Heavy Metals in Human Hair and Teeth

The Correlation with Metal Concentration in the Environment

BARBARA NOWAK^{*,1} AND HENRYK KOZLOWSKI²

'Silesian University of Medicine, Department of Toxicology, 41-200 Sosnowiec, St. 4 Jagiellor~ska, Poland; and 2University of Wroclaw, Institute of Chemistry, Str. 14, Joliot-Curie 14, 50-383 Wroclaw, Poland

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ABSTRACT

Biological samples were collected simultaneously with environmental quality investigations. Studies of metal levels in biological (hair and teeth) and environmental (soil and air) samples were performed in Zwardoń during 1991/1992. Zwardoń is a small mountain resort village, situated on the border pass of Zwardon, in the close proximity of the southwestern border of Poland. Heavy metal levels in soil, air, and chemical metals forms in the soil were examined. Pearson's product correlation in soil (for total concentration of heavy metals and each chemical form) in hair and in teeth was calculated to investigate bioavailability of heavy metals in human organism. We received essential correlations simultaneously between: Pb vs Mn in exchangeable form of metal in soil, in teeth and in soil (total); Cd vs Zn and Mn vs Co in organically bound form in soil and in teeth and soil (total); and Cu vs Zn in all investigated samples (teeth, hair, soil total, and organically bound form in soil); Mn vs Co and Cr vs Mn in residual form in soil, in teeth, and in soil (total) and between Co vs Ni for hair, soil (total), and residual form in soil.

^{*}Author to whom all correspondence and reprint requests should be addressed.

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INTRODUCTION

The impact of heavy metals on biological systems has been widely studied *(1-3).* There are few studies establishing definite correlations between environmental quality and the state of health of the people *(4-8).*

Among many human tissues, human hair, bone, teeth, and nails can be used as a biomarkers of environmental burden of toxic metals *(3,6,7,9-13).*

The bioaccumulation of heavy metals in human hair and teeth is rather a complex process. Factors that influence bioaccumulation include: nourishment, chemical forms of the metal and their binding sites *(7),* age, sex, genetic inheritance, and environmental quality *(9).* Hair color is a variable that is responsible for a level of trace elements in hair and it is determined by the amount of melanin pigments in the cortex. Dark hair has higher amounts of these pigments than does blond or white hair. Many authors reported *(14)* that the Fe content of red hair was higher than that of blond or black hair, because it contained siderin pigments. The other differences were observed: blond hair contained less Zn (significantly) than black (for both sexes), brown, white, or red, and black hair had a lower content of Cd higher of Pb than other colors (for males). Cu is involved in the synthesis of melanin, and some authors give this as argument that color is independent of the concentration of this element in the hair, but Zn in hair does appear to vary with hair color and for other trace elements it is not as clear *(14).* The hair of boys contains higher levels of Pb and Cd (statistically significant) than the girls hair *(15).*

The amounts of metals in the hair in the studied non-industrial region of southern Poland are considerably lower in comparison to those estimated for the population living in the Silesian industry center *(10,16).* The analysis of metal content in the hair and teeth is expected to give different kinds of information, which can be used to predict the total environmental pollution in the region studied *(12).* This work attempts to establish the use of hair and teeth as the first approximation of "biomarkers," which can be used to determine the effect of the environment pollution on the biological objects. Both hair and teeth are easily available biological materials which could be used in biological trials to evaluate heavy metal pollution *(17-19).* Taking into consideration the similarity of histopathological structure of bones and teeth, the concentration of the metals in teeth can be used to estimate long-term environmental contaminants, the same as in bones *(14,20).* Bone Pb levels (tibia and patella) had a strong positive correlation with age *(21),* and in teeth, we can observe an increase in Pb levels with age, too *(16).* Jaworowski et al. *(22)* analyzed Pb, Cd, Zn, and Ca in human bones from the last five millennia. They reported stable level Zn and Cd during this time until it increased recently, and Pb was increased (the main source was via the gastrointestinal tract). Recently, problems of heavy metals intoxication have depended on industrialization level *(17).*

The major focus in these investigations is measurement of metals in biological markers (hair and teeth) and of some parameters in environment (heavy metals in soil, air, chemical form of metals in soil). It can result in obtaining information about the influence of the environment on body burden.

