23$) Ag jewelry involved the following elements: K (31% decrease ↓ Yes vs. No) and Pb (23% ↓ Yes vs. No) and in the group of males, Se (8 times increase ↑ Yes vs. No), Ag (7 times ↑ Yes vs. No), Tl (4 times↑ Yes vs. No), Sb (3 times↑ Yes vs. No), Li (90% ↑ Yes vs. No), Co (63% ↑ Yes vs. No), As (51% ↑ Yes vs. No), Cd (29% ↑ Yes vs. No), Ti (78% ↓ Yes vs. No), Si (75% ↓ Yes vs. No), Sr (68% ↓ Yes vs. No), Mn (47% ↓ Yes vs. No), Al (23% ↓ Yes vs. No), and S (3% ↓ Yes vs. No). Higher excretion of metals in the group of males could occur because men sweat more often than women and the acidic pH of sweat, which can range from 3.5 to 6.0 (Emrich et al. 1968), favors this effect. The especially high level of Ag in the hair of males might be not meaningful because the number of individuals in this group was low.

The content of the main components of alloys in hair was compared with the results presented by Chojnacka et al. (2010b). The contents of Ag, Si, and Zn in hair both in female and male groups were higher in the present study—for females: 9%, 74%, and 18%, respectively; for males: 2.5 times, 2%, and 19%.

It was also found that hair of females (F) wearing jewelry contained more elements that are ingredients of Ag

Table 2 Descriptive statistics for element content in hair depending on gender (mean ± SD; mg/kg)

