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Original Research

Biomonitoring Release of Elements from Water Pipes Using Hair Mineral Analysis

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Abstract

This paper reports the results of a biomonitoring study of exposure to elements released by water pipes by hair mineral analysis with the consideration of gender. Hair of a population of 117 students living in an urban area in Poland was analyzed for the content of elements by ICP-OES (macroelements) and ICP-MS (micro-, toxic and other trace elements). The participants were grouped according to the material of which water pipes in their households were made (steel, copper, plastic). The population was of uniform age (21-22 years). The mean values and standard deviations of the content of 34 elements were reported for the whole population as well as for other populations and the subgroups. The mean level of the following elements was higher: As, Ba, Bi, Ca, Na, and lower: Hg. Statistically significant differences between the subpopulations for which the grouping variable was the type of tap water pipes were found for the following elements: Fe, Mn, Na, Ti (release order: plastic>steel>copper), Mg (copper>plastic>steel), Ni (plastic>copper>steel). The composition of water (from the same water purification station), from pipes made of different materials: steel, copper and plastic was determined. The release of elements to water was confirmed. The results of biomonitoring study by hair mineral analysis were compared with multielemental analysis of water. Plastic pipes were found to release the highest quantities of elements, which was confirmed by both a biomonitoring study and direct analysis of water: Ni, Ti, Al, Hg, Sn, Mo, Li, Ag, Cu, Sr, B. For copper pipelines both types of analyses showed release of: Ag, Cu, Si, As, and in steel: Zr and Zn. Elements, the level of which depended on sex, were indicated. The content of elements in hair and also the effect of gender were compared with other populations reported in the literature. Additionally, ratios between elements in the present and in various groups were investigated. It was found that the content of alkaline earth metals (Ba, Ca, and Mg) was statistically significantly higher in hair of females than males in almost all the groups. The release of elements with gender as additional grouping variable was confirmed for Ag and As, which were eluted in the highest amounts from copper plumbing, Mn and Si from plastic pipes. Hair of males seemed more appropriate for a biomonitoring study since more statistically significant differences were confirmed. This can be explained with the cosmetic treatment of hair by females.

Keywords: exposure to toxic elements, water pipelines, hair mineral analysis, gender

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Introduction

The human population is exposed to various pollutants, among which are toxic elements that are released from environmental background. As the result of rapid development of such branches as food industry, construction engineering, and medical techniques in the vicinity of humans, highly processed materials can be found that may release potentially toxic amounts of various ions. Preservatives in food products, decorative elements of buildings (plasters, paints, pipes, glues, etc.), and materials used in medicine (implants of hip joints, dental implants, orthodontic braces) may be sources of toxins. The latter are made of alloys that contain toxic elements [1]. One method for assessing exposure to those contaminants is hair mineral analysis (HMA), a useful tool in biomonitoring human exposure to elements from food, drink, medicine (surgical elements, implants, orthodontic braces) and environmental media [2-5].

Literature reports the results of many studies on using HMA as the biomonitor [6-9]. Among the advantages listed by the authors, we can mention easiness of sampling and storage, non-invasiveness, high degree of mineralization, known methods of digestion (nitric acid) and analysis (ICP-MS, ICP-OES, AAS). The problems related with HMA include first of all difficulties with the interpretation of the results. There is still a lack of universal reference ranges, probably because each laboratory uses its unique methods of extraction of externally bound fraction of elements [10]. Also, contamination during extraction procedure is possible [10]. There are also differences in the typical composition of hair for populations of various races, living in different locations, having different dietary habits, as well as differences in the composition of hair between sexes, and between natural and treated hair (colored or permed).

HMA provides a large amount of information on the status of a human organism at a relatively low cost. This can be achieved through asking participants, hair of which are to be analyzed, to fill in a questionnaire that includes questions on their lifestyle, types of hair, gender, living environment, and cosmetic treatment of hair. However, the results of studies that link the results of a questionnaire with hair mineral composition are rarely found in the literature.

A general conclusion from the majority of works was that age, sex, and race influence the composition of human hair. Therefore, these factors should be taken into consideration in the interpretation of biomonitoring studies based on human hair. Another conclusion is that chronic exposure is reflected by the composition of hair. An example of such an exposure is the presence of minerals in tap water. Therefore, we assumed that HMA can be found to be useful in the risk assessment of exposure to elements released from potable water transmission pipelines.

Undoubtedly, water leaving a purification station is under strict control. However, it might become contaminated as it flows through pipes made of various materials. Pipelines located inside buildings usually are made of copper, plastic, iron, steel, or cement [11].

There is increasing concern about the release of elements from drinking water supply systems. Zietz et al. [12] studied the contamination of tap water in households by lead in Germany. In other work [13], chronic exposure to copper released by a drinking water supply system, with particular attention paid to children, was reported. Tamasi and Renzo [14] presented the results of a study on risks related to exposure to As in Italy.

There are several studies showing that plastic materials can support the growth of biofilms. The growth is usually similar in iron, steel, plastic, or cement pipes [15, 16]. Roughness of the materials used for drinking water distribution has been identified as an important factor affecting bacterial attachment [17]. Microbial extracellular polymeric substances are among the factors most commonly cited as influencing corrosion in soft waters [18]. Literature presents alloys containing copper, commonly used home-plumbing material, as relatively resistant to corrosion [19]. Many reports discuss the possibilities of minimization of the corrosion problem in water pipes, and different modifications were made to study corrosion in various materials (steel, cooper, lead) [20, 21].

Many studies report examples of using hair as biomarker of exposure to toxic elements, showing its usefulness. Nowak and Chmielnicka [22] investigated the content of Pb and Cd in hair of inhabitants of Katowice (an industrialized region in Poland) and compared it with a non-polluted region. Hair mineral composition was also compared with the level of elements in nails and teeth. The analyses were carried out by atomic absorption spectroscopy. The authors concluded that hair mineral analysis was particularly useful in biomonitoring of Pb pollution, because the content in hair from the polluted and non-polluted regions differed statistically significantly. The level of Pb depended on age (decreased with age) and sex (was higher for males than females). Higher content of Pb caused a reduced level of bio-elements Fe and Ca, which was manifested by higher Pb/Fe and Pb/Ca ratio for environmentally exposed subjects. For Cd, the differences were not statistically significant between environmentally exposed and not exposed individuals. Hair mineral analysis is also a useful tool in determination of occupational exposure. Georgescu et al. [23] investigated the content of metals in hair of metallurgical workers in relation to the control group. The differences in the content of Al, Co, Cu, Fe, Mg, Mn, V, and Zn were statistically significantly higher than in the control group – only for Se were the differences not significant. Georgescu et al. [23] reported the values of hair mineral content for occupationally exposed and non-exposed populations with respect to gender, for subjects living in Romania. In the non-exposed population the level of all the elements in females was higher than in males, but the differences were statistically significant (at $p<0.05$) only for Co, Fe, Mg, and Zn. Khalique et al. [24] studied the content of 10 metals of subjects 3-100 years old living in Pakistan by ICP-AES. The authors concluded that hair was a useful matrix of environmental and occupational exposure.

