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ENVIRONMENTAL AND OCCUPATIONAL EXPOSURE TO Cr, Cu, Pb AND Zn OF POPULATION IN BAIA-MARE USING AS INDEX THE ABSORPTION OF CONTAMINANTS IN HAIR

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ABSTRACT. The extent of environmental and professional exposure to Cr, Cu, Pb and Zn as a result of the industrial activity in the Baia-Mare area was investigated. The environmental exposure was estimated through the metal content in hair samples from five children aged between 7 and 13 years, while the occupational exposure was assessed on 5 adults between 40-70 years. The alert and intervention levels of Cu, Pb and Zn and sometimes Cr in soil were many fold exceeded but in hair only Pb was suited to evaluate the risk to exposure as it was much over the normal value. It has been found an accumulation of Pb in hair with age, but children are a more useful tool for epidemiological assessment of environmental exposure to toxic elements. In high polluted area such as Baia-Mare, the Pb level in hair is less influenced by the distance of the residential zone from polluter and more dependent on people's age. Results underline the relevance of health care preventive measures for children, who are the most sensitive groups to pollution.

INTRODUCTION

Monitoring trace elements in human body is of great concern as their changes can be used as an index of the excess or deficiency of specific nutrients in the diet or as an index of the absorption of contaminants from environment. The levels of trace elements in the human body are often evaluated in blood, urine, hair and tissues [1, 2]. Although blood and urine analysis are the most traditional approaches to evaluate trace element levels in the human body, hair can provide a more permanent record of these elements associated with normal and abnormal metabolism as well as trace elements assimilated from the environment. In addition, hair is easily collected and stored and can be easily digested [3,4]. Various factors influence the level of elements in hair, such as residence place [5], sex and hair color [6], age [7], occupational exposure [8] and hair dyeing. Many authors [9,10] believe that examining hair is a good non-invasive method, which should be used in screening studies of children living in heavily polluted areas. Thus, Jenkins [11] and Chlopicka et al. [12] consider that hair is a material ideally suited to the biological monitoring of As, Cd, Cr, Pb and Hg.

The aim of the study was to investigate the extent of Cr, Cu, Pb and Zn exposure via environmental pollution and occupational exposure as a result of the industrial activity in the Baia-Mare area. To evaluate the exposure to environmental pollution, we determined the metal content in hair samples from children, while the occupational exposure was assessed on adults working or having worked in the processing of non-ferrous ores. The subjects were selected to have different residential locations in Baia-Mare in order to study the relationship between exposure and distance from the polluter in a high-polluted environment. For correlation, heavy metals were also determined in interstitial water and soil samples collected from different locations.

The town of Baia-Mare is situated in a depression in north-west Romania, bordered on the east by a mountain chain and with a wind direction from east to west. At the beginning of the 14^{th} century several foundries were established in the neighborhood to process non-ferrous ores extracted from the mountains in the region. These foundries were unified in 1884 in new plant in the northeastern side of the town, known after 1990 as the Romplumb Company. Nowadays, the main activity of the plant is production of free-copper lead and copper matte by roasting non-ferrous ores. After 1907 another plant under the name of Phoenix Company situated in the south-east of the town was established to produce sulfuric acid, electrolytic copper, lead sheet and tubes, lead oxides, silver and gold ingots. Residual sulphurous gases resulted from the processing of non-ferrous ores are evacuated in the atmosphere through high chimneys. Although the sulphurous gases containing SO_2, SO_3, fog of sulfuric acid are purified during the chemical process, they still contain both traces of heavy metals, especially Cu, Pb, Zn and Cd. Thus, airborne particulate matters deposit and consequently generate pollution with inorganic heavy metal compounds non only in the proximity of the industrial site but also in the town and its surroundings [13]. Previous studies [14, 15] showed a significant pollution with Pb, Zn, Cu, Cd as oxides, carbonates, sulfates, sulfides and silicates of soil collected in Baia-Mare. The sulfides are accumulated in soil and their content in the surface layer in the proximity of the polluting sources is comparable to that of some ores. Generally, for all species, the content decreases with the distance from the polluting source. Thus, these two industrial units became the main polluters of the town for almost a century, with a peak between 50's and early 90's. To these two polluters it should be added the Central Flotation Station situated in the south east of the town and the tailings deposited around it.