Element	Ag jewelry					
	Female			Male		
	No (*N* = 23)	Yes (*N* = 74)	*p*-Value	No (*N* = 46)	Yes (*N* = 12)	*p*-Value
Ag	0.316 ± 0.227	0.529 ± 0.656	0.132	0.210 ± 0.169[a]	1.46 ± 3.53[a]	*0.0173*
Al	8.94 ± 6.02	9.87 ± 11.99	0.723	17.4 ± 15.6[A]	8.65 ± 3.38[A]	*0.0603*
As	0.764 ± 0.264	0.714 ± 0.342	0.523	0.733 ± 0.339[a]	1.11 ± 0.91[a]	*0.0244*
B	0.889 ± 1.683	1.22 ± 1.96	0.468	1.37 ± 1.91	1.55 ± 4.22	0.827
Ba	3.57 ± 2.89	3.56 ± 2.89	0.989	1.90 ± 2.33	1.00 ± 0.72	0.197
Bi	0.281 ± 0.658	0.186 ± 0.435	0.426	0.244 ± 0.576	0.217 ± 0.328	0.880
Ca	2,662 ± 1,522	2,812 ± 1,539	0.682	1,606 ± 963	1,294 ± 726	0.301
Cd	0.102 ± 0.057	0.0817 ± 0.0736	0.229	0.0686 ± 0.0258[a]	0.0882 ± 0.0304[a]	*0.0283*
Ce	0.140 ± 0.209	0.197 ± 0.342	0.451	0.225 ± 0.343	0.256 ± 0.279	0.780
Co	0.765 ± 0.326	0.655 ± 0.330	0.167	0.546 ± 0.418[a]	0.888 ± 0.167[a]	*0.0077*
Cr	1.02 ± 0.35	0.958 ± 0.452	0.515	1.07 ± 1.32	1.13 ± 0.23	0.867
Cu	29.5 ± 51.9	24.4 ± 23.9	0.514	15.8 ± 11.4	11.5 ± 4.6	0.207
Fe	23.3 ± 5.6	23.5 ± 9.1	0.907	23.3 ± 7.67	20.5 ± 5.4	0.239
Hg	0.197 ± 0.168	0.213 ± 0.153	0.654	0.213 ± 0.174	0.191 ± 0.120	0.673
K	84.7 ± 96.3[A]	58.3 ± 47.1[A]	*0.0786*	383 ± 735	70.2 ± 45.8	0.149
La	0.646 ± 0.415	0.708 ± 0.382	0.507	0.381 ± 0.274	0.390 ± 0.226	0.915
Li	0.0830 ± 0.0786	0.0896 ± 0.0774	0.723	0.0716 ± 0.0728[a]	0.136 ± 0.083[a]	*0.0099*
Mg	137 ± 109	144 ± 113	0.813	101 ± 105	51.0 ± 22.0	0.112
Mn	0.992 ± 0.797	1.15 ± 0.93	0.458	1.13 ± 0.85[a]	0.601 ± 0.120[a]	*0.0383*
Mo	0.243 ± 0.328	0.408 ± 1.468	0.595	0.455 ± 1.971	0.565 ± 1.233	0.855
Na	394 ± 220	324 ± 222	0.183	532 ± 428	352 ± 133	0.158
Ni	1.32 ± 1.58	0.940 ± 0.942	0.156	0.801 ± 0.462	0.724 ± 0.392	0.599
P	150 ± 47	149 ± 51	0.916	147 ± 41	155 ± 33	0.520
Pb	3.26 ± 1.87[A]	2.52 ± 1.54[A]	*0.0593*	2.86 ± 2.41	2.71 ± 1.58	0.837
Pt	0.225 ± 0.527	0.391 ± 0.812	0.360	0.250 ± 0.631	0.202 ± 0.687	0.821
Rb	1.29 ± 1.46	2.10 ± 2.60	0.159	2.10 ± 2.49	1.43 ± 1.27	0.369
S	40,349 ± 2,606	40,498 ± 1,698	0.748	40,735 ± 1,905[A]	39,589 ± 1,614[A]	*0.0613*
Sb	0.534 ± 0.899	0.354 ± 0.630	0.285	0.322 ± 0.763[a]	0.917 ± 1.186[a]	*0.0377*
Se	4.06 ± 3.31	4.13 ± 4.41	0.946	2.61 ± 2.92[a]	21.9 ± 48.2[a]	*0.0077*
Si	96.6 ± 87.6	126 ± 171	0.424	149 ± 214[A]	36.7 ± 16.3[A]	*0.0772*
Sn	3.31 ± 3.10	3.35 ± 3.25	0.961	3.74 ± 4.35	2.83 ± 3.42	0.5081
Sr	6.44 ± 4.77	8.22 ± 9.18	0.375	5.96 ± 6.97[a]	1.88 ± 1.24[a]	*0.0495*
Ti	2.19 ± 2.58	2.41 ± 3.14	0.760	2.47 ± 3.23[a]	0.545 ± 0.399[a]	*0.0459*
Tl	0.404 ± 1.080	0.386 ± 0.923	0.937	0.259 ± 0.653[a]	1.14 ± 1.37[a]	*0.00200*
V	1.13 ± 0.90	1.27 ± 1.00	0.559	1.07 ± 0.80	0.928 ± 0.447	0.559
W	2.65 ± 2.00	2.45 ± 2.40	0.715	1.67 ± 1.59	1.89 ± 1.91	0.680
Y	0.0461 ± 0.0286	0.0450 ± 0.0357	0.892	0.0489 ± 0.0518	0.0544 ± 0.0251	0.725
Zn	255 ± 136	285 ± 212	0.520	203 ± 84	247 ± 178	0.224
Zr	0.533 ± 1.019	0.343 ± 0.419	0.197	0.601 ± 1.022	0.913 ± 1.349	0.383

Note: Italics indicate statistically significant differences: [a] $p < 0.05$; [A] $p < 0.1$

alloys than that of males (M): Si (3.5 times↑ F vs. M), Cu (2 times↑ F vs. M), Ni (30% ↑ F vs. M), Sn (18% ↑ F vs. M), and Zn (15% ↑ F vs. M). As it was mentioned earlier, Ag jewelry might be not the only source of elements in hair. The increased level of Si in hair of females might be due to the application of "shine treatment" conditioners, which contain silicon (Jachowicz 2005). In the questionnaire, 55% of the female population declared using conditioners. Bowen et al. (1975) also observed a higher content of Ni in hair of females (4.21 ± 0.54 mg/kg) than in hair of males (1.01 ± 0.23 mg/kg). Khalique et al. (2005) reported a 34% higher content of Ni in female hair (3.18 mg/kg) compared to male hair (2.37 mg/kg). According to the author, the differences in metal content in hair of females and males could be explained on the basis of differences in the metabolism and physiological role of the metals for the two genders. The higher contents of Zn and Cu in females hair than in males agree with the literature data; Khalique et al. (2005) noted a 21% increase of Zn content (F vs. M) and 86% for Cu (F vs. M).