The aim of the present work was to investigate usefulness of hair mineral analysis linked with the direct analysis of water in monitoring elements released by potable water transmission pipelines (copper alloys, steel, and plastic).

Another objective was to point out the material that releases the lowest doses of toxic elements and can be considered as the safest.

Experimental Procedures

Sample

The present research was carried out on hair sampled from 117 subjects. The population was uniform when considering age, which was 21-22 years and consisted of individuals who were students of biotechnology, Department of Chemistry, Wrocław University of Technology. This means that the participants underwent similar environmental and occupational exposure. The population consisted of 41 males and 76 females. The participants were asked to complete a questionnaire that included questions on the material of which their potable water transmission pipelines were made.

Material

The participants cut hair from the nape of the neck by stainless steel scissors directly after four consecutive washings (15 minutes) of their hair with Johnson's Baby shampoo and drying (for cutting hair, new surgical scissors made from stainless steel were used from Hilbro International 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 further washing steps. The goal was to elaborate an easier analytical procedure without additional steps of washing hair with acids, organic solvents, etc., that on one hand are presented in the literature as a method that removes exogenous contamination, but on the other is a source of contamination.

Analytical Methods

The content of 34 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, Rb, S, Si, Sn, Sr, Ti, V, Y, Zn, and Zr) in hair was determined by ICP-OES (macroelements) and ICP-MS (microelements and toxic elements). The procedure has been described in detail in previous studies [25-27]. 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 Milestone Start D microwave oven (USA). After mineralization, the samples were diluted with ultra pure 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 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. 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 China National Analysis Center. The analyses were performed 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 ver. 8.0. Post-hoc comparisons were made by Tukey's and Spjotvoll/Stolin tests. The results were considered significantly different at $p<0.05$ and $p<0.1$.

Results and Discussion

Concern about intake of toxic elements from drinking water has increased in recent years. Chronic effects on humans may be caused by prolonged consumption of water with concentrations of such elements. Monitoring exposure to various elements from water pipes can be important in the assessment of possible health risks [28]. Public concern exists over the possible long-term effects of chronic exposure to elements present in drinking water, which can become contaminated by contact with the distribution network and home plumbing [29, 30].

The aim of the present paper was to discusses the usefulness of hair mineral analysis in biomonitoring exposure to the elements from potable water. The content of elements in hair of subjects who drink water from pipelines made of different materials (steel, copper, and plastic) is presented in Table 1. Statistically significant differences between the groups were found for Mn and Ti for all the groups, and for Fe, Mg, Na, and Ni between two groups. The content of Ti was over two times higher in hair of subjects drinking water from plastic pipelines compared to steel, and three times higher than from copper pipes. The differences between the groups were statistically significant at $p<0.05$. This shows that plastic pipelines are the source of chronic exposure to Ti and this is consistent with the composition of plastic material (TiO_2 as filler). In the case of Mn, the concentration order was as follows: plastic>steel>copper. However, Mn is a microelement and slightly elevated levels would not be of concern. The content of Ni was 46% higher in hair of subjects who declared pipelines made of plastic in their households as compared with steel (at $p<0.1$). The release of this element was also confirmed by a high and statistically significant correlation between hair mineral content and the concentration in water sampled from the same water purification stations, and from houses with pipelines made of different materials (Table 2). The content of Na was the highest in hair of subjects drinking water from steel pipelines (46%) when compared with plastic. It was also higher than from copper pipes (13%), but the latter difference was not statistically significant. Another element, Mg, was present at the highest level in hair of people drinking water from copper pipelines when compared with pipes made of steel (37%). For Fe, statistically significant differ-

Table 1. Hair mineral composition of subjects grouped according to the type of pipelines in their households: steel (N=57), copper (N=25), and plastic (N=35), mg/kg.