Besides industrial pollution by smelting activity there is a continual environmental exposure especially to lead generated by the car traffic. Human exposure occurs mainly through oral (drinking water, food), inhalative and dermal pathways. Lead from environmental pollution is not carcinogenic but even low dose exposure has been shown to have detrimental and long-lasting effects on the renal homeopoetic and nervous system.

EXPERIMENTAL

Apparatus

A scanning inductively coupled plasma atomic emission spectrometer (ICP-AES) SPECTROFLAME type (Spectro Analytical Instruments, Kleve, Germany) was employed (Table 1).

Table 1.

Operating conditions for the SPECTROFLAME ICP -AES

Equipment	Characteristics
Generator	Free – running 27.12 MHz, manually controlled power level between 750 – 1400 W, 1200 W in this experiment.
Plasma torch	Water-cooled copper induction coil inductively coupled plasma, radial viewing through an optical fiber for the VIS range and 8 optical fibers for the UV range (10 μm wide), observation height 15 mm.

Equipment	Characteristics
	Ar flow rates: - Outer gas 12 L min^{-1}. - Intermediate gas 0.6 L min^{-1}. - Nebulizer gas 1 L min^{-1}.
Torch cooler system	Cooling water without automated control of the temperature.
Sample introduction system	2 channel peristaltic pump, 2 mL min^{-1} solution up-take rate, concentric nebulizer Meinhardt type K (TR-30-K3), double pass Scott type spray chamber mounted in a thermostated room controlled by the computer.
Optics	Double scanning monochromator. UV range 160 – 336 nm chamber filled with high purity nitrogen, grating with 3600 lines mm^{-1}, focal length 750 mm, thermostated at 15 ± 0.5 ^{0}C, entrance slit width 15 µm, resolution 15 pm. Vis range 335 – 800 nm, grating with 2400 lines mm^{-1}, focal length 750 mm, thermostated at 15 ± 0.5 ^{0}C, resolution 15 pm. Optical detector: 9781 R photomultiplier tube supplied at 1000 V (Thorn EMI, Ruislip, Middlesex, UK).
Data processing	Soft: Smart Analyzer, Pentium III CPU 450 MHz, background correction two points linear model, integration time 10 s, 3 successive measurements for each sample.

Reagents and standard solutions

The stock solutions (1000 µg mL^{-1}) of the elements determined in this study (Cr, Cu, Zn, Pb) were prepared from high purity metals. Amounts of 1.0000 g powder were dissolved in 1+1 HNO_3 (Cu, Pb and Zn) or in 1+1 HCl (Cr) and filled up to 1 L with 2 % (v/v) HNO_3. All solutions were prepared using analytical-grade reagents (Fluka-Germany) and double distilled water.

Preparation of calibration standards

Dilution of the most concentrated multielement standard solution in order to prepare the lower concentration solutions is not permitted because of unknown error propagation. The analytes concentrations ought to be distributed randomly in such a way that the overall analyte concentration is approximately constant in all solutions. Ideally, the analyte concentrations should lie between a half and two-fold the concentration of real samples. In order to correct drifts and fluctuations of the spectral device during calibration and sample measurement the external standardization (recalibration) was used after the analysis of each sample. The external standard used for this purpose had a concentration corresponding to the medium calibration standards for each analyte. To each standard solution the acid amounts used for hair samples digestion (25 mL 65% HNO_3 and 5 mL 80% $HClO_4$) were added for a final volume of 50 mL. The dilution was made with 2% HNO_3 (v/v). The same solution without analytes was used as blank. A list of Cr-Cu-Zn-Pb calibration solutions used in this investigation is given in Table 2.

Table 2.