Zwardoń is a resort village, situated on the border pass of Zwardoń, in the close proximity of the southwestern border of Poland. The resort village has about 1400 inhabitants and contains no industrial centers. The wind for those regions shows the dominance of southwestern directions, and this may be reason for the transport of pollution emitted by the industrial plants of Třinec and Čadča (Slovakia). Local emission sources were: traffic exhaust (33 cars/hr), railway tracks, and domestic coal combustion. The average of the suspended dust in Cieszyn (situated 40 km from the north of Zwardon) in 1995 was 41 mg/m⁻³ and the average dust deposition was 75 g^{-2}/yr (Report WSSE Bielsko-Biała, 1996, Poland, unpublished data). During last 10 yr in the Cieszyn region, a decrease in pollutants in air was reported.

EXPERIMENT

The hair samples (without color or permanent wave treatment) and teeth of the healthy (medical history of donors, but no medical examination) Zwardoń inhabitants were analyzed simultaneously with environment samples in 1991/1992.

Hair ($n = 40$ samples) was collected from a nape of the neck. After washing with acetone and then with distilled water for 10 min, hair samples were dried at 85° C for 4 h and then 1 g of cut hair was burnt at 450° C for 24 h. The ash samples thus obtained were digested in a Teflon vessel with 3 mL nitric acid in 120°C for 3 hr. Perchloric acid (0.5 mL) was added to the obtained solution.

We examined only carious teeth excluding teeth with metallic fillings. Only those samples, in which the donor was born and was a resident of the given town, and was healthy were used in the measurement. Teeth were extracted at dentists' offices. The type of teeth (incisive, canine, molar, premolar) and a place of residence were determined for each donor.

Samples of teeth ($n = 40$ samples) were dried at 85°C to a constant weight and pulverized using a porcelain pestle and mortar. They were dried again at 85° C for 4 h immediately prior to digestion. A 500-mg sample of the dried and powdered teeth was digested with 3 mL of concentrated nitric acid in the Teflon vessel at 120° C for 3 h. The obtained solution was diluted with distilled water to 10 mL, and analyzed by AAS method. For Ca determination, lanthanum chloride was added to a final concentration of 1%.

The suspended dust ($n = 144$ samples) was taken within 1 h using a Staplex dust counter with a flow range of $16-35$ m³/h. Glass filters (TFGAF-810 type) with a diameter of 10 cm and 99.95% effectiveness for particle size above 3 mm were used. The samples of the air were taken at 60-70 cm and 100 cm above the soil surface.

The soil ($n = 52$ samples) layer of the thickness of 5 cm from 100-cm² area was taken simultaneously at the points of dust sampling. Chemical forms of heavy metals in the soil were examined according to the method of Tessier (N = 48 samples) *(23,36).* According to the Tessier method, the general scheme of metal analysis was as follows: $F(1)$ —exchangeable $(1 g)$ soil samples was extracted with 20 mL of 1 mol/L MgCl₂ at pH 7.0 for 30 min), $F(2)$ —carbonates or specifically adsorbed (leached for 5 h with 1 mol/L sodium acetate and adjusted to $pH = 5.0$); F(3)—sorbed on Mn oxides (leached for 30 min at room temperature with 0.1/mol/L hydroxylamine hydrochloride in 0.01 mol/L $HNO₃$); F(4)—sorbed on Fe-Mn oxides (extracted at 96°C for 6 h with 0.04 mol/L hydroxylamine chloride in 25% $[v/v]$ acetic acid); $F(5)$ —organically bound (was extracted at 85°C for 5 h with 30% H₂O₂ adjusted to pH = 2.0 with HNO₃, then extracted at room temperature $[v/v]$ HNO₃), F(6)—residual (digested with mixture HF-HClO₄ 5 + 1).