	Element	Steel	Copper	Plastic	All
Mean	Ag	0.369	0.915	0.475	0.518
SD		0.290	2.466	0.874	1.252
Mean	Al	7.92	6.95	9.88	8.30
SD		4.92	3.44	7.97	5.83
Mean	As	0.813	0.896	0.823	0.834
SD		0.166	0.649	0.119	0.325
Mean	B	0.90	0.77	0.90	0.87
SD		2.18	2.91	2.14	2.32
Mean	Ba	1.92	2.50	1.95	2.05
SD		1.41	1.77	1.60	1.56
Mean	Bi	0.245	0.141	0.198	0.209
SD		0.577	0.305	0.493	0.503
Mean	Ca	1,969	2,666	2,089	2,154
SD		1,097	1,766	1,430	1,378
Mean	Cd	0.1004	0.0853	0.0777	0.0904
SD		0.0807	0.0440	0.0242	0.0618
Mean	Ce	0.135	0.124	0.241	0.164
SD		0.224	0.196	0.270	0.237
Mean	Co	0.856	0.836	0.844	0.848
SD		0.139	0.122	0.111	0.127
Mean	Cr	1.16	1.09	1.35	1.20
SD		0.31	0.20	1.42	0.81
Mean	Cu	17.3	28.8	23.1	21.5
SD		18.1	52.1	22.4	29.8
Mean	Fe	22.4	21.0^{a}	25.3^{a}	23.0
SD		6.2	4.1	8.8	6.9
Mean	Hg	0.195	0.187	0.245	0.208
SD		0.153	0.146	0.178	0.160
Mean	K	61.0	47.8	73.1	61.8
SD		43.4	20.4	71.5	50.8
Mean	La	0.521	0.703	0.519	0.559
SD		0.321	0.469	0.413	0.389
Mean	Li	0.104	0.100	0.119	0.108
SD		0.083	0.077	0.060	0.075
Mean	Mg	73.1^{a}	100.8^{a}	89.4	83.9
SD		35.5	68.5	56.1	51.3
Mean	Mn	0.682^{b}	0.614^{A}	0.890^{Ab}	0.730
SD		0.210	0.175	0.670	0.414
Mean	Mo	0.577	0.351	0.607	0.538
SD		1.801	0.874	2.053	1.723
Mean	Na	420^{a}	373	287^{a}	370
SD		345	254	154	285
Mean	Na	420^{a}	373	287^{a}	370
SD		345	254	154	285
Mean	Ni	0.810^{a}	0.939	1.190^{a}	0.951
SD		0.335	0.541	1.323	0.809
Mean	P	161	153	142	154
SD		46	52	31	44
Mean	Pb	3.12	3.18	2.96	3.08
SD		1.72	1.85	1.57	1.69
Mean	Rb	2.10	1.92	2.86	2.29
SD		2.23	1.85	3.23	2.51
Mean	S	40,112	40,044	40,219	40,129
SD		2,011	1,762	1,842	1895
Mean	Si	56.5	67.5	59.3	59.7
SD		45.0	54.8	45.9	47.2
Mean	Sn	3.08	3.29	4.00	3.40
SD		3.00	3.88	3.44	3.33
Mean	Sr	4.41	5.00	4.83	4.66
SD		4.33	4.09	5.63	4.68
Mean	Ti	1.46^{AB}	1.08^{B}	3.22^{A}	1.91
SD		1.79	1.29	4.54	2.95
Mean	V	0.868	0.810	0.831	0.845
SD		0.381	0.329	0.255	0.335
Mean	Y	0.0482	0.0435	0.0423	0.0454
SD		0.0311	0.0298	0.0321	0.0310
Mean	Zn	233	254	208	230
SD		158	171	78	142
Mean	Zr	0.412	0.337	0.339	0.374
SD		0.839	0.328	0.425	0.645
Mean	Ca/Cd	23,788	31,667	27,140	26,475
SD		16,484	18,429	18,850	17,750
Mean	Cu/Cd	212	322	295	261
SD		267	455	266	317
Mean	Zn/Pb	111	96.3	93.3	102
SD		130	66.3	62.9	102
Mean	Zn/Cd	2,753	3,228	2,782	2,863
SD		2,243	1,922	1,086	1,891
Mean	Zn/Cu	22.2	23.5	14.2	20.1
SD		29.3	35.1	11.6	26.9
Mean	Na/K	8.7	9.6	6.4	8.2
SD		9.0	9.6	5.4	8.2
Mean	Ca/P	13.5	20.4	15.9	15.6
SD		9.8	18.0	13.1	13.0
Mean	Ca/Mg	26.8	27.5	24.6	26.3
SD		8.0	8.0	8.0	8.0

A, B, C, D – significant at $p<0.05$,
a, b, c, d – significant at $p<0.1$

Table 2. Elements released to water from pipelines made of different materials.

Material	Elements released to a higher extent	Elements released to a lower extent
By hair mineral analysis		
Steel	Pb, Bi, Na, Cd, Zr	Mo, Y, P, B, V, Zn, Co
Copper	Ag, Cu, La, Ca, Ba, Mg, Si, Zn, As, Sr	Na
Plastic	Ti, Ce, Ni, Rb, Mn, Al, K, Hg, Sn, Mo, Cr, Li, Fe	Ag, Cu, Mg, Sr, B
By water analysis		
Steel	Ba, Ce, Fe, Hg, Mg, Mn, Sn, Zn, Zr	K, Si
Copper	As, Cd, Cu, K, Mo, P, Si, Ti	Ag, Mn, Ni, Pb, S
Plastic	Ag, Al, B, Bi, Ca, Co, La, Li, Na, Ni (very high), P, Pb, S, Sr, Ti, Zn	Ba, Cu, Hg, Mo, Sn, Zr

ences were observed between plastic and copper pipelines (20%). The mean content of Fe in the hair of subjects who drank water from steel pipes was intermediate, showing that Fe transferred to the solution by, e.g., microbiological corrosion either was not bioavailable nor contributed significantly to the overall intake of this element.

The results of a biomonitoring study were compared with the results of direct analysis of water sampled from the same water purification station but from households with different pipelines. For some elements they stay with an agreement. HMA showed undoubtedly the release of Ti and Ni from plastic pipelines. For the remaining elements, further analysis needs to be carried out.

Correlation coefficients between the content of elements in hair and in tap water were determined (Table 3a). Statistical significance (at $p<0.01$) was found only between the level of Ni and Li (synergism) and Ba (antagonism) in human hair and in water from a given transmission line. High, but not significant correlation coefficients were found for Al, As, Cu, Si, and Zr. Antagonisms showed that either it is necessary to consider additional factors (such as sex or other sources of exposure) or HMA is not valid to investigate exposure to these elements. Interactions between a given element in water and the remaining in human hair are presented in Table 3b. Synergism might mean a similar occurrence, which is a similar source of exposure. Many synergistic effects were identified (water-hair): Ag-Sn, Ni-Sn, Pb-Sn, Mn-Na, Fe-Zr.

Multielemental analysis of potable water from various transmission lines shows that some groups of elements, the concentrations of which are interrelated, can be distinguished. This is shown in Table 4. The following groups were identified: (Al, B, Bi, Co, Li, Sr), (Ag, Na, Ni, Pb). Within each group, the same release order from various installations was identified. For the first group, the highest level of all the elements was found to be released by plastic pipes, then by steel, and then copper lines were found in the lowest extent. For the second group, the release order was as follows: plastic>copper>steel. The first group was antagonistic to K, which was released in the highest extent by copper, subsequently by steel and plastic materials. This release order for K was the opposite to the first group of interrelated elements. Also, many correlated pairs of elements were found, together with the material from which they were released in the highest and the lowest extent: Sn-Zr (released by steel lines) antagonistic to Mo (released by copper pipes), Hg-Ba (released by steel installations), and Cd-Ti (released by copper pipes, antagonistic to Zn, which was released by steel and plastic lines). Also, many antagonistic dependencies between elements were detected: (Ca, Si) (Ca released by plastic, Si by copper pipes), (Fe, P) (Fe: steel, P: copper and plastic), (La, Mn) (La: plastic, Mn: steel).

