Original Research

Effects of Local Industry on Heavy Metals Content in Human Hair

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Abstract

In the present work hair mineral analysis of 110 individuals was carried out to determine environmental exposure based on the distance from a subject's residence to a pollutant source. The subjects were asked to fill in a questionnaire concerning their place of living in the city of Wrocław (lower Silesia, Poland), which was divided in 12 sectors. The content of minerals in hair was determined by ICP-OES and ICP-MS technique in a laboratory certified by the Polish Centre for Accreditation and ILAC-MRA (No. AB 696). The results were elaborated statistically. Each person served as the experimental unit. Post-hoc comparisons were made by Tukey's test and the Spjotvoll/Stolin test. Results were considered significantly different when $p<0.1$. The differences in the content of As were statistically significant between IV-V regions ($p=0.0182$), IV-VII ($p=0.0720$), and IV-XII ($p=0.0586$). In the case of Cd, statistically significant differences were found between II and XII region ($p=0.0377$). Hair has been found to be a valuable indicator of environmental pollution in Wrocław. The highest content of Al was found in sector VII, As – IV, Cd – II, Hg – VIII, Ni – V, and Pb – IX. The explanation could be the vicinity to a heat and power generating plant and a non-ferrous metals plant or other industrial units, as well as interactions between elements in a human organism. Additionally, statistically significant differences between Ni content ($p=0.0591$) in hair of males and females were found. These results showed that hair mineral content reflected exposure to elements from the environment.

Keywords: hair mineral analysis, human biomonitoring, ICP-OES, ICP-MS, Wrocław city

Introduction

There are 35 metals, the presence of which is of concern because of occupational or residential exposure. Twenty-three are so-called toxic elements or "heavy metals": antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [1]. These elements occur naturally in the environment, and additionally are emitted from anthropogenic sources [2]. Heavy metals may enter the human organism body through food, water, air, or absorption through the skin. Exposure can be from agriculture and from manufacturing, pharmaceutical, industrial, or occupational exposure. Industrial exposure accounts for a common route of exposure for adults [3].

This paper discusses toxic elements that pollute the environment of Wrocław. Briefly covered are four elements that are included in the ATSDR's "Top 20 Hazardous Substances" list (As – first rank, Pb – second

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rank, Hg – third rank, and Cd – seventh rank). Nickel and aluminum also will be discussed even though they appear on the Top 20 list, but respectively at 53rd and 187th places.

Wrocław is the largest city in southwestern Poland, situated on the Oder River. According to official population figures for June 2009, its population is 632,240, making it the fourth largest city in Poland. Investments in the Wroclaw agglomeration, observed in recent last years, can cause environmental problems. Among the most important emitters, the following can be mentioned: automotive, chemical and power industries, household appliances, metallurgy, pharmaceuticals, printing, manufacture of printing inks, and sugar mill. The main enterprises in Wrocław that emit pollution are as follows: a producer of non-ferrous metals (A) that emits Al, Ag, Ca, Cd, Cu, Mg, and Pb; a chemical plant (B) – Al, As, and Pb; heat and power generating plant (C) – As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn; a chemical plant (D) – As, Cu, Hg, Pb, and Zn; producer of paints (E) – As, Cd, Cu, and Pb; heating plant (F) – As and Cd; producer of domestic appliances (G) – Pb and Hg; producer of furniture (H) – Al and Hg; a gas power plant – As, Pb, Ni, Cr, and Zn; and a manufacturer of home appliances (J) – Cd and Pb. Literature describes only a single study that attempts to biomonitor the Wrocław environment [4].

Human hair has gained considerable attention in recent years for its use as a biomonitor of trace elements investigating environmental exposure [5, 6]. It is used to monitor public health [7, 8]. Hair is a keratin-rich tissue with an abundance of cysteine residues and the sulfhydryl groups, which bind cations such as lead and cadmium in hair [9]. Analysis of hair samles reflects the total body intake of certain elements better than biological fluids, even though careful evaluation of exogenous contamination is mandatory [10]. The advantages of utilization of hair as a biomonitor are as follows: noninvasive sampling, stable matrix, easy collection, short and long-term investigation of exposure tracings [8].

