Article submitted to the Proceedings Book of the VI[th]. International Symposium– 2022, *Theme: "Biosphere & Environmental Safety"*	Biosphere and Environmental Safety VI.th International Symposium-2022	ISBN: 978-963-449-285-6 Online May 5-6, 2022 ICEEE, Óbuda University, Budapest, Hungary

HEAVY METAL CONCENTRATIONS IN THE HAIR SAMPLES

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Since the industrial revolution, human activity has continued to cause significant pollution all over the world. Some of the various pollutants released into the environment take the form of heavy metals. These substances present a major threat to the biosphere by entering the food chain and causing toxic effects on living organisms. Our interest has been turned to the heavy metal exposure of Csepel residents in Budapest. Csepel is the site of the Weiss Manfred Steel and Metal Works, which has had various pollution problems over the years. In the present work, human hair was chosen as a tool to detect the above-mentioned heavy metal pollution. The concentrations of some heavy metals (copper, selenium, iron, zinc, cadmium, manganese) was measured in the hair of Csepel residents and compared them with the results of a control group, namely people living in "Erzsébet" district. It is a known fact, that hair testing is a good indicator of heavy metal pollution, because it is simple to perform without internal intervention and does not exposure the person being tested. The collected hair samples were cut into 2-3 mm pieces. The samples were washed, dried, digested and finally the heavy metal content was measured using a Unicam 923 QZ AA spectrometer. Statistical evaluation was done by SPSS 14.0. The results showed that the heavy metal concentrations of the Csepel hair samples were on average higher than the control samples for copper, iron, manganese, cadmium and selenium.

***Keywords**: biological indicator, environmental pollution, GFAAS, hair samples, heavy metals, SPSS*

INTRODUCTION

Since the industrial revolution, humans have continued to cause massive pollution. This pollution has a major impact on the biogeochemical processes taking place on Earth, which processes ensure the proper functioning of the Earth's ecosystem and climate. Some of the various pollutants released into the environment take the form of heavy metals. These substances pose a major threat to the biosphere by entering the food chain and causing toxic effects on living organisms.

This is why the role of environmental protection is becoming increasingly important today, both to minimize the release of these substances into the environment and to reduce the concentrations of those already released to the lowest possible levels through technical interventions.

Csepel is the site of the "Weiss Manfred" Steel and Metal Works, established in the early 20th century, which has faced various environmental pollution problems. In the years before the change of regime, the Ironworks, which operated with the technology of the time, paid huge fines in Budapest as the largest air polluter in Budapest [1].

Csepel Works was also the source of the large-scale pollution of galvanic sludge that caused a nationwide outcry. As a result, over the years, the Csepel Works area has been the source of various levels of heavy metal pollution into the environment and the bodies of Csepel residents, due to inadequate technologies and human negligence.

As it is known, the hair accumulates trace elements in the body over time as it grows, so testing can be used to assess the trace element status of the previous few months. Hair samples are easy to take and are safe to work with. When taking hair samples, the sampling site must be fixed, as different areas of the hair are not equally affected by environmental influences and cosmetics. After sampling, hair samples can be stored at room temperature, but some authors suggest that samples should be frozen, according to Pereira et al. [2], and collected hair samples should be placed in a polyethylene bag and kept at -20 °C until cutting.

For trace element analysis, samples are usually taken from the back of the head, which is relatively protected from contamination sources. For sampling, Manson and Zlotkin [3] recommended the use of a plastic or quartz cutting instrument to eliminate contamination, while Senofonte et al. [4] recommended the use of a titanium nitride-coated scalpel. However, these instruments are fragile, expensive and difficult to access. Storage may also contaminate the sample and therefore the storage vessels should previously be inspected to check whether the sample may leach contamination from the vessel or whether elements may bind to the vessel wall.

The next step in the preparation of the hair samples is washing, which is still an unresolved issue in hair analysis and the main source of error in results. The aim of washing is to remove as much as possible exogenous impurities from the surface of the hair fiber without affecting the endogenous composition of the sample. This is also complicated by the fact that different trace elements may accumulate in different forms of mobility or in different parts of the hair shaft. An inappropriate washing procedure may also alter the concentration of each trace element and their relative proportions to each other.

Several washing methods are described in the literature. The International Atomic Energy Agency recommends washing with acetone followed by washing with deionized water, both for at least 10 minutes with continuous stirring at room temperature. Senofonte et al. [4] recommended a washing procedure with diethyl ether-acetone (3:1), 5% EDTA solution followed by deionized water. The above examples illustrate the wide variation in washing operations, but most authors agree that a perfect washing method that has been shown to remove exogenous contamination and not affect the endogenous trace element composition has not yet been developed.

The next step in sample preparation is destructive washing. Humid atmospheric shredding and incineration are not suitable for trace element analysis due to the high risk of contamination and loss of certain trace elements. Today, the most commonly used method is microwave shredding, of which several variants are used. Koplík et al. [5] compared the microwave destructive method with cremation and found that out of a reference sample of about 500 mg of plant origin used, significant losses (10-75%) of most of the trace elements tested were found in the samples prepared by cremation, whereas the trace element composition of the samples prepared in a closed microwave system was in good agreement with the guaranteed values.

The methods used in the literature for the analysis of biological samples are very diverse. For the analysis of solid samples, non-destructive analytical methods such as neutron activation analysis (NAA) can be used. The advantage of these multi-element methods is that they do not require sample digestion.

Non-destructive methods are generally used for clinical research. Clayton and Wooller [6] and Tomza et al. [7] tested the hair of workers exposed to heavy metals in the workplace and obtained high concentrations of As, Cr, Co, Se, Zr and Cd. Zeng et al. [8], also examining hair samples from cancer patients, reported significant differences in Mn, Cu, Zn and As concentrations and Cu/Zn ratios between cancer patients and controls.

For the determination of trace element content in biological samples, non-destructive methods are much more widely used than destructive methods. It is commonly used being FAAS (Flame Atomic Absorption Spectrometry), ZAAS (Zeeman Atomic Absorption Spectrometry), ETAAS (Electrothermal Atomic Absorption Spectrometry), ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry), GFAAS (Graphite Furnace Atomic Absorption Spectrometry) and more recently ICP-MS (Inductively Coupled Plasma - Mass Spectrometry), ID-ICP-MS (Isotope Dilution - Inductively Coupled Plasma - Mass Spectrometry) and LC-ICP-MS (Liquid Chromatography-Inductively Coupled Plasma - Mass Spectrometry).