Also, inter-element ratios in human hair were investigated – between essential and toxic elements (Ca/Cd, Cu/Cd, Zn/Pb, Zn/Cd) and among essential elements (Zn/Cu, Na/K, Ca/P, Ca/Mg). Generally, knowledge of ratios between elements is not full, but in many papers an increasing role of investigating ratios rather than the absolute level of elements as a future trend is underlined. It is thought that the content of an element in hair might be individual, while ratios reflect balance between minerals in the human organism. For instance, high values of the ratio Ca/Mg reflect hypertonia while low values reflect hypotonia [31]. Low values of the ratio Ca/P show elevated levels of P when related to Ca. Such imbalance may cause problems with teeth, arthritis, and demineralization of bones [31]. High value of Na/K means increased excretion of aldosterone and increased retention of sodium [32]. A high ratio of Zn/Cu reflects hypercholesterolemia, ischeamic heart disease, arterial hypertension, overweight or psychic disturbances [33]. Low values are found in hair of vegetarians and can be an early prognosis of heart attack [34], and can show hepatic failure and cholestasis. Low Zn/Cd can lead to deficiency of histamine and can cause food and other allergies [31].

A low ratio of essential vs. toxic elements is disadvantageous because it shows inhibitory activity of toxic metals toward nutritive elements. Low ratios were found in hair of subjects drinking water from steel (Ca/Cd, Cu/Cd, Zn/Cd) and plastic (Zn/Pb, Zn/Cd) pipelines. Higher values of the coefficients were found for copper pipes (Ca/Cd, Cu/Cd, Zn/Cd, Zn/Pb). However, in this case this also means that copper pipes release Ca, Cu, and Zn. Values of ratios of

Table 3. Inter-element interactions between hair and water level of elements.
a) Correlation coefficients between concentrations of a given element in tap water and in hair.

Element	Correlation coefficient	Element	Correlation coefficient
Statistically significant (at $p<0.1$)		Not significant, but high	
Ni	0.99	Fe	-0.87
Li	0.99	K	-0.90
Ba	-0.99	Mg	-0.94
Not significant, but high		Mn	-0.84
Al	0.97	Na	-0.99
As	0.89	P	-0.80
Cu	0.93	Pb	-0.90
Si	0.70	W	-0.98
Zr	0.85	Zn	-0.84
Ca	-0.78		

b) Correlation coefficients (significant at $p<0.05$) between the concentration of elements in water and the content of other elements in hair.

Water	Hair	+*)/-**)	Water	Hair	+*)/-**)	Water	Hair	+*)/-**)
Ag	Sn	+	K	Ce, Hg, Rb, Ti	-	S	Cd	-
Al	Ce, Hg	+	La	Ni	+	Si	W, Zn	+
B	Ce, Hg	+		Na, P	-	Si	K	-
Ba	Ag, As, Ca, Si	-	Li	Ce, Hg	+	Sn	Bi	+
Bi	Ce	+	Mg	Ag	-		Cu	-
Ca	K	+	Mn	Na	+	Sr	Ce	+
	W, Zn	-		Ni	-	Ti	Ba, La	+
Cd	Ba, La	+	Mo	Bi	-	W	Al, Cr, Fe, S	+
	B	-	Na	Sn	+		Pb	-
Ce	Co, V	+	Ni	Sn	+	Zn	B	+
	Mg, Sr	-	P	Zr	-		Ba, La	-
Co	Ce	+	Pb	Sn	+	Zr	Bi	+
Fe	Zr	+	P	Zr	-		Cu	-
Hg	Ag, As, Ba, Ca	-	Pb	Sn	+			

*) + - synergism
**) - - antagonism

essential *vs*. other essential elements were as follows. Low values: plastic (Zn/Cu, Na/K, Ca/P), and steel (Ca/P, Ca/Mg). High values: copper (Zn/Cu, Na/K, Ca/P, Ca/Mg), steel (Zn/Cu), plastic (Ca/Mg).

To make the technique more valid, another grouping variable (gender) was considered. It was then assumed that environmental and occupational exposure of the participants was similar. *Post-hoc* comparisons between the subpopulations were made by Tukey's test and the Spjotvoll/Stolin test. Results were considered significantly different when $p<0.05$ and $p<0.1$. The population was divided into a subpopulation of males and females. Within each subpopulation a group of subjects which declared steel, copper, and plastic installations were distinguished (Table 5). Since gender is an important factor determining hair mineral content, another grouping variable, sex, was included. For this reason, the whole population was divided into six subpopulations, between which statistical significance of differences was assessed.

Table 4. Inter-element correlations between the concentration of various elements in water (statistically significant at $p<0.05$).

Groups of inter-related elements	Type of pipes	Elements in the group are antagonistic to	Type of pipes	Correlation pairs (synergistic)	Correlation pairs (antagonistic)
Synergisms					
(Al, B, Bi, Co, Li, Sr)	Plastic>Steel>Copper	K	Copper>Steel> Plastic	Al-B, Al-Bi, Al-Co, Al-Li, Al-Sr, B-Bi, B-Co, B-Li, B-Sr, Bi-Co, Bi-Li, Bi-Sr, Co-Li, Co-Sr, Li-Sr	K-Al, K-B, K-Bi, K-Co, K-Li, K-Sr,
(Ag, Na, Ni, Pb)	Plastic>Copper>Steel			Ag-Na, Ag-Ni, Ag-Pb, Na-Ni, Na-Pb, Ni-Pb	
(Sn, Zr)	Steel>Plastic>Copper	Mo	Copper>Plastic>Steel	Sn-Zr	Mo-Sn, Mo-Zr
(Hg, Ba)	Steel>Plastic>Copper			Hg-Ba	
(Cd, Ti)	Copper>>Plastic, Steel	Zn	Steel, Plastic>>Copper	Cd-Ti	Cd-Zn, Ti-Zn
Antagonisms					
(Ca, Si)	Ca: Plastic>Steel>Copper		Si: Copper>Steel> Plastic		Ca-Si
(Fe, P)	Fe: Steel>>Copper, Plastic		P: Copper, Plastic>>Steel		Fe-P
(La, Mn)	La: Plastic>Copper>Steel		Mn: Steel>Copper> Plastic		La-Mn

Therefore, the level of elements within the group of males and, separately, females drinking water from various sources was assessed.

Two grouping variables were included – gender and the type of plumbing material (Table 5). Statistically significant differences were found for the following elements: Ag (males, copper pipes vs. steel 6 times higher, copper vs. plastic 10 times higher; in females – Ag from jewelry is another important source of exposure), As, Ba, La, Mg (statistically significant differences only between genders), K (females steel>copper; similarly males, but differences were not significant statistically), Mn (females plastic>copper; males – similarly, not significant), Si (males plastic>steel; similarly females, but not significant), Sr (males steel>plastic; females – no dependence), Ti (males and females: plastic, but not significant). These results are summarized in Table 6.