In spite of many advantages of using hair in biomonitoring studies, there are also some disadvantages. In the literature, some problems related to using human hair as a biomonitor of environmental pollution are described [11]. One of the major disadvantages in the application of hair as a biomonitor is the problem of contamination and poorly understood mechanisms of uptake, incorporation and binding of trace elements in the hair matrix, and hence distinguishing between endogenous and exogenous depositions [12]. In the literature, many examples of the use of mineral content of hair in biomonitoring environmental pollution are described [13, 14].

The aim of the present work was to examine the influence of local industry in Wrocław on the content of toxic elements in human scalp hair. Data were analyzed in terms of gender and specific place of residence, taking into consideration the vicinity of the industrial/chemical enterprises.

Experimental Procedures

Sampling and Preparation

The content of elements in hair was determined by ICP-OES (macroelements) and ICP-MS (microelements and toxic elements). The performed experiments were not conducted on human subjects. The samples of hair were provided by volunteers, who previously filled in a questionnaire that included questions on their individual characteristics – in particular places of living in Wrocław. The present research was carried out on 110 subjects, including 40 males and 70 females. The chosen population for mineral hair analysis was uniform when considering environmental and occupational exposure, because the experimental unit (donor of hair sample) were students of the same department, and the same field of study (Department of Chemistry, Wrocław University of Technology). The population was also uniform when considering age, which was 21-22 years. According to the administrative division of the Wrocław region, samples of scalp hair were collected from 38 districts (names presented in Table 1, column 2) located in the city center. In order to get at least six experimental units in each sector, 38 districts were grouped into 12 sectors (Table 1). This enabled us to point out the sources of exposure to toxic metals.

The participants cut hair from the nape of the neck (5 cm long) directly after four consecutive washings using Johnson's Baby Shampoo and drying. For cutting hair, new, surgical scissors made from stainless steel were used (Hilbro International (Pvt) Limited). The selection of the shampoo was determined by its composition – among the metal cations, only sodium was present. The hair was stored in a paper envelope and underwent digestion without additional washing steps. The goal was to elaborate upon an easier analytical procedure without additional steps of extraction from hair with acids, organic solvents, etc., [15], which on one hand are presented in the literature as a method that removes exogenous contamination, but on the other hand is a 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 ICP-OES Varian-Vista MPX (Australia) with pneumatic nebulizer (macroelements) and ICP-MS Thermo Fisher Scientific (microelements and toxic elements), as described previously [16-18]. The samples of hair (0.5 g) were solubilized with concentrated nitric acid (69%; m/m) suprapur grade from Merck and digested in a Milestone Start D microwave oven (USA). After mineralization, the samples were diluted with ultra pure water deionized by Aquadem 50 L, Wilhelm Werner 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

Table 1. Districts from Wroclaw city divided into 12 sectors with the type of pollutant.

No.	Districts within the sectors	Type of enterprise	Type of pollutant
I	Plac Grunwaldzki, Olbin	C	As, Cd, Cu, Cr, Hg, Ni, Pb, Zn
II	Stare miasto, Szczepin	Close to C	As, Cd, Cu, Cr, Hg, Ni, Pb, Zn
III	Grabiszyn, Grabiszynek, Oporów, Gajowice	A	Al, Pb, Cd, Ca, Mg
		H	Al, Hg
IV	Gadow, Kozanów, Kuzniki, Popowice	Close to B	Al, As, Pb
		C	As, Cd, Cu, Cr, Hg, Ni, Pb, Zn
V	Kleczkow, Kowale, Psie Pole, Rozanka, Soltysowice	G	Pb, Hg
		D	As, Cu, Hg, Pb, Zn
		E	As, Cd, Cu, Pb
		J	Cd, Pb
		F	As, Cd
VI	Sepolno, Szczytniki, Zacisze, Zalesie	Close to E	As, Cd, Cu, Pb
		D	As, Cu, Hg, Pb, Zn
		I	As, Pb, Ni, Cr, Zn
VII	Bartoszowice, Biskupin	Close to E	As, Cd, Cu, Pb
		D	As, Cu, Hg, Pb, Zn
		I	As, Pb, Ni, Cr, Zn
VIII	Dabie, Rakowiec, Bierdzany	Close to E	As, Cd, Cu, Pb
		D	As, Cu, Hg, Pb, Zn
		I	As, Pb, Ni, Cr, Zn
IX	Południe, Huby, Przedmiescie	Close to I	As, Pb, Ni, Cr, Zn
X	Borek, Gaj, Tarnogaj	I	As, Pb, Ni, Cr, Zn
XI	Jagodno, Oltaszyn, Partynice,Wojszyce	Close to I	As, Pb, Ni, Cr, Zn
XII	Klecina, Krzyki	Close to A	Al, Pb, Cd, Ca, Mg
		H	Al, Hg