The results obtained are compared with reference ranges established from control samples. The results may be influenced by a number of factors other than health status, such as age and gender, while environmental factors include place of residence, occupation and lifestyle.
Zakrgynska-Fontaine et al. [9] studied the dependence of the composition of hair samples on sex and age and found that men's hair had higher concentrations of Fe and Pb, while women had higher concentrations of Ca, Mg, Zn and Cu. In hair samples collected from young people, Al, Ag, Cu and Co were found in higher concentrations, while Zn, Ca and Mg were found in higher concentrations in adults. Despite the problems encountered, trace element analytical methods are becoming increasingly common, not only to detect environmental effects, but also to test subjects suffering from various diseases.
The aim of these tests is to facilitate the early detection of diseases associated with changes in trace element status, preferably before the onset of clinical symptoms, and to investigate their biological and biochemical background and consequences.
Ely et al. [10] investigated the relationship between air pollutants and children's learning problems and found that although the hair of children with learning problems had a different trace element composition to that of controls, the differences were not due to air pollutants. Ryan et al. [11], analyzing hair samples from patients with multiple sclerosis, found that the concentration of V and Se in hair samples from patients was significantly higher, while the concentration of Cu, I, Mn and S was significantly lower than in control samples [12]. Keratin makes up 97% of the hair and the remaining 3% is water. Keratin is nothing more than the amino acid protein structure that makes up the horns.
The hair consists of three layers: the cortex, cuticle and medulla. The outer layer is made up of a series of overlapping plates, which are coated with hair oil produced by the sebaceous glands. The elasticity of the hair is ensured by a cortex of keratin fibers.
The hair is divided into two main parts, one is the living hair root in the scalp, the lower part of which is the hair follicle and the other is the lifeless hair shaft [13]. The lifelessness of the hair makes it a good choice for trace element analysis. Hair testing is much simpler and less inconvenient for the subjects than testing blood, urine, skin, plasma or other tissues. During the growth of hair, it continuously stores trace elements absorbed by the body, which allows the trace element content of the subject's body to be determined for several months, thus providing a good measure of the subject's heavy metal contamination [14].
Care should be taken during sample collection prior to testing to ensure that samples do not suffer from trace element loss or external contamination, as this may affect the measurement results later on. Due to the concentration of trace elements in $\mu g/dm^3$, a highly sensitive analytical method of analysis should be used. In our case, the residents of the study area were the residents of Csepel and the control sample were the residents of “Erzsébet”.
Due to its high sensitivity, the GFAAS (Graphite Furnace Atomic Absorption Spectrometry) method is often used for trace analysis of biological substances. We used this method for the analysis of the hair samples we obtained. The advantage of using this method is that by using a suitable heating program in the graphite furnace, the organic matter content of the sample can be destroyed before atomization, so that not only liquid but also solid samples can be analyzed [12].
In this article, human hair has been chosen as a tool to detect the above-mentioned heavy metal pollution. The concentration of some heavy metals (copper, zinc, selenium, iron, cadmium, and manganese) in the hair of Csepel residents was measured and compared with the results of a control group, namely persons living in “Erzsébet”.
An answer was sought to the question whether people living in Csepel were indeed exposed to higher levels of heavy metals compared to people living in the surrounding districts. It is a known fact that hair testing is a good indicator of heavy metal pollution; it is simple to perform without internal intervention and does not burden the person being tested.
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MATERIALS AND METHODS

Description of the sampling site

Csepel is located on the northern part of the island of Csepel, one of the southernmost districts of Budapest. Its population is 76 911 according to 2016 data. It covers an area of 25.75 km^2, of which 23.02 km^2 is internal [15].

It is bordered by the Danube to the west and the "Ráckeve"-Danube branch to the east, which is a NATURA 2000 site of "Nature of Special Importance for Nature Conservation". The only protected area in Csepel was the "Tamariska" hill in the King's Forest, which was protected from 1994. It became a Metropolitan Nature Reserve in 1999 and a National Nature Reserve in 2012 [16].

The area is named after the Tamarisk plant that grows here, and among the sandy plant and animal species, Red Book and Pannonian endemic species can also be found in this 5.2-hectare area. The first thing most people think of when they think of Csepel is not its natural values, but rather the "Weiss Manfred" Steel and Metal Works, founded in Csepel in 1892.

The name of the metalworks was changed in 1956 to Csepel Iron and Metal Works, a name that has remained to this day. Over the years, the factory site has been home to many different plants and industries. These included, for example, a munitions and ammunition plant, a metal foundry and metalworks, a power plant, a hydraulic press shop, a carpentry plant, a fine wire plant, a vehicle factory, an iron foundry, a steel foundry, a military vehicle plant, a gas generator plant, a bell foundry, a bicycle plant and many others [15].

These are all industries that have a high potential to pollute their environment with heavy metals, even today, let alone in the early 19th century, when there were no such strict or even no environmental standards for manufacturing technologies.

Indeed, the beginning of environmental protection can only be dated back to 1962, with the publication of Rachel Carson's Silent Spring. This work opened the eyes of intellectuals in time to the fact that what you do to your environment can have very serious consequences later on.

Since the early 1990s, the factories of the time have been slowly closing, fragmenting and transforming themselves as a result of the economic difficulties.

Today there are more than 200 companies operating in the Csepel Works area. The companies have acquired ownership of the buildings and have started to modernize and renovate them.

Waste water treatment plant in Csepel

Untreated wastewater can be one of the sources of heavy metals in soil, surface water and groundwater. Wastewater generally contains low concentrations of toxic metals, but they can enter the food chain during its passage into the biomass and accumulate in high concentrations once it reaches the human body [17].

With the construction of the Csepel wastewater treatment plant, this source of pollution seems to be decreasing. Wastewater from Budapest, and thus from Csepel, is now treated in a total of 4 treatment plants.

The largest of these is the Csepel wastewater treatment plant, built in 2009, which can treat an average of 350 000 m^3 of wastewater biologically. Together, the plants operated by North Pest, South Pest, Csepel and BKSZT Ltd. can treat 95% of Budapest's wastewater [18]. The contamination limits for heavy metals in wastewater and sludge are shown in Tables 1 and 2, based on the Government Decree 50/2001 (IV. 3.).