The concentrations of heavy metals were determined by atomic absorption spectrometry with an AAS-3 (Zeiss Jena, Germany) spectrometer using an air-acetylene flame. The absorption lines used for the analyses were: 324.75 nm (Cu), 248.4 nm (Fe), 217 nm (Pb), 213.9 nm (Zn), 279.5 nm (Mn), 232 nm (Ni), 240.7 nm (Co), and 357.9 nm (Cr). The concentrations of metals: Ca, Na, and K were determined by flame photometer (Carl Zeiss Jena 1, FLAPHO 4) with an air-acetylene burner.

The quality control was compared with the certified soil reference material CTA-FFA-1 from the Institute of Nuclear Chemistry and Technology Warsaw (Poland). For quality control, the results of certified soil reference material CTA-FFA-1 and for hair CRM-397 (Brussels) were used.

The experimental values for certified soil reference material CTA-FFA-1 are given as follows:

The 1-g soil samples were digested with a mixture of hydrofluoric and perchloric acids $(5 + 1)$. The average recoveries for average (nitride or chloride salt concentrations of 0.5, 1, 3, 4 μ g/mL were used, n = 6) samples for each concentration were of 98% for Cu, 89% for Cd, 97% for Ni, 87% for Pb, 102% for Zn, 89% for Co, and 105% for Cr.

RESULTS AND DISCUSSION

The hair samples were classified into age groups (0-20, 21-40, 41-60, and above 60), sex (male, female), and hair color (fair, dark). The changes in the average concentration of metal in the hair of the healthy inhabitants of Zwardofl are shown in Fig. 1 *(24).* These results show that the highest level of Pb content occurs in the oldest humans, showing that bone Pb level changes with age *(21).* We observed a similar result of Pb level increase with age in teeth, too *(16,18). The* oldest investigated group cumulated the highest level of Pb in the human organism. Using the Statgraphics program, we calculated regression analysis ($p < 0.1$) The regression equations for different age groups were calculated and collected. Then we calculated concentration ratios for each essential correlated ($p < 0.1$) pair of heavy metals. These results are presented in Fig. 2. Two groups of the metal/metal relationships in human hair can be distinguished: (1) In this age 61-80 group, the ratios Cu/Cr, Pb/Mn, Pb/Fe, Pb/Ni, Pb/Cu, Pb/Cd, Pb/Zn and Mn/Fe are of maximum value for the, whereas the minimum values are observed for the ratios Cd/Zn, Cd/Mn, Cu/Zn for this oldest age group. (2) In the age group 21-40, the maximum ratio is obtained for Ni/Cu ratio and the minimum value for the Cu/Mn and Pb/Ni ratios.

Fig. 1. Heavy metals concentrations in the hair of inhabitants of Zwardon $(\mu g/g)$.

Fig. 2. Ratios of heavy metals concentrations in hair in relation to age.

The mechanism of the interrelationships between heavy metals in human organism and the function of age is still being studied. The changes in the metal ratios for different age groups are certainly dependent on the metal homeostasis in human organisms, and they can be used as indicators of the physiological processes occurring in the living systems, e.g., Cd, Cu, and Zn show the similarities in biochemical behavior, and that is why the study on the Cd/Zn or Cu/Zn ratios are already reasonably well established *(25,26). The* Cd/Zn and Cu/Zn ratios in the kidneys increase with age, whereas our results obtained for the hair samples show a decrease of these ratios with age (Fig. 2). This lack of the correlation between the hair and kidney metal concentrations was reported recently *(3).*