macroelements and after 10-times dilution, by ICP-MS Thermo Scientific (Germany) for the content of microelements, toxic elements, and other trace elements. Mercury was determined by atomic absorption spectroscopy AMA-254 (Czech Republic). 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 a laboratory certified by ILAC-MRA and the Polish Centre of Accreditation (No. AB 696) according to ISO/IEC 17025. According to this standard, our quality management system in particular validation procedures followed the requirements of EURACHEM. Elements to be investigated were chosen on the basis of their relationship with the current industrial activities in the Wrocław region.

ArcGIS ver. 9.2 software was used in preparation of maps.

Statistical Methods

The results were elaborated statistically by Statistica ver. 8.0. The normal distribution and uniformity of variance of the variable were tested. W Shapiro-Wilk test was used for verification of normality of the distribution of all analyzed variables. Equality of variance for two independent samples being compared was verified using the Brown-Forsythe statistics. If the significance level from Brown-Forsythe test was smaller than the set level of significance $p < 0.05$, the hypothesis of equal variances in both groups was rejected, then the alternative test Cochran-Cox was used. In the case of non normality assumption of the analyzed variable, nonparametric Mann-Whitney U test was used.

Results and Discussion

Wrocław is an example of urban agglomeration, where within a relatively small area, with a high-density road network, a large number of industrial and energy facilities, plus heat and power plants, are located. All these industrial units are potential sources of contaminants that can affect health and can cause changes in the environment, including land degradation, pollution of abiotic elements like air, water and soil, and biotic elements of the environment.

Because of this, the Lower Silesia Voivodship Inspectorate for Environmental Protection conducted an investigation that confirmed increased contamination with toxic metals (Cd, Hg, Pb) in soil in the proximity of the main emitters (Table 1). The effect of environmental exposure, based on the distance from a subject residence to a pollutant source, on the content of macro-, microelements, and toxic elements in hair was determined.

The obtained results are reported in Fig. 1 and Table 2. In discussion about the influence of local industry on mineral content of hair, the route of exposure of certain toxic elements should be investigated. The most significant source of exposure to Al is only by gastrointestinal tract (GT), As – respiratory system (RS) and GT, Cd – RS and GT, Hg and Ni – RS, GT and skin, and Pb – RS and skin. With the exception of Al, all of the mentioned toxic metals are transported to the human body by respiratory system, with inhalation the primary route of exposure [19].

The highest content of Al was found in sector VII (Fig. 1). The most significant source of exposure to Al is by contaminated food and water. A reasonable explanation of high content could be dietary habits. The presence of local industry could be affected indirectly, for example by correlations between Al, Ni and Cd that were found to be statistically significant in that region (Table 2). This may explain the highest content of Al, although no industrial units that could emit Al were located in the neighborhood. High levels of Al in hair samples could be enhanced by the presence of Ni and Cd that were emitted by a gas plant (Table 2, Fig. 1), producer of paints (E), and heating plant (F) in the discussed region (Table 1).

Chemical plant (B) and heat and power generating plant (C) are placed close to sector IV. This might be a reason for the high level of As in hair samples from experimental units living in that region (Fig. 1). Similar levels of As were found in sector X, where the gas plant is located. Moreover, levels of As could be increased by the presence of Al (Al-As, r=0.809) in sector IV and by the presence of Cd (As-Cd, r=0.785), as well as Pb (As-Pb, r=0.919) in sector X (Table 2). Significant differences in hair contents of As were found in relation to the location, between V-IV region, IV-VII, and IV-XII (Table 2).