Table 1. Limit values for toxic elements and harmful substances in waste water for agricultural use

Name of materials	Limit value mg/dm^3

Zinc	**5.0**
Cadmium	**0.02**
Manganese	**5.0**
Copper	**2.0**
Iron	**20.0**

Table 2. Limit values for toxic elements and harmful substances in sludge for agricultural use

Name of materials	Limit value mg/kg dm.
Zinc	**5.0**
Cadmium	**0.02**
Manganese	**5.0**
Copper	**2.0**
Iron	**20.0**

Csepel drinking water base

Csepel is home to the second largest shore-filtered water base in Budapest. There are nearly 150 drinking water wells on the island, and the water extracted from these wells supplies 30% of the drinking water needs of the capital and the surrounding municipalities.

The quality of the drinking water from the Csepel Island area (Table 3) is heavily influenced by agriculture, waste management, sewage disposal and various industrial activities, as the drinking water bases are vulnerable. This is because there is no impermeable layer above the water storage medium to protect the vulnerable coastal filtered water from upstream contamination [19].

Fortunately, Csepel Works has so far not contaminated this vulnerable drinking water base, although the area adjacent to the Danube has sometimes polluted the Danube water to a greater or lesser extent.

Table 3. Limit values for harmful substances in drinking water

Description	Quantity	Limit value
Free active chlorine	0.34 mg/l	-
Chloride	34 mg/l	100 mg/l
Iron	46 µg/l	200 (µg/l)
Manganese	17 µg/l	50 (µg/l)
Nitrate	13.1 mg/l	50 mg/l
Nitrite	<0.03 mg/l	0.1 mg/l
Ammonium	<0.04 mg/l	0.2 mg/l
Conductivity	704 µS/cm	2500 (µS/cm)
pH	7.42	6.5-8.5

Sampling

Hair samples were obtained with the help of hairdressers from 3 different hairdressing salons in Csepel. The control samples were taken from 1 hairdresser in Erzsébet. A total of 30 hair samples were collected, of which unfortunately 2 were destroyed during the analysis. One was the control and one was from the tested group.

Thus, a total of 28 hair samples were tested. Hair samples were taken only from local residents and a short questionnaire was completed by them. The questionnaire contained the following questions:

- Gender
- Age
- Do you dye your hair? If yes, with what?
- Do you smoke? If yes, for how many years?
- Do you take medication regularly? If yes, what?

These questions were necessary because smoking, hair dyeing and taking certain medicines can affect the results of the measurements. For example, the control site was particularly interested to see if there was a measurable difference between the hair dyes they use and those used by other hairdressers. It was also important for them to know the quality of the hair dye packs their customers were receiving and to know what they were working with. Unfortunately, we did not get any valuable answers about their medication habits. Data for the Csepel study (A) and „Erzsébet" control (K) groups are shown in Tables 4 and 5.

Preparing the hair samples

After collection, the hair samples were stored in separate polyethylene bags together with the questionnaires until the start of the study. The first step was to cut the hair samples to 2-3 mm using stainless steel scissors [20].

After that, the cut hair samples were placed in beakers with hair sample code numbers. After the chopping, the hair samples were placed in an ultrasonic water bath first once in bidistilled water, then three times in diethyl ether, and then again in bidistilled water for 5-5 minutes for each washing phase. The washed samples were placed in coded petri dishes and placed in a drying chamber at 70 °C for 24 hours.

Table 4. Responses to the questions in the questionnaire from persons providing hair samples (A) living in Csepel

Code	Age	Gender	Smoking	Hair dyeing
A-01	57	Female	no	LK (lisap)
A-02	23	Female	yes (2-3 years)	HI Richesse (L'oreal)
A-03	80	Female	no	Regal Bes
A-04	60	Female	no	Regal Bes
A-05	32	Male	no	no
A-06	63	Female	yes (40 years)	Bes Regal
A-07	16	Male	no	no
A-08	84	Female	no	no
A-09	36	Female	no	no
A-10	40	Male	no	no
A-11	64	Male	no	no
A-12	57	Female	no	Regal Bes
A-13	50	Male	yes (35 years)	no
A-14	33	Male	no	no

Table 5. Responses to the questions in the questionnaire from people living in "Erzsébet" (K) who provided a hair sample

Code	Age	Gender	Smoking	Hair dyeing
K-01	43	Female	no	Joico
K-02	25	Female	yes (7 years)	Joico
K-03	47	Female	no	bleaching + dye
K-04	10	Male	no	no
K-05	19	Male	no	no
K-06	53	Male	no	no
K-07	18	Female	yes (6 years)	bleaching Kallos
K-08	46	Female	no	Joico
K-09	53	Female	no	Joico
K-10	33	Female	yes (15 years)	Joico
K-11	38	Male	yes (20 years)	no
K-12	38	Male	no	no

K-13	27	Female	no	Joico
K-14	44	Female	no	no

Digestion of samples

Digestion of samples was performed in a Milestone 1200 MEGA microwave oven (Table 6).
For digestion the samples 5 cm^3 of 65% nitric acid and 2 cm^3 of 30% hydrogen peroxide were used.

Table 6. The microwave hair digestion program was as follows

Number·of·steps¤	Time·required·(minutes)¤	Operation¤
1.¤	2¤	Digestion,·250·watts¤
2.¤	2¤	Ventilation¤
3.¤	6¤	Digestion,·250·watts¤
4.¤	5¤	Digestion,·400·watts¤
5.¤	5¤	Digestion,·600·watts¤
6.¤	5¤	Ventilation¤

RESULTS AND DISCUSSION

Changes in copper concentration values in hair samples

At the copper concentration (Figure 1), it can be seen that the concentration values in µg/g are higher for the control samples labelled "K" compared to the samples labelled "A". In particular, sample "K13" with a value of 39.70±0.34µg/g is outstanding. The lowest of these is sample "K12" with 1.70 ± 11.10µg/g. The average of the control samples is 12.37µg/g, while the average of the Csepel samples is only about half of 6.45 µg/g. Among these, the lowest was also sampling "A4" with 0.55µg/g, while the highest was also only 10.60µg/g, which was sample "A3".