The mean values of levels of elements within each subpopulation and each group were compared with the average for the subpopulation. The mean content of level of elements in hair of males drinking water from steel, copper and plastic pipes was compared with the mean for males and the same was done for females. This enabled us to point out elements released in the highest and the lowest quantities as determined by human hair, within a group of males and females, separately. When taking into consideration the content of elements in hair of males and females from various installations, the following release patterns can be distinguished. In both sexes drinking water from steel pipelines, higher levels of Na, Cd, and P were found. Hair of males showed higher contents of Mo and Zr, but hair of females: Bi, B, Y. The lowest level of the following elements was found in hair of males drinking water from steel pipes: Ag, Ti, Si, Ce, Ni, Pb, Mg, Cu, Cd and in females: Cu, Ag, Mg, Hg, Ni, Zr, Sn, Ca, Pb, Sr, Ba, Al, Si when compared with males and females who declared the other pipes. In both sexes drinking water from steel transmission lines, the following elements were released at the lowest extent: Ag, Si, Ni, Pb, Mg, Cu. For installations made of copper, the release patterns were as follows. The elements were released in the highest extent in both sexes: La, Zn, Ba, Ca. Hair copper level was very high in females, but in males was not elevated. Elements released in the smallest extent when compared with individuals using water from other than copper installations: males – Ti, Rb, Zr, Al, Bi, K, Hg, Cr, Ce, Cu, Fe, Mn, Co, Si, S, and females: B, Mo, Ti, Bi, Ce, Li, Mn, Y, V, K, Fe, Al, As, S. Elements common for both sexes as those released in the lowest quantities: Ti, Al, K, Ce, Fe, Mn, S. Hair of the subpopulation of subjects' drinking water from installations made of plastic contained more Ti, Ce, K, Al, Ni, Sn, Fe, Hg, Mn, Pb. Elements released in the lowest quantities based on male hair analyses: B, Mo, Ag, Na, Y, Sr, P, Ba, Cd, V, La, As, Zn, Ca and based on analysis of hair of females: Bi, Na, Cd, Zn, La, Pb, P. Elements common in both sexes: Na, P, Ba, La, Zn.

The level of the following elements statistically significantly differed between the subpopulations who declared various pipes, for both sexes: K (steel>copper), Mn (plastic>steel), Si (plastic>steel), Ti (plastic>steel, copper – not significant difference). The following differences were found statistically significant only for the group of males (not confirmed by the comparisons in the group of

Table 5. Hair mineral composition from subjects' drinking water from various potable water transmission pipelines with respect to gender, mg/kg.

Sex		Male			Female			Total population	
Tap water from:		Steel	Copper	Plastic	Steel	Copper	Plastic	Min	Max
N		*22*	*7*	*12*	*35*	*18*	*23*		
Mean	Ag	0.327^{a}	2.000^{ab}	0.194^{b}	0.396	0.493	0.622	0.00	12.6
SD		0.265	4.70	0.168	0.305	0.349	1.05		
Mean	Al	8.98	6.17	12.73	7.25	7.25	8.39	1.31	39.9
SD		5.80	3.20	9.14	4.23	3.58	7.04		
Mean	As	0.847	1.21^{a}	0.836	0.792	0.775^{a}	0.816	0.65	4.0
SD		0.176	1.214	0.123	0.158	0.134	0.118		
Mean	B	0.81	2.35	0.17	0.96	0.15	1.28	0.00	14.4
SD		2.40	5.36	0.56	2.06	0.60	2.55		
Mean	Ba	1.00^{ABC}	1.13^{a}	0.87^{DEF}	2.50^{AD}	3.03^{BEa}	2.51^{CF}	0.22	6.8
SD		0.59	0.80	0.63	1.48	1.77	1.68		
Mean	Bi	0.180	0.135	0.306	0.287	0.144	0.141	0.00	2.7
SD		0.369	0.288	0.725	0.678	0.319	0.320		
Mean	Ca	$1,372^{ABa}$	1,569	$1,296^{C}$	$2,344^{a}$	$3,093^{AC}$	$2,503^{B}$	336	7,433
SD		921	862	832	1,040	1,858	1,513		
Mean	Cd	0.0857	0.0734	0.0707	0.1097	0.0899	0.0814	0.05	0.5
SD		0.0259	0.0213	0.0131	0.1004	0.0499	0.0279		
Mean	Ce	0.119	0.146	0.271	0.145	0.115	0.225	0.00	1.1
SD		0.217	0.198	0.266	0.230	0.201	0.276		
Mean	Co	0.882	0.829	0.846	0.840	0.839	0.843	0.77	1.3
SD		0.167	0.095	0.129	0.119	0.134	0.103		
Mean	Cr	1.16	1.12	1.80	1.16	1.08	1.12	0.81	9.4
SD		0.25	0.27	2.40	0.34	0.18	0.30		
Mean	Cu	14.1	11.6	12.0	19.3	35.5	28.8	3.03	243
SD		12.9	3.9	3.6	20.7	60.5	25.9		
Mean	Fe	21.4	21.4	26.6	23.1	20.9	24.6	8.41	62.8
SD		5.5	2.7	12.1	6.7	4.6	6.8		
Mean	Hg	0.224	0.167	0.230	0.176	0.195	0.252	0.03	0.8
SD		0.192	0.114	0.203	0.122	0.159	0.168		
Mean	K	73.9	52.0	107^{ab}	52.9^{Aa}	46.1^{Ab}	55.2	13.8	351
SD		43.1	25.3	87.3	42.2	18.8	55.9		
Mean	La	0.352^{A}	0.418	0.328^{B}	0.627	0.813^{AB}	0.619	0.00	2.0
SD		0.263	0.245	0.286	0.312	0.493	0.439		
Mean	Li	0.096	0.138	0.106	0.109	0.085	0.126	0.00	0.3
SD		0.082	0.092	0.074	0.084	0.068	0.053		
Mean	Mg	52.8^{AB}	53.2^{a}	56.3^{Cb}	85.9	119^{ACa}	107^{Bb}	25.1	301
SD		19.8	28.2	36.9	37.4	71.0	57.2		
Mean	Mn	0.611^{A}	0.591	0.642	0.727	0.623^{B}	1.02^{AB}	0.42	4.1
SD		0.154	0.147	0.167	0.229	0.188	0.793		
Mean	Mo	0.883	0.764	0.210	0.384	0.191	0.815	0.00	13.3
SD		2.80	1.60	0.549	0.639	0.277	2.50		
Mean	Na	481	416	277	382	356	293	56.7	1,630
SD		435	204	184	275	274	141		

Table 5. Continued.