Calibration standards for Cr-Cu-Zn-Pb

	Blank*	STD 1	STD 2	STD 3	STD 4	STD 5
Element	Concentration / µg mL^{-1}					
Cr	0	0.020	0.005	0.030	0.010	0.040
Cu	0	0.6	0.2	0.5	0.4	0.1
Zn	0	0.5	2	4	6	8
Pb	0	2.0	1.2	0.8	0.4	0.2

* 25 mL 65 % HNO_3, 5 mL 80% $HClO_4$ diluted to 50 mL with 2% HNO_3 (v/v)

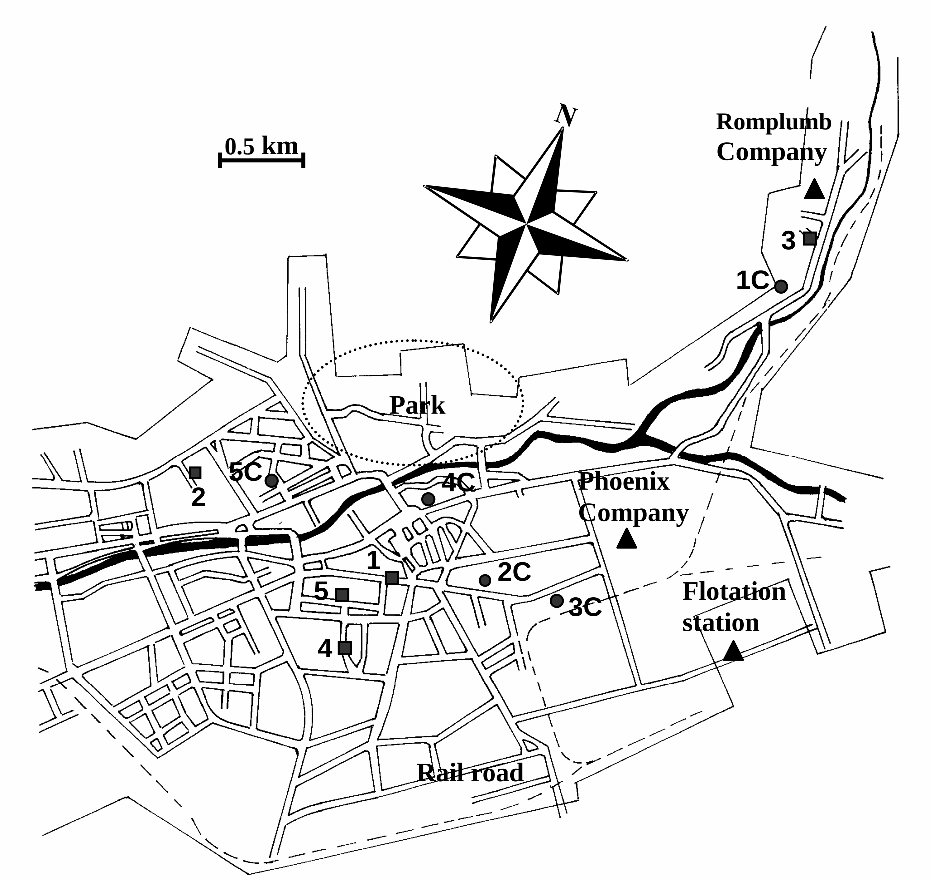

Fig. 1. Residence of subjects in the Baia-Mare town
- • children
- ▪ adults

Hair samples collection and digestion procedure

The subjects involved in this study live in Baia-Mare near Romplumb and Phoenix Companies as well as in the center of the town and next to the park (Fig. 1). Human hair samples were collected in hairdressing establishments from 10 persons, 5 children aged between 7-13 years and 5 men aged between 40-70 years. The adult subjects have been living at their residence for at least 30 years, while children from birth. Adults admitted to be or to have been subjects of an occupational exposure to heavy metals. Hair samples were taken from various parts of the scalp, 1 – 1.5 cm measured from the root and cut to 2 – 5 cm long using a stainless-steel scissors. The collected samples were stored in bags in a cool and dry place until analysis. The adult donors were asked to fill out a detailed questionnaire concerning age, address, occupation, smoking habits.