In Table 3, *p*-Values for the comparison of mineral content of hair in the four examined groups [Female-Yes ($N = 74$), Female-No ($N = 23$), Male-Yes ($N = 12$), Male-No ($N = 46$)] wearing or not wearing Ag jewelry are presented. The elements for which statistically significant differences were observed (Ag, Al, As, Ba, Ca, Co, K, La, Na, Se, Tl, and Zn) are shown in Fig. 2. Analyzing the effect of gender wearing Ag jewelry (Female-Yes and Male-Yes) on hair composition, it was found that statistically significant differences were determined for the

Table 3 *p*-Values for the comparison of mineral content of hair in the four examined groups wearing or not wearing Ag jewelry

Element	Female-No	Female-Yes	Male-No	Male-Yes	*p*-Value
Ag	b		a	a, b	a 0.0209 b 0.0422
Al	A	a	a, A		a 0.0161 A 0.0864
As		B	A	A, B	A 0.0954 B 0.0717
Ba	A	a, B	a	A, B	a 0.0132 A 0.0794 B 0.0811
Ca	a, A	b, c	a, b	A, c	a 0.0379 b 0.000099 c 0.0283 A 0.0600
Co			A	A	A 0.0780
K		a	A, a	A	a 0.000705 A 0.0598
La	a	b	a, b		a 0.0492 b 0.000048
Na		a	a		a 0.00385
Se	b	c	a	a, b, c	a 0.00269 b 0.00676 c 0.00705
Tl			A	A	A 0.0855
Zn		A	A		A 0.0932