Sex		Male			Female			Total population	
Tap water from:		Steel	Copper	Plastic	Steel	Copper	Plastic	Min	Max
N		*22*	*7*	*12*	*35*	*18*	*23*		
Mean	Ni	0.664	0.893	1.084	0.901	0.957	1.25	0.35	8.3
SD		0.206	0.453	0.621	0.369	0.583	1.58		
Mean	P	167	151	135	157	154	146	86.5	356
SD		51	46	25	44	55	34		
Mean	Pb	3.07	3.43	3.24	3.15	3.08	2.82	0.00	10.9
SD		2.12	2.59	1.74	1.45	1.55	1.49		
Mean	Rb	2.03	1.06	3.26	2.14	2.26	2.66	0.00	2.5
SD		2.18	1.06	3.27	2.29	2.00	3.26		
Mean	S	39,960	39,916	40,444	40,208	40,093	40,101	34,962	47,720
SD		1,815	1,573	2,203	2,145	1,871	1,665		
Mean	Si	35.9^{Aa}	35.3	36.5^{a}	69.5	80.0^{A}	71.3	8.72	213
SD		19.2	20.8	16.4	51.5	59.0	51.8		
Mean	Sn	2.94	3.28	3.87	3.16	3.29	4.07	0.00	15.7
SD		2.27	3.54	4.24	3.41	4.10	3.05		
Mean	Sr	2.62^{a}	2.17	1.98^{a}	5.53	6.10	6.32	0.43	32.2
SD		3.29	1.50	1.57	4.56	4.28	6.40		
Mean	Ti	0.93^{a}	0.68	3.13	1.80	1.23	3.26^{a}	0.00	15.4
SD		1.25	0.39	4.52	2.00	1.48	4.65		
Mean	V	0.838	0.996	0.778	0.887	0.738	0.858	0.63	2.3
SD		0.317	0.576	0.147	0.420	0.124	0.295		
Mean	Y	0.0449	0.0517	0.0345	0.0502	0.0404	0.0464	0.00	0.1
SD		0.0264	0.0202	0.0286	0.0339	0.0327	0.0337		
Mean	Zn	205	243	194	251	258	216	95.7	1053
SD		100	181	97	185	172	68		
Mean	Zr	0.594	0.245	0.344	0.297	0.373	0.337	0.00	4.8
SD		1.077	0.228	0.304	0.638	0.359	0.483		
Mean	Ca/Cd	17,311^{Aa}	20,481	18,787	27,860	36,018^{A}	31,498^{a}	4,862	116,210
SD		14,428	7,351	12,378	16,575	19,719	20,362		
Mean	Cu/Cd	166	170	172	242	381	359	16.0	2,217
SD		126	70	51	325	527	309		
Mean	Zn/Pb	97.3	94.5	75.2	119	97.1	103	12.7	820
SD		93.8	75.2	44.5	150	64.9	70		
Mean	Zn/Cd	2,563	3,092	2,796	2,873	3,281	2,775	627	16,332
SD		1,500	1,508	1,379	2,618	2,098	933		
Mean	Zn/Cu	19.7	31.5	18.1	23.7	20.4	12.2	0.54	180
SD		19.4	44.4	13.8	34.3	31.7	9.9		
Mean	Na/K	8.8	10.1	3.0	8.7	9.4	8.1	1.32	63.7
SD		13.0	7.7	2.2	5.4	10.4	5.8		
Mean	Ca/P	9.4^{Aa}	11.9	9.9^{b}	16.0	23.6^{Ab}	18.9^{a}	1.90	78.2
SD		9.9	9.4	6.5	8.9	19.6	14.7		
Mean	Ca/Mg	24.8	29.6	25.8	28.0	26.7	23.9	4.64	48.3
SD		7.9	8.6	10.2	7.9	7.9	6.7		

A, B, C, D – significant at $p<0.05$
a, b, c, d – significant at $p<0.1$

Table 6. Elements released to water from pipelines made of different materials by hair mineral analysis with respect to gender.

Material	Elements released to a higher extent
Steel – males	Mo, Zr, Na, Cd, Cd, Cu, P, Co
Steel – females	Bi, Cd, B, Na, Y, V, Pb, Cr, P, S
Copper – males	Ag, B, As, Li, Y, V, La, Zn, Ba, Ca, Pb
Copper – females	Cu, La, Ca, Mg, Ba, Zr, Si, Zn
Plastic – males	Ti, Ce, Rb, Bi, K, Cr, Al, Ni, Sn, Fe, Hg, Mg, Mn, Pb, Si, S
Plastic - females	Mo, Ti, B, Ce, Mn, Ag, Hg, Ni, Sn, Li, Pb, Al, Sr, Fe, K, As, Co

females): Ag (copper>steel>plastic), Sr (steel>plastic). For the following water pipes the elements for which the differences between genders were found but were not statistically significant:

- plastic: highest level (Ti, Ce, K, Al, Ni, Sn , Fe, Hg, Mn, Pb), lowest: (Na, P, Ba, La, Zn)
- steel: highest level (Na, Cd, P), lowest (Ag, Si, Ni, Pb, Mg, Cu)
- copper: highest level (La, Zn, Ba, Ca (Cu only in males)), lowest (Ti, Al, K, Ce, Fe, Mn, S).

A comparison of the level of elements between a group of males and females drinking water from the same source enabled us to point out differences between sexes. It was found that the level of the following elements differed: As (males>females, 56%), Ba, La and Mg (males<females, 2.7, 1.9, 1.9 times, respectively). The differences in the level of elements between sexes that were not statistically significant were found for the following elements: females>males – Sr (2.5 times), Si (2 times), Cu (2 times), La (1.9 times), Ti (40%), Mn (30%), Ni (20%),Cd (20%), Zn (16%), Y (9%), Sn (6%), Rb (4.5%), males>females – K (54%), Mo (42%), Zr (41%), Al (26%), Cr (19%), Ag (18%), Na (18%), Hg (6%), Pb (5%). These differences were compared with the literature data (Table 7). The following found the confirmation: females>males – Ca, Cd, Cu, Mn, Mg, Ni, Sn, Zn, lower level in females: Al, Co, Lin, Na, Pb, similar level in females as in hair of males: Hg, Fe.