In sector II the highest density of road network is observed, therefore, the highest content of Cd was found in this region. Mehra et al. [20] reported that the level of cadmium in the hair of 25 workers of metal finishing units and metal recycling units of the State of Rajasthan, India, was 26 times higher than it was found in this paper. At the same time Gil et al. [21] found in the samples of hair of 178 individuals working in the iron and steel industry during at least 6 consecutive months that the level of cadmium was 0.07 mg/kg. They were occupationally exposed to welding fumes from various activities (production, polishing, and shaving of stainless steel vessels and other metallurgical processes). Additionally, the content of Cd could be increased by the presence of Ni released by a heat and power generating plant (C) (statistically significant correlation between Cd and Ni, r=0.532, Table 2). Statistically significant difference in hair content of Cd was found between II and XII sectors, with a low-density network of roads. Patra et al. [22] found significantly higher cadmium residues in hair from cows reared around lead-zinc smelter and a closed lead operational zinc smelter.

The highest content of Hg in hair samples was found in regions VIII and V (0.359 mg/kg). The level of content of Hg in Polish students was two times lower than that found by Kim et al. [23], where mean maternal hair mercury level

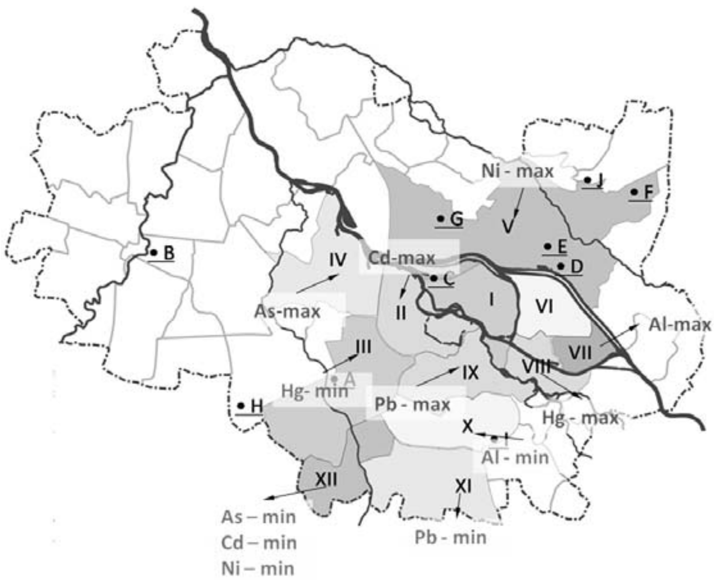

Fig. 1. The distribution of average content of toxic elements within the districts of Wrocław of Al, As, Cd, Hg, Ni, and Pb (mg/kg).

Table 2. The average content (mg/kg) of toxic elements in 12 regions in hair of individuals living in Wrocław ($\bar{X}$ – average, SD – standard deviation, SE – standard error) and reference values for human hair according to the literature [28].