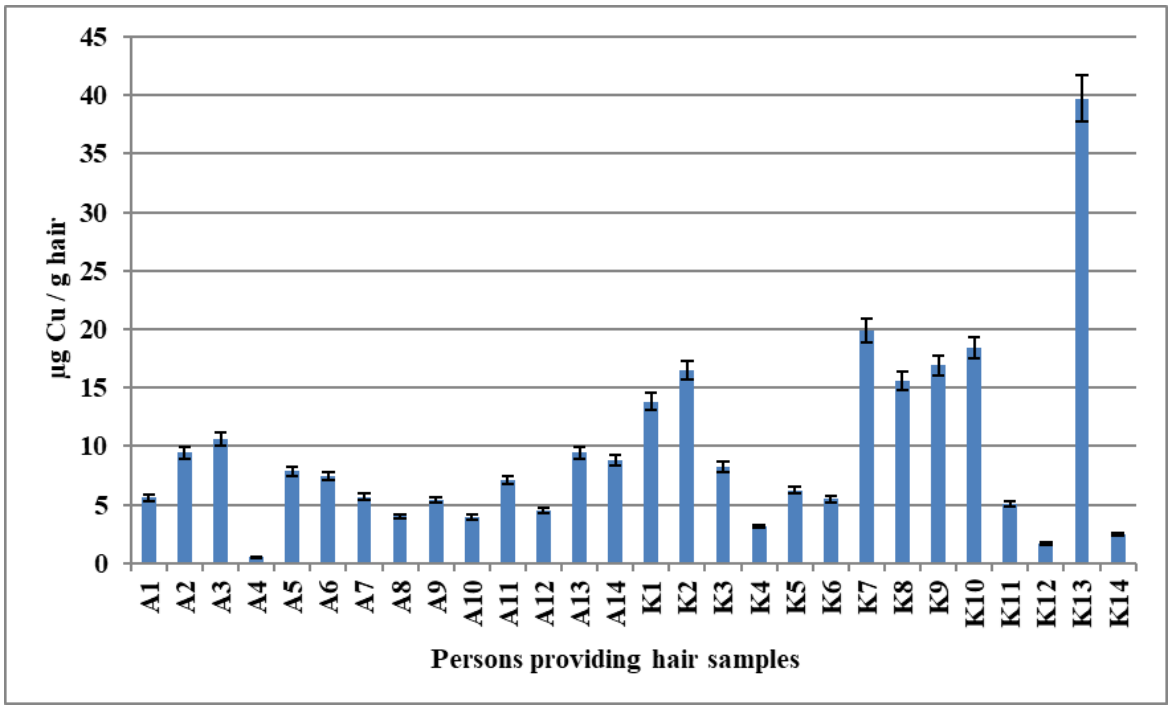

Figure 1. Cu concentration in hair samples

Statistical analysis (Table 7) showed that the Cu concentration of hair samples by residence (Figure 1) was significant ($LSD_{5\%}$= 4.36). On average, Cu concentration in hair of "Erzsébet" residents is significantly higher (A: 6.44µg/g hair; K: 12.63µg/g hair).

Table 7. Cu concentration variance table by residence

Factor	SQ	df	MQ	F	Sig.	$LSD_{0.5}$
Modell	507.589	2	253.795	4.111	0.022	
Correction Factor	4800.502	1	4800.502	77.753	0.000	
Residence	505.921	1	505.921	8.194	0.006	4.365
Repeat	3.029	1	3.029	0.049	0.826	
Error	3087.013	50	61.740			
Total	8485.368	53				
Corrected total	3594.603	52				

Table 8. Cu concentration variance table by gender

Factor	SQ	df	MQ	F	Sig.	$LSD_{0.5}$
Modell	432.468	2	216.234	3.419	0.041	
Correction Factor	3702.923	1	3702.923	58.551	0.000	
Residence	430.800	1	430.800	6.812	0.012	3.858
Repeat	8.190	1	8.190	0.130	0.720	
Error	3162.135	50	63.243			
Total	8485.368	53				
Corrected total	3594.603	52				

Statistical analysis (Table 8) showed that the Cu concentration in hair samples was significant ($LSD_{5\%}$= 3.86) according to the sex of the samplers (Figure 1).
On average, Cu concentration in hair of women is significantly higher than in hair of men (women: 11.72µg/g hair; men: 5.76µg/g hair).
Based on statistical analysis (Table 9), the Cu concentration in hair samples was not significant ($LSD_{5\%}$= 6.28) according to the smoking habits of the sampled individuals (Figure 1).

Table 9. Cu concentration variance table for smoking habit

Factor	SQ	df	MQ	F	Sig.	$LSD_{0.5}$
Modell	142.866	2	71.433	1.035	0.363	
Correction Factor	4509.091	1	4509.091	65.316	0.000	
Residence	141.198	1	141.198	2.045	0.159	6.282
Repeat	2.871	1	2.871	0.042	0.839	
Error	3451.737	50	69.035			
Total	8485.368	53				

Corrected total	3594.603	52				

Based on statistical analysis (Table 10), the concentration of Cu in hair samples according to the hair dyeing habits of the sampled individuals (Figure 1) is significant ($LSD_{5\%}$= 3.87).
The concentration of Cu in hair of hair dryers was significantly higher on average than that of men who did not dye their hair (hair dryers: 14.37µg/g hair; hair non-dyers: 4.97µg/g hair).
As the ladies were the overall proportion of people who dye their hair so the trend was similar for the ladies in the past.
Further investigation is needed to determine whether the ladies had higher Cu levels in their hair because they dyed their hair or whether the ladies had higher Cu concentrations by design.
The statistical analysis (Table 11) showed that the Cu concentration in hair samples was significant ($LSD_{5\%}$= 7.54) according to the age of the samplers (Figure 1).
The highest hair sample concentrations were found in those aged between 20 and 30 years (1: 8.75µg/g hair; 2: 21.89µg/g hair; 3: 7.42µg/g hair; 4: 10.04µg/g hair; 5: 7.24µg/g hair).