Also, ratios between elements with respect to gender were investigated: high steel males: Zn/Pb, females: Zn/Cu, Zn/Pb, Ca/Mg; in common: Zn/Pb; low males: Zn/Cd, Ca/P, Ca/Cd, Ca/Mg, females: Cu/Cd, Ca/P, Ca/Cd; in common: Ca/P, Ca/Cd. Copper High males: Zn/Cu, Na/K, Ca/P, Ca/Mg, Zn/Cd, Ca/Cd, females: Ca/P, Cu/Cd, Ca/Cd, Zn/Cd, Na/K; in common: Na/K, Ca/P, Zn/Cd, Ca/Cd. Low males: none, females: Zn/Pb. Plastic High males: Cu/Cd, females: none; low males: Na/K, Zn/Pb, Zn/Cu, females: Zn/Cu, Ca/Mg, Na/K, Zn/Cd. In common: Na/K, Zn/Cu.

Other statistically significant differences were related to gender. The following were found statistically different. The content of As was 56% higher in hair of males than females in the group drinking water from copper pipes. In hair of males that declared the remaining installations, the content of As was also higher than in females. The level of Ba was higher in hair of females than of males. The differences were statistically significant for all types of water pipes: plastic (2.9 times), copper (2.7 times), and steel (2.5 times). Results were similar for Ca, but in this case the differences were significant only for steel installation (1.7 times). Copper and steel pipes were not significant and evaluated as 2 and 1.9 times, respectively. The content of other alkaline earth metal – Mg was also higher in hair of females than males. The differences were statistically significant between the content of this element in hair of individuals drinking water from copper (2.2 times) and plastic installations (1.9 times). The difference was high but not significant for steel water pipes (1.6 times). When comparing means for males and females, the highest differences between genders were found for the following elements. The elements, the content of which was higher in females than in males are as follows: Ba (2.7 times), Sr (2.5 times), Si (2 times), Si (2 times), La (1.9 times), Co (1.9 times), Mg (1.8 times), Ti (40%), Mn (30%), Ni (20%), Cd (20%), Zn (16%), Y (9%), Sn (6%), and Rb (4.5%), and higher in males than in females: K (54%), Mo (42%), Zr (41%), Al (26%), Cr (19%), Ag (18%), Na (18%), Na (18%), As (14%), Hg (6%), and Pb (4.9%).

In the literature, the information on the levels of elements in 20-year-old subjects with respect to gender are scarce. The majority of works investigating the effect of sex on the level of elements in hair studied populations of children (Table 7). When comparing the mean level of elements with other populations, the level of the following elements was higher: As, Ba, Bi, Ca, and Na; and lower: Hg. Unkiewicz-Winiarczyk et al. [37] investigated the effect of gender, age, and smoking on the content of Ca, Mg, Fe, Zn, and Cu in the population of Polish individuals. The analytical technique used was ICP-AES. The population was divided into two age groups: 20-30 and 50-60. The following means of investigated elements were reported for the first group (in mg/kg): Ca (males (m): 528, females (f): 549), Mg (m: 37.1, f: 52.5), Fe (m: 26.0, f: 22.7), Zn (m: 179, f: 240), and Cu (m: 11.5, f: 10.6). When compared with the present work, the consistent are information about higher levels of Ca, Mg, and Zn in hair of females. It was concluded that the content of bio-elements in hair of tobacco-smokers was lower and that the levels of Ca, Mg, and Fe decreased with age. Sakai et al. [38] studied the content of Cu, Fe, Mn, and Zn in a population of children (age 0.5-20 years) by flameless atomic absorption spectrometry, and Zn by ICP-AES with respect to age and sex. The following contents of elements were found (geometric mean, in mg/kg): Cu (m: 14.5, f: 13.3, total: 13.7), Fe (m: 43.8, f: 43.7, total: 43.8), Mn (m: 2.5, f: 2.3, total: 2.3), and Zn (m: 116, f: 108, total: 111). In the present work, a similar trend was found for Fe. The gender differences were significant for Cu and Mn. It was concluded that the content of all the elements decreased with age. Kozielec et al. [39] investigated the content of Cu in hair of people of different age and sex in Poland (Szczecin region) by atomic absorption spectrometry. The authors found no statistically significant differences between sexes. The content of copper changed

Table 7. Effect on gender of the content of elements in hair (mean, mg/kg).

Reference	[35]		[10]		[36]		[23]		[24]	
Age, years	9-10		11-13		3-6		20-60		3-100	
Sex	Males	Females	Males	Females	Males	Females	Males	Females	Males	Females
Country	Italy		Italy		Korea		Romania		Pakistan	
Analytical technique	ICP-MS and ICP-AES		ICP-AES		ICP-MS		INAA		ICP-AES	
Al			9.18	7.54	8.99	8.56	14.1	15.1		
As	0.144	0.169	0.09	0.07	0.12	0.11				
Ba					0.33	0.32				
Bi					0.03	0.05				
Ca	290	455	382	601	198	228			462	870
Cd	0.04	0.052	0.17	0.24	0.10	0.06			1.15	1.54
Co	0.034	0.044	1.07	0.79	0.01	0.01	0.0014*	0.00151*	1.25	0.916
Cr	0.776	0.663	0.54	0.66	0.48	0.45			2.08	3.44
Cu	13.1	11.4	29.7	19.3	15.1	16.0	10.4*	12.2*	13.2	24.5
Fe	13.4	11.4	17.2	15	12.4	12.9	20	31	82.7	62.8
Hg					0.49	0.51				
K					32.7	35.6				
Li					0.01	0.01				
Mg	19.9	52.7	22.8	29.3	12.1	12.5	83.6*	150.0*	113	243
Mn	0.459	0.338	0.37	0.33	0.30	0.27	0.590	0.860	4.02	6.32
Mo			0.36	0.31	0.07	0.07				
Na					27.8	26.4				
Ni	0.767	0.912	0.76	1.74					2.38	3.18
P	139	142	212	196	124	118				
Pb	1.90	1.48	7.22	7.58	1.89	1.45				
Sb	0.062	0.028					0.042	0.052		
Se	0.410	0.442	0.87	1.41	0.75	0.74	0.496	0.481		
Sr			0.77	0.97						
Ti			0.83	0.94						
Tl	0.0011	0.0008								
U					0.04	0.04				
V	0.141	0.211	1.57	1.63	0.08	0.07	0.0285	0.0320		
Zn	160	188	153	166	72.5	67.2	161*	185*	251	208