Sec.	Al			As			Cd			Hg			Ni			Pb		
	$\bar{X}$	SD	SE	$\bar{X}$	SD	SE	$\bar{X}$	SD	SE	$\bar{X}$	SD	SE	$\bar{X}$	SD	SE	$\bar{X}$	SD	SE
I	11.2	8.5	2.6	$0.720^{-a,b}$	0.263	0.079	0.0772^{b}	0.0310	0.0094	$0.169^{-a,c}$	0.104	0.031	0.794^{c}	0.321	0.097	3.19	2.05	0.62
II	$9.89^{a,b}$	8.22	2.37	$0.755^{c,d}$	0.149	0.043	**0.126^{e}**	**0.126**	**0.036**	0.173	0.098	0.028	$0.748^{a,c,d,e}$	0.262	0.076	2.15b	1.10	0.32
III	12.0^{a}	6.9	3.1	0.784^{b}	0.043	0.019	0.0728^{b}	0.0210	0.0094	0.143	0.107	0.048	0.973^{a}	0.280	0.125	2.94	0.64	0.29
IV	7.68^{a}	3.17	1.12	**$0.948^{a}_{A,B,C}$**	**0.281**	**0.099**	0.0880	0.0320	0.0113	0.183	0.124	0.044	0.911	0.294	0.104	2.43	1.23	0.44
V	15.4	13.1	4.6	0.487^{a}_{A}	0.284	0.100	0.0827^{b}	0.0579	0.0205	0.254^{b}	0.253	0.089	**2.24^{c}**	**2.54**	**0.90**	$2.75^{a,c}$	1.86	0.66
VI	7.01	4.84	2.16	0.775^{-a}	0.035	0.016	0.0724	0.0120	0.0054	$0.309^{-a,b}$	0.151	0.068	0.977	0.728	0.326	2.81^{b}	0.57	0.26
VII	**$19.2^{a,b}$**	**25.1**	**7.2**	0.546_{B}	0.311	0.090	0.0666^{b}	0.0372	0.0108	0.206	0.199	0.057	0.760^{a}	0.438	0.126	2.17	1.71	0.49
VIII	8.41^{a}	3.68	1.64	0.755	0.386	0.173	0.0770^{b}	0.0376	0.0168	**$0.359^{a,b}$**	**0.288**	**0.129**	0.905	0.477	0.213	2.04	1.53	0.68
IX	$8.57^{a,-b}$	6.36	1.36	0.754^{-b}	0.223	0.047	0.0826	0.0385	0.0082	0.281^{-c}	0.172	0.037	1.22	1.62	0.35	**$3.80^{a,-c}$**	**2.80**	**0.60**
X	6.48	2.62	1.07	$0.890^{a,b}$	0.177	0.072	0.0784^{a}	0.0257	0.0105	0.149	0.114	0.047	0.909	0.337	0.138	2.23^{b}	1.57	0.64
XI	7.48	4.32	2.16	0.759^{a}	0.032	0.016	0.0686^{b}	0.0148	0.0074	0.206^{a}	0.127	0.063	0.728	0.126	0.063	1.38^{b}	2.09	1.05
XII	14.6	11.7	3.4	0.536^{a}_{C}	0.331	0.0956	0.0553^{b}_{B}	0.0264	0.0076	$0.186^{a,b}$	0.102	0.030	0.716^{c}	0.187	0.054	2.03^{c}	1.60	0.46
Average	10.7			0.726			0.079			0.218			0.990			2.29		
[28]	>20			>10			>1			>3.0			>2.2			>20		

^{a,d,c,} …– statistical significant inter-sector correlations

$_{A,B,C,}$…– statistical significant differences at p<0.05

was 0.91 mg/kg. In the sectors VIII and V producers of paints (Fig. 1 E) and chemical plant (Fig. 1 D) are placed. All of them emit Hg. Another issue is the presence of Al and Cd. These elements could additionally increase the content of Hg (Al-Hg, r=0.909 in sector VIII and Cd-Hg, r=0.708 in sector V (Table 2)).

The samples of hair collected from region V had the highest content of Ni (Fig. 1), despite the fact that in that region no Ni emitters were found. Statistically significant correlation between Ni-Pb (Table 2) was found, which might explan the high levels of that element, as well as hair often being contaminated with Ni from hair treatments, dyes, and hair products [19].

Pb was the highest in sector IX (Fig. 1), close to the gas plant. Furthermore, the content of Pb could increase with the presence of Al (Al-Pb, r=0.381) and Hg (Hg-Pb, r=-0.391) (Table 2). There was a significant correlation (region IX) between Pb and Cd content in hair. This suggests that Cd accumulation in hair was influenced by hair lead content in individuals environmentally exposed to Pb. Similar results were found by Patra et al. [22] in tail hair of cows.

The negative correlation was found between As and Hg in sectors I, VI, and XII. According to the results obtained by Salonen et al. [24], Hg intake and especially hair Hg content were remarkably independent of intakes of other elements, the hair mercury content correlated only with As levels. On the other hand, it was found that the content of Hg was strongly correlated with the levels of Cd, Pb, and Ni in hair (Table 2).