The average metal concentrations and standard deviation in hair, taking into account sex and color, are collected in Table 1. These results differ distinctly from those obtained by Paschal et al. in the US *(27).* In this study, the amount of Cd (male) is found to be twice as high as in the Paschal et al. study, whereas Cr (male) concentrations are up to 12 times higher than in ref. *(27).* The comparison of male and female hair samples shows that the amount of Pb, Cu, and Cr is higher in the male hair, although the reason for higher concentration in male is not yet known. As shown in Table 1, the fair hair samples contain more Pb and Cu than the dark hair samples. However, the sex is also a factor influencing the amount of these metals, and the results obtained for the groups divided only according to color are misleading *(9,28).* Prucha *(24)* have shown that the Cd and Pb content in boys' hair increases with the amount of pigment, whereas in the case of girls, only the Pb amount is increasing. The essential correlation, taking into account sex and hair color, is presented in Table 2. Using one-way ANOVA for different hair colors, we received essential differences ($p < 0.05$) only for Cu ($p = 0.022$) and lower $(p = 0.06$; not essential) for Cr. A Levene Test (homogeneity of variance) was performed, and high variance within a group was found for particular metals, indicating the necessity to use a full multivariate analysis. Using the test MANOVA to investigate the influence of all effects (age, sex, and color of hair), we have not found essential differences for these factors. The lowest ($p = 0.15$; not essential statistically) we received was for sex, but differences in concentrations of heavy metals in hair for sex were very often reported.

The teeth were divided into incisive, canine, premolar, and molar teeth. No essential differences are observed between the concentrations of metals for a particular group (one-way ANOVA, $p > 0.05$). The group of the canine teeth was rather small, and that is why confidence interval and standard deviation are considerable in comparison to the other group of teeth studied *(8).* The essential correlation between metals in teeth, for $(p < 0.1)$ using the T-test is presented in Table 3. The lack of literature of the extensive studies in this field does not allow us to reach too many conclusive remarks. From the data obtained in this work, the

variables	n-quantity of samples	r-correlation coefficient $(p=0.1)$	regression equation
male	23	0.61	$C_{\rm Zn}$ =96.7+6.4* $C_{\rm Mn}$
female	17	0.78	$C_{Mn} = 0.69 + 0.03$ *C _{Fe}
		0.65	C_{2n} =79.01+6.51* $C_{C_{n}}$
dark hair	27	0.77	$C_{\text{Mn}} = 0.37 + 0.03 \times C_{\text{Fe}}$
fair hair	$\overline{13}$	0.68	$C_{Cd} = 0.37 + 0.03 \times C_{Mn}$
		0.95	C_{Ph} = -20.4+37.1*C _{Ma}
		0.75	$C_{\text{Pb}} = -59.7 + 373 \times C_{\text{Cd}}$

Table 2 Regression Equation for Heavy Metals in Human Hair

correlation is found for Ni and Zn (except for molar teeth). The concentrations of Cu, Pb and Cr are in the same range *(27),* whereas Mn level is about three times higher (Table 4).

The essential ratios of Pb/Ca in the studied teeth are the following: 8.9×10^{-4} , 8.3×10^{-4} , 8.8×10^{-4} , and 8.0×10^{-4} for incisive, canine, premolar and molar teeth, respectively. These ratios are about 20 times higher than those found by Manea-Krichten in the Netherlands *(13) in* bone. It should be mentioned that the biological level of Pb in bone is about 1.1×10^{-7} (29).

The main reason for very high Pb/Ca ratios is low Ca level in teeth of Zwardofi inhabitants, whereas the Pb level is close to that reported by Manea-Krichten *(13).*

Simultaneously with the study of metal levels in the hair and teeth samples, the evaluation of the ecological state of Zwardoń environment was performed. The hazardous risk of the population expressed in the doses of metals absorbed within I yr by inhabitants of this town was calculated according to following equation *(30):*

$$
\sum_{i=n}^{m} Ki = Ci^*W^*P^*I[mg]
$$
 (1)

where *Ci* is an average concentration of metal "i" in air, *W* is a lung ventilation (22 m³/d), P is a number of inhabitants, and I is a number of days in a year.