* reported as statistically significant

with age and was higher in the group of 11-15-year-old subjects. For the 21-30-year-old group the mean content was 11.7±5.9 mg/kg. It was found that the content of Pb in Sardinian children statistically differed between sexes and was higher in girls [40]. Ferré-Huguet et al. [41] found no statistical differences between sexes in the level of (mean, in mg/kg): Cr (m: 1.28, f: 1.34), Hg (m: 0.56, f: 0.55), Mn (m: 0.20, f: 0.22), Ni (m: 0.34, f: 0.63), Pb (m: 0.60, f: 0.52), and Sn (m: 0.12, f: 0.20). The results presented in this work confirm higher levels of Mn, Ni, and Sn in females, lower levels of Pb in females than in males, and similar level of Hg. Ashraf et al. [42] studied the content of Cu, Ni, Pb, and Zn in an urban Pakistaniani population that was divided with respect to gender and age (6-60 years). The analytical technique was ICP-AES. Within the age group 23-30, the content of elements was as follows (reported as average concentrations in mg/kg): Cu (m: 12.9, f: 18.2), Ni (m: 3.18, f: 3.57), Pb (m: 7.12, f: 12.7), and Zn (m: 132, f: 216). In the present work this was confirmed for Cu, Ni, and Pb. In another study [43] the effects of age, sex, food habits, and family occupation on Pb and Cd level in hair of children was investigated. The results showed that the level of metals decreased with age and that hair of females contained more Pb (16.5 mg/kg) than males (12.5). In the case of Cd the situation was the opposite: males contained more (2.9 mg/kg) than females (2.2). However, the differences were not statistically significant.

The general conclusion from the studies on the effect of sex is that the content of alkaline earth metals in females is higher than in males: Ca (54%), Mg (78%), and Sr (26%). Less obvious, but reported in the majority of papers, was higher content of the following elements in hair of females when compared with males (in%): Ni (60%), Cr (17), Cd (16), V (13), Mn (11), and Cu (11). Hair of males contained higher levels of the following (in%): Co (6), Al (5), and Na (5). The content of U and Li was similar. The sources, however, do not agree on the levels of As, Fe, P, and Zn *vs.* gender. In the present work, similar results were obtained for the differences of the following elements with respect to gender. Higher levels in females, (Ca, Cd, Cu, Mn, Mg, Ni, Sn, and Zn) and lower levels in females (Al, Co, Li, Na, Pb), and similar levels in females as in hair of males: Hg, Fe.

Conclusions

Hair analyses of groups of individuals drinking water from pipelines made of different materials showed statistically significant differences for the following release order: plastic>steel>copper (Fe, Mn, Na, Ti), copper>plastic>steel (Mg), and plastic>copper>steel (Ni). The content of Ti in hair of subjects that declared plastic pipes was over 3 times higher than participants who declared copper, and over two times than for steel pipes. Nickel was also released by plastic pipes (46% higher level than in steel and 27% than in hair of subjects using copper pipes). Other elements released by plastic installations were Fe and Mn, but since these are microelements and their levels did not increase substantially, they were not of particular concern. Steel pipes were found to release Na (a 46% higher level in hair of subjects that declared plastic pipes and 13% higher than copper). Hair of subjects who used copper pipelines contained more Mg. The differences between the levels of elements found but which were not significant statistically are as follows. Plastic pipes released: Ce, Rb, Mn, Al; steel: Pb, Bi, Na, Cd, Zr; copper: Ag, Cu, La. Also, the role of inter-element ratios was underlined, but it is necessary to carry out further research to confirm the hypotheses.

The composition of water from various pipes was determined. The elements released (by both biomonitoring by HMA and by water analysis) are as follows – plastic: Ni, Ti, Al, Hg, Sn, Mo, Li, Ag, Cu, Sr, B; by steel: Zr, Zn; by copper: Ag, Cu, Si, As. For these elements the results of hair mineral analysis were confirmed by the analysis of water, which was the source of exposure. The analysis of tap water enabled us to find several groups and pairs of inter-related elements, which shows their common occurrence and release: (Al, B, Bi, Co, Li, Sr) released by (plastic>steel>copper) and antagonistic to K, (Ag, Na, Ni, Pb) released by (plastic>copper>steel), (Sn, Zr) (steel> plastic>copper), antagonistic to Mo (copper>plastic>steel). Also, antagonistic pairs of elements were found: (Ca, Si), (Fe, P), (La, Mn).

Inter-element interactions between elements occur in humans. This means that exposure to a given element might result in excessive accumulation or lower accumulation of another element. Knowledge on inter-element interactions may also help uncover remedies against toxic elements by studying antagonistic dependencies (water-hair): Ca-W, Ca-Zn, K-Ti, Mg-Ag, P-Zr, S-Cd.

The obtained results confirmed that currently used materials (in particular plastic pipes) for water transmission pose a risk related to the release of various ions to potable water. This creates the need for the elaboration of new, innovative technologies of production of modern materials. The present work showed that both hair mineral analysis and direct analysis of water are useful techniques of exposure assessment.

Hair mineral analysis is a useful biomonitoring technique. Due to the problems with the interpretation of the results, the method has not yet been fully validated. One of the problems is the effect of gender on the content of elements in hair. In our opinion it is worth carrying out further research to improve the technique and to learn more about the factors that influence mineral composition of hair.

The studied group of individuals was of uniform age and exposure. Therefore, it was possible to divide it into subpopulations with respect to gender and the material of which water pipes are made. Using these two grouping variables helped us obtain valid information and distinguish among the elements, the level of which depended either on sex or exposure from water pipes.

Based on the analyses of male hair, statistically significant differences were found for Ag. The release pattern was as follows: copper>plastic>steel. Based on hair analysis of females, Mn was released to a higher degree from plastic than copper pipes and Si from plastic when compared with steel (analysis of male hair). From the analysis male hair, Sr was released in statistically higher amounts from steel pipes when compared with plastic. Statistically significant differences between genders were found for the following elements, the content of which was lower in hair of males than females: Ba (all the materials), Ca (steel), and Mg (copper, plastic). The content of As in male hair was statistically significantly higher in copper pipes, showing that perhaps male hair would be more appropriate for biomonitoring epidemiological studies, since male hair does not undergo as many hair treatments as female hair.

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