The mean value of Cu, K, La, Mg, Na, and Ni content in hair of female subjects was found to be two times higher than in males. However, in these studies no significant difference in heavy metals content in the hair of both sexes was found. This outcome is consistent with the reported findings in the literature, that there was no significant difference between As in hair and gender. Contradictory findings are cited elsewhere [13, 14]. For example, Ferré-Huguet et al. [25] reported 2.5 times lower content of Pb in female hair samples and lower content of As.

It is believed that the uptake of essential metals, such as Ca, Cu, Fe, and Zn, occurs through processes that include energy-independent carrier mechanisms, as well as ion channels. Cd and Hg inhibit the uptake of these metals [26]. Blazka and Shaikh [26] indicated that mentioned metals inhibited Cd accumulation in a competitive manner. In comparison, neither the essential metals nor Cd had any significant effect on Hg accumulation. The essential metals reduced Cd accumulation by inhibiting its uptake. On the other hand, Hg reduced Cd accumulation by both inhibiting its uptake and enhancing its efflux. Reported by Blazka and Shaikh [26], this type of interaction was not found in presented work, although in sector XII negative correlation between Cd and Hg (r=0.808) was indicated. Additionally, many positive correlations between Cd and Fe, and Zn and Cu, as well as Hg and Cd were found in a few sectors.

Ni usually competes with Fe for DMT (divalent metal transporter) and other import/export [27]. In the presented results, strong positive correlation between Ni and Fe was found in the following sectors: I, II, VII, XI, and XII.

It is believed that Pb interferes with the ability of Ca to trigger exocytosis of neurotransmitters [27]. Statistically significant correlation between Pb and Ca (r=0.456) was found in sector IX, where the highest content of Pb was registered. The similarity of size of Pb 0.117 nm to Ca 0.100 nm may be a reason for this substitution. Al likewise would bind too strongly with catalytic residues such as carboxylate and serine/threonin-OH, and replace Mg inhibiting Mg-dependent enzymes. This fact found the confirmation in significant correlation between Al and Mg in sector VII, where the highest content of Al was noted.

The acute toxicity of thallium is known to be more severe than those of Hg, Cd, Pb, and Cu in mammals. The negative correlation between Tl and K was found in all considered sectors with the exception of XII and X sectors. This can be confirmed by the similarity of Tl to K in electric charge and size, and hence Tl interferes with K-related enzymes [27].

The measured content of Al, As, Cd, Hg, Ni, and Pb were compared with data from the literature. The results were found to be within the range of concentrations published in the literature (Table 2) [28]. The reference range and possible health consequences have been discussed in previous papers [29-32].

The Voivodship Inspectorate for Environment Protection in Wrocław monitored the concentrations of the following substances: sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitrogen oxide (NO), nitrogen oxides (NO_x), particulate matter PM_{10}, particulate matter $PM_{2.5}$, benzene (C_6H_6), benzo(a)pyrene, carbon monoxide (CO), and ozone (O_3).

There is lack of monitoring of environmental contamination by toxic elements in Wrocław. Biomonitoring shows not only the degree of contamination but also risks to humans, since the degree of elimination from the body is assessed. In the literature, environmental biomonitoring research that considers the distribution of contamination acording to the districts in urban areas are missing.

This paper provides the new information about the distribution of heavy metals in Wrocław.

Concluding Remarks

Human biomonitoring is one of the most important approaches to monitoring. This is also an important tool in environmental medicine to assess and evaluate the level of internal exposure of the general population and individuals to the environmental pollutants [33]. The obtained data were analyzed in terms of specific place of residence and sex. Sector V was the most contaminated region. Contents of all considered toxic elements were high, moreover the highest content of Hg and Ni was registered in this region, with the exception of As (its content in that region was the lowest). In the current study, significant differences depending on the specific place of residence of the subjects were noted in the hair levels of As and Cd. These were higher for subjects living in the vicinity of the industrial/chemical complexes emitting these elements, while Ni levels were two times higher in female hair samples. Additionally, presented mineral content of scalp hair reflected the environment/residence of the subjects and can serve as an indicator of environmental pollution from local industry.

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