Table 10: Cu concentration variance table for hair dyeing

Factor	SQ	df	MQ	F	Sig.	$LSD_{0.5}$
Modell	1167.044	2	583.522	12.019	0.000	
Correction Factor	4938.803	1	4938.803	101.724	0.000	
Residence	1165.376	1	1165.376	24.003	0.000	3.866
Repeat	10.168	1	10.168	0.209	0.649	
Error	2427.559	50	48.551			
Total	8485.368	53				
Corrected total	3594.603	52				

Table 11. Cu concentration variance table by age

Factor	SQ	df	MQ	F	Sig.	$LSD_{0.5}$
Modell	1077.293	5	215.459	4.023	0.004	
Correction Factor	5531.923	1	5531.923	103.285	0.000	
Residence	1075.625	4	268.906	5.021	0.002	7.542
Repeat	4.874	1	4.874	0.091	0.764	
Error	2517.309	47	53.560			
Total	8485.368	53				
Corrected total	3594.603	52				

Changes in selenium concentration values in hair samples
Selenium concentrations (Figure 2) are relatively low in all except three samples from Csepel ("A1", "A2" and "A3"). A1 is 0.42 µg/g, A2 is the highest at 1.06 µg/g and A3 is 0.27 µg/g.
Apart from the three outliers, the average of the different samples labelled "A" is 0.059 µg/g. The overall average is 0.17 µg/g.
The control samples all show very low selenium concentrations with none of them reaching 0.2 µg/g.
On average, 0.05 µg/g selenium is found in the “Erzsébet” hair samples.
Statistical analysis (Table 12) shows that the Se concentration in hair samples by residence (Figure 2) is significant ($LSD_{5\%}$= 0.117). Se concentrations in the hair of Csepel and Elisabeth residents are significant, on average (A: 0.186 µg/g hair; K: 0.056 µg/g hair).
Based on statistical analysis (Table 13), the Se concentration in hair samples was significant ($LSD_{5\%}$= 0.117) according to the sex of the samplers (Figure 2).

On average, Se concentration in hair of women is significantly higher than in hair of men (women: 0.150 µg/g hair; men: 0.065 µg/g hair).
Based on statistical analysis (Table 14), Se concentrations in hair samples were significant ($LSD_{5\%}$= 0.163) according to the smoking habits of the sampled individuals (Figure 2).

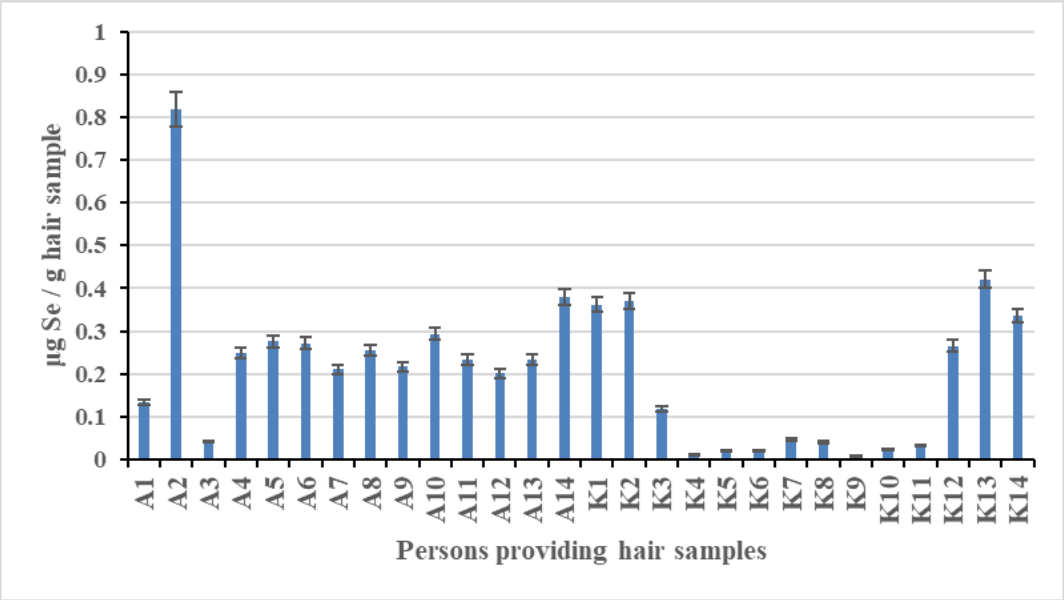

Figure 2. Se concentration changes in hair samples
Table 12. Se concentration variance table by residence

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.226	2	0.113	2.565	0.087	
Correction Factor	0.774	1	0.774	17.578	0.000	
Residence	0.222	1	0.222	5.049	0.029	0.117
Repeat	0.005	1	0.005	0.109	0.742	
Error	2.203	50	0.044			
Total	3.184	53				
Corrected total	2.429	52				

Statistical analysis (Table 15) showed that the Se concentration in hair samples was significant ($LSD_{5\%}$= 0.119) according to the hair dyeing habits of the sampled individuals (Figure 2). The Se concentration in the hair of hair dryers is significantly higher on average than that of men who do not dye their hair (hair dryers: 0.172 µg/g hair; hair non-dyers: 0.069 µg/g hair).

Table 13. Se concentration variance table by gender

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.092	2	0.046	0.982	0.381	
Correction Factor	0.561	1	0.561	11.996	0.001	
Residence	0.088	1	0.088	1.888	0.176	0.117
Repeat	0.001	1	0.001	0.030	0.864	
Error	2.337	50	0.047			
Total	3.184	53				

Corrected total	2.429	52				

Table 14. Se concentration variance table for smoking habit

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.100	2	0.050	1.074	0.349	
Correction Factor	0.837	1	0.837	17.959	0.000	
Residence	0.096	1	0.096	2.071	0.156	0.163
Repeat	0.002	1	0.002	0.052	0.820	
Error	2.329	50	0.047			
Total	3.184	53				
Corrected total	2.429	52				

Statistical analysis (Table 16) showed that the Se concentration in hair samples was significant ($LSD_{5\%}$= 0.195) according to the age of the samplers (Figure 2). The highest hair sample concentrations were found in those aged between 20 and 30 years (1: 0.060 μg/g hair; 2: 0.417 μg/g hair; 3: 0.063 μg/g hair; 4: 0.040 μg/g hair; 5: 0.120 μg/g hair).