$^{a, b, c}$ for $p < 0.05$; $^{A, B}$ for $p < 0.1$

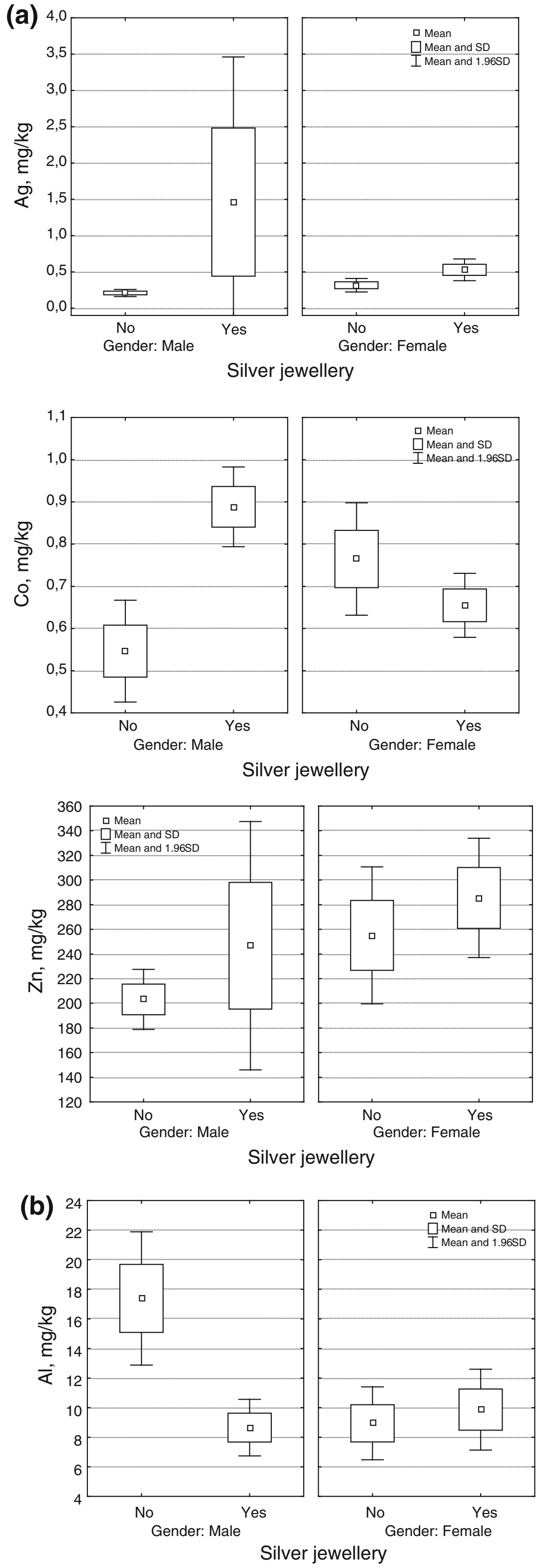


Fig. 2 The effect of two grouping variables: gender and wearing Ag jewelry on the content of elements (**a** elements present in Ag alloys; **b** other elements) in human hair (mg/kg) (Female-Yes: $N = 74$, Female-No: $N = 23$, Male-Yes: $N = 12$, Male-No: $N = 46$)