Hair samples were washed threefold with acetone, then with double distilled water and dried at a temperature between 40 - 60℃. After drying, an amount of 1.0000 g of each hair sample was placed in a 150 mL Pyrex glass with cover and soaked with 25 mL 65% HNO_3 overnight at room temperature. Afterwards, the sample was heated at 120℃ and kept at this temperature fo r about 5 – 6 h until fading of solution. After cooling, 5 mL of 80 % $HClO_4$ were added and the solution was heated again at 120℃ for 2 h. The residue was trans ferred in a 50 mL volumetric flask and the volume was adjusted with 2 % HNO_3 (v/v), then filtrated. The blank solution was subjected to the same procedure.

Limits of detection for Cr, Cu, Zn and Pb in hair by ICP-AES

Table 3 presents the limits of detection (LODs) for Cr, Cu, Zn and Pb (3σ) by ICP-AES in human hair samples. The LODs were calculated in $\mu g\ g^{-1}$ dry mass taking into account the amount of hair sample and the dilution factor.

Table 3

Limits of detection for Cr, Cu, Zn and Pb by ICP-AES in human hair

	Cr	Cu	Pb	Zn
λ (nm)	283.563	324.754	283.307	213.586
LOD (ng mL^{-1})	0.2	2	30	4
LOD (μg g^{-1})*	0.01	0.1	1.5	0.2

* expressed in dry mass taking into account the amount of sample and the dilution factor

The method allows the quantitation of at least ($\mu g\ g^{-1}$): 0.05 Cr, 0.5 Cu, 7.5 Pb and 1.0 Zn.

Evaluation of soil and water pollution in the Baia-Mare area

Table 4 presents the total content of Cr, Cu, Zn and Pb in soil from different sites at 20 cm depth extracted in *aqua regia* and the leachable content in water, while Table 5 indicates the contents of these elements in the interstitial water in soil at the same depth.

Table 4

Mean results ±s of heavy metals in soil at 20 cm depth determined by ICP-AES (n= 3 successive measurements)

Area	Cr	Cu	Zn	Pb
	Aqua regia extractable contents (mg Kg^{-1})			
Around Romplumb	294±20	8320±330	21400±360	41242±829
	457±32	4154±130	5760±130	17090±230
	84±13	21647±420	14720±330	26112±860
Around Phoenix	300±5	31200±540	11586±310	12800±300
	595±26	9503±1400	54000±3100	10509±2400
	349±18	22490±520	9805±300	14195±300
Park	75±10	257±32	418±28	320±193
	19±5	314±33	444±29	366±19
Town Center	388±14	607±43	1333±47	1503±70
	434±26	593±40	514± 36	2560±44
	130±15	609±40	1086± 80	920±50
	Water leachable contents (mg Kg^{-1})			
Town Center	< 0.02	45±5	433±36	526±44
Alert/Intervention limits for sensitive soils	100/300	100/200	300/600	50/100

Table 5

Content of heavy metals in interstitial water (mg L^{-1}) at 20 cm depth determined by ICP-AES (n= 3 successive measurements)

	Cr	Cu	Zn	Pb
	mg L^{-1}			
Interstitial water	< 0.0002	0.10	0.10	0.16
Maximum admitted level (STAS 4706/88)	0.05	0.05	0.03	0.05

According to data in Table 4, soil is highly polluted with Cu, Zn and Pb especially around the Romplumb and Phoenix Companies, where the alert and intervention limits are much exceeded. Although the amounts of these metals are lower in soils collected from the town and the park, here also the limits are many fold surpassed. In the case of Cr, both the alert and intervention limits are exceeded around Phoenix and Romplumb (2 samples), while in the town the amounts are higher than the alert limits. In the park area the Cr level in soil is not over the alert value. For all elements the lower contents were found in the park area.