Table 15. Se concentration variance table for hair dyeing

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.146	2	0.073	1.596	0.213	
Correction Factor	0.768	1	0.768	16.828	0.000	
Residence	0.142	1	0.142	3.112	0.084	0.119
Repeat	0.002	1	0.002	0.033	0.856	
Error	2.283	50	0.046			
Total	3.184	53				
Corrected total	2.429	52				

Table 16. Se concentration variances table by age

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.651	5	0.130	3.439	0.010	
Correction Factor	0.887	1	0.887	23.445	0.000	
Residence	0.647	4	0.162	4.275	0.005	0.195
Repeat	0.002	1	0.002	0.052	0.820	
Error	1.778	47	0.038			
Total	3.184	53				
Corrected total	2.429	52				

Changes in iron concentration values in hair samples

The Figure of the iron concentration (Figure 3) shows that there is an exceptionally high value of around 980 ± 26.45µg/g among the hair samples from Csepel; this is sample "A13". The other samples from Csepel vary between 97µg/g and 6µg/g.

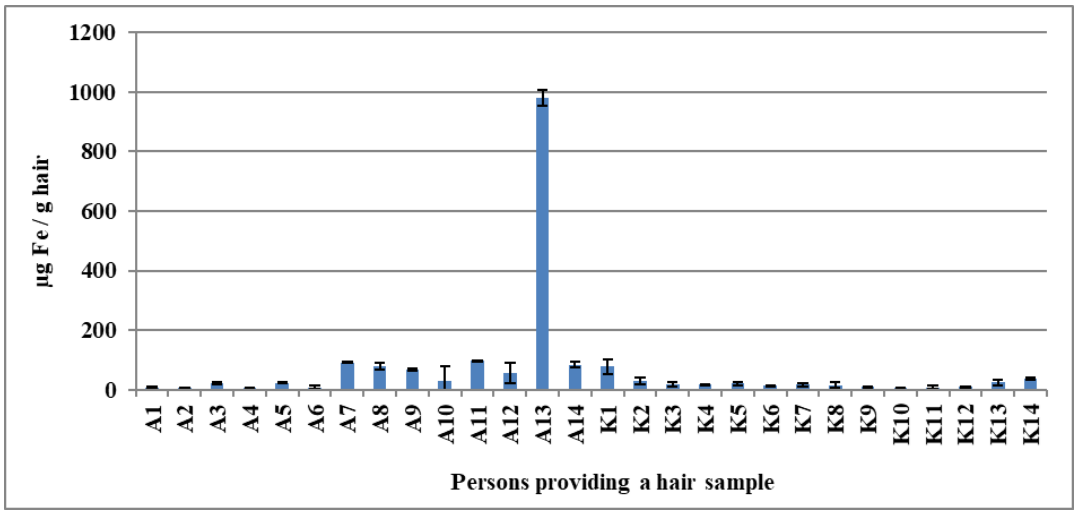

Figure 3. Changes in Fe concentration in hair samples

The average of these is 62.71µg/g, excluding the outlier. For the control samples, there is no outlier with the highest value being 77µg/g, the other values are all below this value, the lowest of which is 5µg/g. The average for the control samples is 22.05 µg/g. The statistical analysis (Table 17) shows that the Fe concentration in hair samples by residence (Figure 3) is not significant ($LSD_{5\%}$= 118.218). The Fe concentration in the hair of Csepel residents is higher than that of „Erzsébet" residents, on average (A: 137,040/g hair; K: 19,600µg/g hair).

Table 17. Table of variance of Fe concentration by residence

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	160369.777	2	80184.888	2.204	.122	
Correction Factor	283943.173	1	283943.173	7.803	.008	
Residence	160191.399	1	160191.399	4.402	.042	118.218
Repeat	56.422	1	56.422	.002	.969	
Error	1601055.315	44	36387.621			
Total	2005094.027	47				
Corrected total	1761425.092	46				

Statistical analysis (Table 18) shows that the Fe concentration in hair samples is significant ($LSD_{5\%}$= 102.896) according to the gender of the samplers (Figure 3). The Fe concentration in women's hair is significantly lower on average than in men (women: 26.929µg/g hair; men: 138.415µg/g hair).
Based on statistical analysis (Table 19), the Fe concentration in hair samples was significant ($LSD_{5\%}$= 118.218) according to the smoking habits of the sampled individuals (Figure 3).
Based on statistical analysis (Table 20), the concentration of Fe in hair samples is significant ($LSD_{5\%}$= 120.496) according to the hair dyeing habits of the sampled individuals (Figure 3). The Fe concentration in the hair of non-dyers was significantly higher on average than that of men who dye their hair (hair dryers: 21.384µg/g hair; non-dyers: 113.190µg/g hair).
Based on statistical analysis (Table 21), the Fe concentration in hair samples was significant ($LSD_{5\%}$= 196.030) according to the age of the samplers (Figure 3). The highest concentration of Fe in hair

samples was found in those aged 50 years and over (1: 37.045µg/g hair; 2: 20.801µg/g hair; 3: 28.544µg/g hair; 4: 28.378µg/g hair; 5: 172.808µg/g hair)

Table 18. Table of variance of Fe concentration by gender

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	142538.675	2	71269.337	1.937	0.156	
Correction Factor	311315.068	1	311315.068	8.461	0.006	
Residence	142360.297	1	142360.297	3.869	0.056	102.896
Repeat	1815.728	1	1815.728	0.049	0.825	
Error	1618886.417	44	36792.873			
Total	2005094.027	47				
Corrected total	1761425.092	46				

Table 19. Table of variance of Fe concentration by smoking habit

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	160369.777	2	80184.888	2.204	0.122	
Correction Factor	283943.173	1	283943.173	7.803	0.008	
Residence	160191.399	1	160191.399	4.402	0.042	118.218
Repeat	56.422	1	56.422	0.002	0.969	
Error	1601055.315	44	36387.621			
Total	2005094.027	47				
Corrected total	1761425.092	46				

Table 20. Table of variance of Fe concentration for hair dyeing

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	98071.317	2	49035.658	1.297	0.284	
Correction Factor	209579.049	1	209579.049	5.544	0.023	
Residence	97892.939	1	97892.939	2.590	0.115	120.496
Repeat	321.197	1	321.197	0.008	0.927	
Error	1663353.775	44	37803.495			
Total	2005094.027	47				
Corrected total	1761425.092	46				

Table 21. Table of variance of Fe concentration by age

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	203569.754	5	40713.951	1.072	0.390	
Correction Factor	139850.264	1	139850.264	3.681	0.062	

Residence	203391.377	4	50847.844	1.338	0.272	196.030
Repeat	32.309	1	32.309	0.001	0.977	
Error	1557855.338	41	37996.472			
Total	2005094.027	47				
Corrected total	1761425.092	46				

Changes in cadmium content in hair samples

The samples from Csepel contained higher levels of cadmium than those from Erzsébet. The highest levels were found in samples "A1" and "A11", both above 0.15µg/g. The average for the Csepel samples was 0.07µg/g and for the Erzsébet samples 0.02µg/g. Among the "Erzsébet" samples, only one with the "K7" symbol is above 0.15 µg/g. Statistical analysis (Table 24) shows that the Cd concentration of hair samples by residence (Figure 9) is not significant (SD5%=0.044). On average, Cd concentrations are higher in the hair of „Erzsébet" residents (A: 0.068 µg/g hair; K: 0.022µg/g hair).