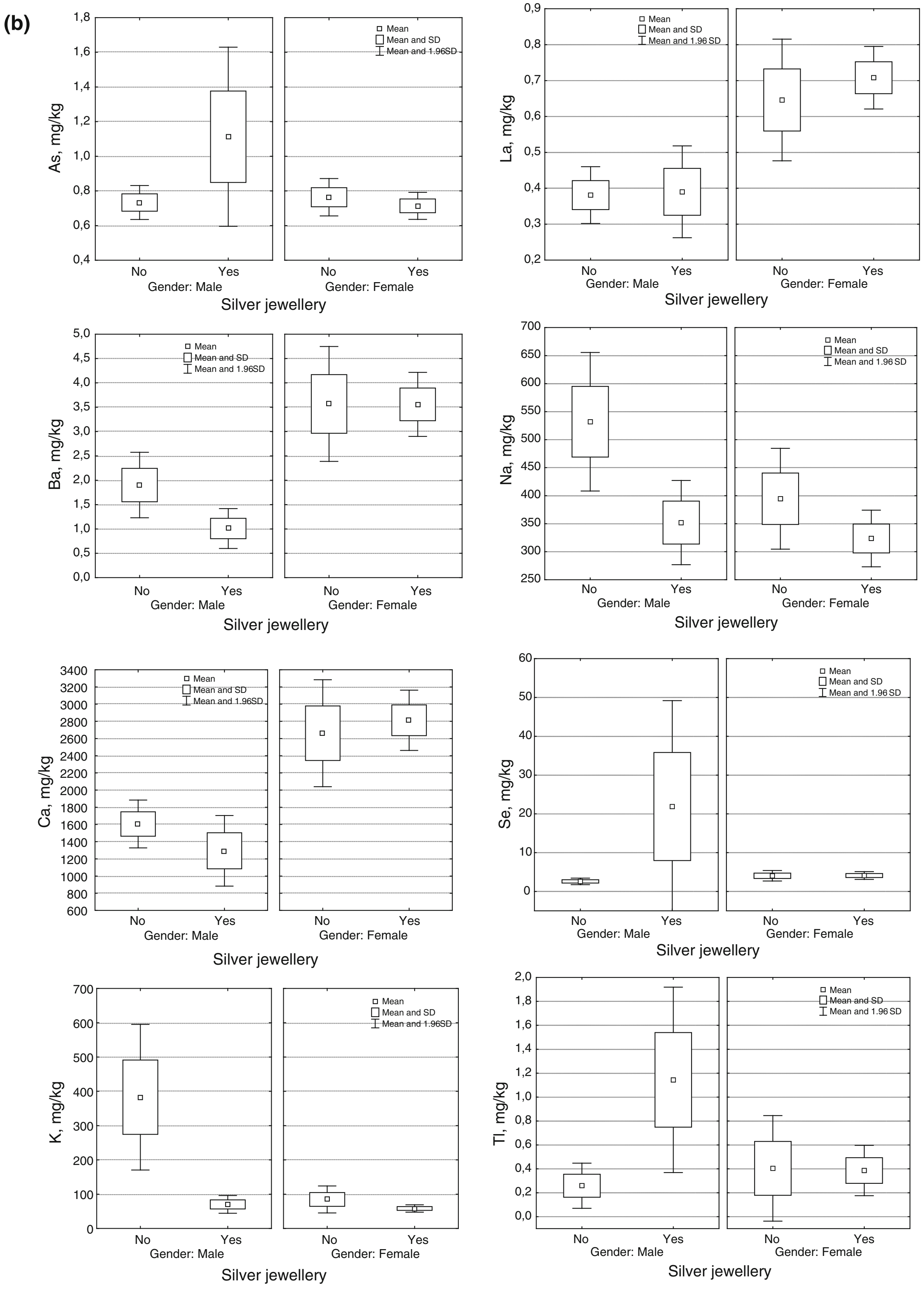


Fig. 2 continued

following elements: As, Ba, Ca, and Se. Female hair contained two times more Ca, four times more Ba, 36% less As, and five times less Se. As was mentioned earlier, there might be different sources of human exposure to the elements. The especially high content of Se in male hair could result from the application of medicated shampoos, which contain very high levels of Al and Se (1000 times higher than regular shampoos; the form: selenium sulfide), Fe (50–100 times higher), Zn (5–10 times higher; the levels can be 1000 times higher; the form: zinc pyrithionate) (LeBlanc et al. 1999). Additionally, a man's scalp, on an average, has 33% more dandruff than a woman's because men tend to sweat more, leading to an oily scalp. In our study, the mean content of Se in hair of 22 males (38% of male population) who declared using antidandruff shampoo was 12.9 ± 36.4 mg/kg, whereas in hair of males who had no dandruff, the Se content was 2.77 ± 3.18 mg/kg. In the case of females, the Se content in the first group ($N = 33$; 34% of the female population) was 4.73 ± 5.36 mg/kg, and in the group that had no dandruff, it was 3.80 ± 3.40 mg/kg.

In the literature, there is also known interaction between Se and As. The content of Se in the diet and/or Se supplements might have an ameliorating effect on As toxicity. For example, in a study of arsenicosis in China, exposure to As from water was shown to closely correlate with As deposition in hair. Furthermore, the Chinese researchers gave the arsenicosis patients a dietary Se supplement of 100–200 μg Se/day as Se–yeast and measured the As content of the new hair growth over 14 months of supplementation with the Se–yeast. Prior to treatment, the As content of hair was 2.970 μg As/g, and after dietary supplementation with Se, the hair As content dropped 73%, to 0.798 μg As/g (Wang et al. 2001; Yang et al. 2002).

Conclusions

The analysis of mineral composition of human hair enables the assessment of human exposure to toxic metals. In the present article, the effect of wearing Ag jewelry on the content of elements in hair depending on gender is presented. It was found that some components of Ag alloys, which are used in the manufacture of jewelry, were released (Ag, Cu, and Zn) and some were not (Ni, P, Si, Sn). Subjects who declared wearing jewelry had increased level of Ag, Ba, Ca, La, Li, and Zn in their hair in comparison with the group that did not wear jewelry. For these two groups, the reference values for Ag were determined: 0.123–1.01 mg/kg and 0.000–0.567 mg/kg, respectively. In the present study, 34% of the population wearing Ag jewelry had Ag content in their hair that was higher than the upper value of the RVs for subjects who did not wear jewelry.

The present study also showed a distinct difference in metal content in hair depending on gender. It was found that hair of females wearing jewelry contained more elements that are components of Ag alloys (Si, Cu, Ni, Sn, Zn) than hair of males. Statistically significant differences were determined for the following elements: As, Ba, Ca, and Se. Female hair contained two times more Ca, four times more Ba, 36% less As, and five times less Se. It was also noted that hair of both genders wearing jewelry had increased levels of Ag, La, Se, and Zn and decreased levels of K and Na. It was shown that hair of females wearing Ag jewelry had higher contents of Al and Ca and hair of males had higher contents of As, Co, and Tl. The opposite effect was observed for As, Ba, Co, and Tl for hair of females and for Al, Ba, and Ca for hair of males. The differences in metal content in hair of females and males could be explained on the basis of differences in metabolism and physiological role of the metals in both genders.

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