The average level of water leachable metals in soils collected from the center of the town were (mg Kg^{-1}): 45 Cu, 433 Zn, 526 Pb and below 0.02 Cr. Thus, the levels of Cr and Cu were not over the alert limit, while that of Zn exceeded it 1.5 times and that of Pb was more than 5 times the intervention value. Copper, Zn and Pb exceeded approximately 2; 3 and 3 times respectively, the admitted level in surface water (Table 5).

The high level of heavy metals in soil and relatively high level of Cu, Zn and Pb in water represent a high pollution of all environment compartments and a risk to long-time exposure of population in Baia-Mare via oral, dermal and inhalative pathways.

Levels of Cr, Cu, Zn and Pb in human hair of individuals in Baia-Mare area

The mean results and standard deviations (n = 3 successive measurements) for hair samples collected from 10 subjects are shown in Table 6.

Table 6

Mean results ±s ($\mu g\ g^{-1}$) in human hair analyzed by ICP-AES (n= 3 successive measurements)

Sample	Age/ years	Smoking habits	Occup. exposure	Cr	Cu	Zn	Pb
5 C	7	-	-	0.96±0.26	10.53±0.42	114.5±3.5	27.92±5.96
3 C**	7	-	-	0.52±0.29	10.83±0.33	188.6±7.4	23.14±5.85
2 C**	8	-	-	< 0.03	12.56±0.24	235.9±9.3	25.72±6.35
4 C	10	-	-	1.14±0.34	12.81±0.51	169.7±8.3	30.82±7.2 3
1 C*	13	-	-	< 0.03	11.05±0.25	129.6±5.2	27.15±7.12
1	40	yes	yes	< 0.03	12.28±0.42	133.1±5.3	28.50±4.25
4	44	yes	yes	0.65±0.23	15.65±0.27	79.6±2.6	33.37±5. 24
5	54	no	yes	1.12±0.31	11.52 ±0.43	141.2±9.5	28.47±6 .93
2	55	yes	yes	< 0.03	10.12±0.36	130.2±1.4	34.12±4.48
3*	70	no	yes	1.05±0.25	10.16±0.24	129.4±1.2	43.07±2.38
Normal values in human hair (group of 21 persons) [16]				0.814±0.401	11.54±1.237	171.1±41.16	4.476±7.295

* residence next to Romplumb; ** residence next to Phoenix; the others in the center and next to the park

According to data in Table 6, only the contents of Pb, a toxic element, are much over the normal values, while Zn, Cu and Cr are close to normal values in human hair. Thus, the average content of Zn was 145.2±6.2 $\mu g\ g^{-1}$, with higher values for children as compared to adults. Hair Zn concentrations were lower in anorexic patients (adult 44 years, 79.6±2.6 $\mu g\ g^{-1}$; one of the two children of 7 years, 114.5±3.5 $\mu g\ g^{-1}$). The average content of Cu was 11.75±0.36 $\mu g\ g^{-1}$, while that of Cr was 0.91±0.29 $\mu g\ g^{-1}$ and there was no significant difference between the concentration levels for adults and children. The results were in good agreement with those reported in literature [17,18].

Although there is an advanced pollution with Cu and Zn in the Baia-Mare area, the levels of these metals in hair do not reflect it and consequently they can not be employed as an index of the exposure assessment. Copper, Zn and Cr are considered to be essential elements for organism and their levels are influenced by diet and health status. The level of Cr in hair could be a good indicator for occupational exposure to chromate but it was not the case of our subjects.