Statistical analysis (Table 22) showed that the Cd concentration in hair samples was significant ($LSD_{5\%}$=0.040) according to the gender of the sampled individuals (Figure 4). The Cd concentration in hair of women is significantly higher on average than in hair of men (women: 0.044 µg/g hair; men: 0.043 µg/g hair).

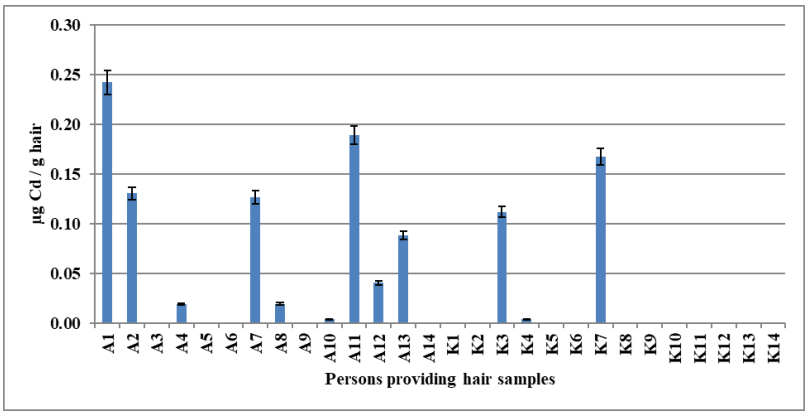

Figure 4. Changes in cadmium content in hair samples

Based on statistical analysis (Table 23), the Cd concentration in hair samples was significant ($LSD_{5\%}$= 0.062) according to the smoking habits of the sampled individuals (Figure 4). Smokers (0.058 µg/g, non-smokers (0.039µg/g). Based on statistical analysis (Table 24), Cd concentrations in hair samples according to hair dyeing habits of the sampled individuals (Figure 4) are significant ($LSD_{5\%}$= 0.046) in non-dyeing hair in men (hair dryers: 0.056 µg/g hair; non-dyers: 0.033 µg/g hair).

Extensive hair sampling was carried out in Beijing [21], using only samples of men and women with undyed hair. A common element in the studies conducted there was Cd. Comparing our results, we can say that the Cd content of the hair samples is of similar magnitude. We also came to almost similar conclusions in terms of age classification. Statistical analysis (Table 25) showed that the Cd concentration in hair samples was significant ($LSD_{5\%}$= 0.080) according to the age of the samplers (Figure 4). The highest hair sample concentrations were found in those aged between 20 and 30 years (1: 0.075 µg/g hair; 2: 0.038 µg/g hair; 3: 0.000026 µg/g hair; 4: 0.031 µg/g hair; 5: 0.065 µg/g hair).

Table 22. Cd concentration variance table by residence

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.029	2	0.015	2.337	0.107	
Correction Factor	0.108	1	0.108	17.285	0.000	

Residence	0.029	1	0.029	4.672	0.035	0.044
Repeat	8.26E-005	1	8.26E-005	0.013	0.909	
Error	0.319	51	0.006			
Total	0.452	54				
Corrected total	0.348	53				

Changes in manganese content in hair samples

The average value of manganese content in the sample labelled "A" is 0.6788 μg/g and in the sample labelled "K" 0.1817 μg/g. The highest Mn concentration was measured in sample A4 with 2.6187 μg/g. Samples "A1" to "A3" also had values above 1 μg/g. "Samples 'A5' to 'A14' were all below 1 μg/g.

Table 23. Cd concentration variance table by gender

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	3.57E-005	2	1.78E-005	0.003	0.997	
Correction Factor	0.096	1	0.096	14.065	0.000	
Residence	2.93E-005	1	2.93E-005	0.004	0.948	0.040
Repeat	5.07E-006	1	5.07E-006	0.001	0.978	
Error	0.348	51	0.007			
Total	0.452	54				
Corrected total	0.348	53				

Table 24. Cd concentration variance table for smoking habit

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.004	2	0.002	0.272	0.763	
Correction Factor	0.097	1	0.097	14.397	0.000	
Residence	0.004	1	0.004	0.543	0.465	0.062
Repeat	1.41E-006	1	1.41E-006	0.000	0.989	
Error	0.345	51	0.007			
Total	0.452	54				
Corrected total	0.348	53				

Table 25. Cd concentration variance table for hair dyeing

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.007	2	0.003	0.512	0.602	
Correction Factor	0.106	1	0.106	15.802	0.000	
Residence	0.007	1	0.007	1.023	0.316	0.046
Repeat	1.95E-007	1	1.95E-007	0.000	0.996	
Error	0.342	51	0.007			
Total	0.452	54				
Corrected total	0.348	53				

Table 26. Cd concentration variance table by age

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.041	5	0.008	1.274	0.290	
Correction Factor	0.079	1	0.079	12.329	0.001	
Residence	0.041	4	0.010	1.593	0.191	0.080
Repeat	8.86E-005	1	8.86E-005	0.014	0.907	
Error	0.308	48	0.006			
Total	0.452	54				
Corrected total	0.348	53				

The concentration of Mn in the hair of women and men (women: 1.049 µg/g hair; men: 0.404 µg/g hair).