The average level of Pb was 30.23±5.76 µg g^{-1} with an almost systematic increase with age revealed by the difference between children and adults values attributed to the supplementary occupational exposure of adults besides the indirect exposure of children to environmental pollution. In the case of children, the average Pb level was 26.95±6.53 µg g^{-1}, six fold higher than the normal value. For adults, 30-45 years after childhood age, Pb accumulation in hair was only up to 1 fold the normal value. Our results exhibited also a more accentuated Pb accumulation for individuals over 60 years compared to those of medium age, similarly with As accumulation [19]. Thus, in the case of the 70 years old subject, the accumulation index was 2.7 fold the normal value (4.476) in the last 15 years of life. Therefore, in this study the Pb content in children's hair was found to be a useful tool in the environmental study of pollution and epidemiological purposes. However, the permanent stay of people in the highly polluted areas causes an accumulation of Pb in hair that represents a risk factor of morphofunctional abnormalities and chronic diseases. From this point of view, hair analysis seems to be a useful tool for epidemiological assessment of environmental exposure to toxic elements (Pb) and occupational exposure. In high polluted area such as Baia-Mare, the Pb level in hair is less influenced by the location of residential zone relative to polluter and more dependent on the age. These results underline the relevance of health care preventive measures for children, who are the most sensitive groups to pollution.

REFERENCES

1. K. Bencze, *Fresenius' J Anal Chem*, **1990**, *337*, 867-876.
2. K. Bencze, *Fresenius' J Anal Chem*, **1990**, *338*, 58-61.
3. P. Bermejo-Barrera, A. Moreda-Pineiro, T. Romero-Barbeito, J. Moreda-Pineiro, A. Bermejo-Barrera, *Talanta*, **1996**, *43*, 1099-1107.
4. J.E. Tahan, V.A. Granadillo, R.A. Romero, *Anal. Chim. Acta*, **1994**, *295*, 187-197.
5. Y. Takagi, S. Matsuda, S. Imai, Y. Ohmuri, T. Masuda, J.A. Vinson, M.C. Mehra, B.K. Puri, A. Kaniewski, *Bull. Environ. Contam. Toxicol*., **1986**, *36*, 793-800.
6. V. Valkovic, "Trace Elements in Hair", CRC Press, Boca Raton, Fl, 1988.
7. D.C. Paschal, E.S. DiPietro, D.L. Phillips, E.W. Gunter, *Environ. Res*., **1989**, *48*, 17-28.
8. I.A. Randall, R.S. Gibson, *Br. J. Ind. Med.,* **1989**, *46*, 171-175.
9. A.A.E. Wibowo, R.F.M. Herber, H.A. Das, N. Roeleveld, R.L. Ziehuis, *Environ. Res*., **1986**, *40*, 346-356.
10. N. Limic, V. Valkovic, *Bull. Environ. Contam. Toxicol.*, **1986**, *37*, 925-930.
11. D.W. Jenkis, "Toxic Trace Metals in Mammalian Hair and Nails", EPA ReportNo. 600/4-79-049, 1979.
12. J. Chlopicka, P. Zagrodzki, Z. Zachwieja, M. Krosniak, M. Folta, *Analyst*, **1995**, *120*, 943-945.
13. E. Cordos, R. Rautiu, C. Roman, M. Ponta, T. Frentiu, A. Sarkany, L. Fodorpataki, K. Macalik, C. McCormick, D. Weiss, *Eur. J. Mineral. Proc. Environ. Prot.* **2003**, *3*, 324-335.
14. T. Frentiu, M. Ponta, A.M. Rusu, S.D. Anghel, A. Simon, E.A. Cordos, *Anal. Lett.,* **2000***,* *33*, 323-335.
15. E.A. Cordos, T. Frentiu, A.M. Rusu, G. Vatca, *Analyst*, **1995**, *120*, 725-731.
16. Y. Ren, Z. Zhang, Y. Ren, W. Li, M. Wang, G. Xu, *Talanta*, **1997**, *44*, 1823-1831.
17. X. Dong, Y. Nakaguchi, K. Hiraki, *Analytical Sciences*, **1998**, *14*, 785-789.
18. F. Watt, J. P. Landsberg, J. J. Powell, R. J. Ede, R. P. H. Thompson, J. A. Cargnello, *Analyst*, **1995**, *120*, 789-791.
19. G. Bozsai, *Microchem. J*., **1992**, *46*, 159-166.