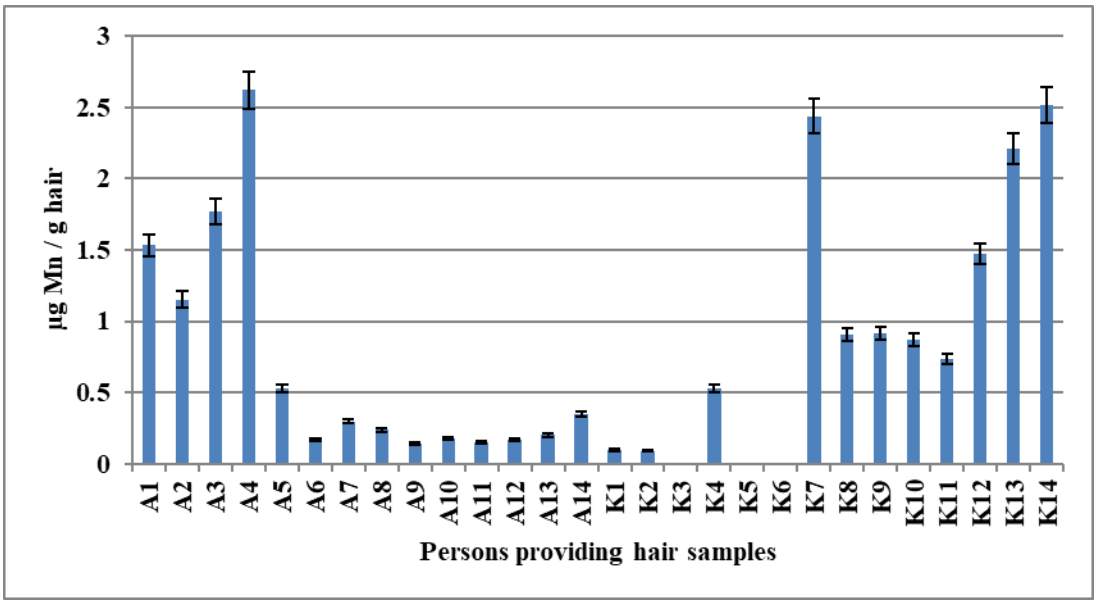

Figure 5. Changes in Mn concentration in hair samples

Table 27. Mn concentration variance table by residence

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.767	2	0.383	0.422	0.658	
Correction Factor	35.433	1	35.433	39.045	0.000	
Residence	0.761	1	0.761	0.838	0.364	0.508
Repeat	0.006	1	0.006	0.007	0.935	
Error	48.097	53	0.907			
Total	84.296	56				
Corrected total	48.863	55				

Table 28. Mn concentration variance table by gender

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	5.555	2	2.777	3.399	0.041	
Correction Factor	28.191	1	28.191	34.499	0.000	
Residence	5.549	1	5.549	6.790	0.012	0.622
Repeat	0.006	1	0.006	0.008	0.931	
Error	43.308	53	0.817			
Total	84.296	56				
Corrected total	48.863	55				

Based on statistical analysis (Table 29), the concentration of Mn in hair samples was significant ($LSD_{5\%}$=0.725) according to the smoking habits of the sampled individuals (Figure 5). Smokers (0.808 μg/g, non-smokers (0.791 μg/g). Based on statistical analysis (Table 30), Cd concentrations in hair samples according to hair dyeing habits of the sampled individuals (Figure 5) are significant ($LSD_{5\%}$= 0.526) in non-dyeing hair in men (hair dyers: 0.947 μg/g hair; non-dyers: 0.664 μg/g hair). Statistical analysis (Table 31) showed that the Cd concentration in hair samples was significant ($LSD_{5\%}$= 0.975) according to the age of the samplers (Figure 5). The highest hair sample concentrations were found in those aged between 20 and 30 years (1: 0.816 μg/g hair; 2: 1.150 μg/g hair; 3: 0.611 μg/g hair; 4: 0.878 μg/g hair; 5: 0.777 μg/g hair).

Table 29. Mn concentration variance table for smoking habit

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	0.009	2	0.004	0.005	0.995	
Correction Factor	26.844	1	26.844	29.122	0.000	
Residence	0.003	1	0.003	0.003	0.957	0.725
Repeat	0.006	1	0.006	0.007	0.935	
Error	48.854	53	0.922			
Total	84.296	56				
Corrected total	48.863	55				

Table 30. Mn concentration variance table for hair dyeing

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	1.127	2	0.563	0.625	0.539	
Correction Factor	36.155	1	36.155	40.142	0.000	
Residence	1.121	1	1.121	1.244	0.270	0.526
Repeat	0.006	1	0.006	0.007	0.935	
Error	47.737	53	0.901			
Total	84.296	56				

Corrected total	48.863	55				

Table 31. Mn concentration variance table by age

Factor	SQ	df	MQ	F	Sig.	$LSD_{5\%}$
Modell	1.302	5	0.260	0.274	0.925	
Correction Factor	33.288	1	33.288	34.994	0.000	
Residence	1.296	4	0.324	0.341	0.849	0.975
Repeat	0.006	1	0.006	0.006	0.936	
Error	47.561	50	0.951			
Total	84.296	56				
Corrected total	48.863	55				

CONCLUSIONS AND RECOMMENDATIONS

In the case of heavy metal contaminants analyzed from a residential point of view, all the substances analyzed were present in higher concentrations in the Csepel area than in the "Erzsébet" area, except for copper and manganese. These were selenium, iron and cadmium, shown in Tables 14, 19 and 24. This may be due to Csepel's history in the manufacturing industry. From the late 1800s onwards, there was extensive metal processing in the area, from which the people living here could have benefited.

In terms of age groups, most heavy metals accumulated in the bodies of people aged between 20 and 30. This may be due to unhealthy lifestyles or to the large-scale development of industry and transport.

When looking at the gender distribution, only iron concentrations were higher in men than in women. For men, this may be due to occupational pollution. For women, it is due to the high use of various cosmetics. Concentrations of manganese, cadmium and copper were compared with measurements in other literature. Their measurement results were of the same order of magnitude as ours. One of the articles is about the analysis of heavy metals accumulated in the bodies of people living in the environment of an electronic waste recycling area [22] The other one was about the accumulation in the occupational environment [23] Therefore, together with the measured results, we conclude that people living in the area of Csepel Works, including people living and working in Csepel, are more contaminated with heavy metals than people living in other cities. Studies by Salih and Aziz [24] also showed that workers in contaminated areas had higher concentrations of different heavy metals in their hair. Our suggestions are the next:

- Regular testing of soil and groundwater in Csepel.
- Investigate the heavy metal exposure of workers in the current Csepel Works area and reduce or eliminate the causes of exposure.

It would be advisable to carry out a future study of heavy metals in the Danube sludge surrounding the island of Csepel. This would show how much heavy metal has been released from the Csepel Works into the Danube over the years.

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