Taking into account the different emission sources (car traffic, railway traction, villa areas, and regions situated far from the emission sources, which represent transport pollution), the average hazard for the population of Zwardoń was:

The population hazardous risk values for the Zwardoń area are distinctly lower than those obtained for the Silesian Beskid, which is closer to the Silesian industrial region *(31). The* population hazardous risk is useful for comparison of different pollutions and population density, because this factor indicates a degree of hazard for the investigated population in the region.

The soil samples were collected at the same sites as air pollution was studied. Concentrations of heavy metals in soil is presented in Fig. 3. We received typical levels of heavy metal for Pb and Cu for unpolluted region in Poland and higher concentration for Ni, Cr, and Co *(16,32),* but we took into consideration soil near different emission sources (traffic intensity [33 cars/h], railway tracks, and domestic coal combustion) as well as what is the reason for higher contamination of soil near local emission sources. Pearson's product correlation in soil is shown in Table 5 for different contamination sources. We received many essential correlations ($p < 0.05$) between metals: Pb vs (Co, Mn, Cr), Ni vs (Co, Mn, Cr), Cd vs (Zn, Cu), Cu vs (Zn), Co vs (Mn, Cr), and Mn vs (Cr). These correlations indicate that pollutants come from transport from industry center, and from car transport and geochemical composition. Total metal

Fig. 3. Concentrations of heavy metals in soil (μ g/g) (Zwardoń $n = 52$).

	Pb	Ni	Cd	Zn	Co	Cu	Mn	\mathbf{C} r
Pb	1.0000	.0880	-1665	-0382	.2962	.2209	.4646	3100
	$p = -1$	$p = 535$	$p = 238$	$p = 788$	$p = 0.033$	$p=.116$	$p = 001$	$p = 025$
Ni	.0880	1.0000	.0658	0426	.8203	.1878	.3291	.7072
	$p = 535$	$0 - -$	$p = 643$	$p = 764$	$p = 000$	$p = 183$	$p = 017$	$p = 000$
C_{d}	-1665	.0658	1.0000	8071	-0483	.8427	-1120	-0745
	$p = 238$	$p = 643$	$p = -1$	$p = 000$	$p = 734$	$p = 000$	$p = 429$	$p = 600$
Zn	-0.382	0426	8071	1.0000	-0482	.7442	-1398	-0851
	$p = 788$	$p = 764$	$p = 000$	$p = -1$	$p = 734$	$p = 000$	$p = 323$	$p = 549$
Co	2962	.8203	-0483	-0482	1,0000	.1459	5990	.7791
	$p = 033$	$p = 000$	$p = 734$	$p = 734$	D^{\pm} ---	$p = 302$	$p = 000$	$p = 000$
Cu	2209	.1878	.8427	.7442	.1459	1.0000	.1177	.0563
	$p = 116$	$p = 183$	$p = 000$	$p = 000$	$p = 302$	$p = -$	$p = 406$	$p = 692$
Mn	.4646	.3291	-1120	-1398	.5990	.1177	1.0000	.5518
	$p = 001$	$p = 017$	$p = 429$	$p = 323$	$p = 000$	$p = 406$	$p =$ \cdots	$p = 000$
$_{\rm Cr}$	3100	.7072	-0745	-0851	.7791	.0563	5518	1.0000
	$p = 025$	$p = 000$	$p = 600$	$p = 549$	$p = 000$	$p = 692$	$p = 000$	$p = - -$

Table 5 Pearson's Product Moment Correlation in the Soil

analyses (HF, HC104) give information about levels of contamination of the soil, but are not useful for bioavailability of heavy metals for the human organism, where pH is essential. The average pH for soil of "clean" (far from local emissions, sources--mountain peaks) areas was 6.56, near the railway station 6.89, and close to the main street 7.6. These

pH values indicate contamination of soil far from local emissions, which is influenced also by transport pollution from the industry center *(32,33).*

Better information for bioavailability of heavy metals for the human organism can provide selective extraction procedures in soil. The sequential extraction procedure of heavy metals from the soil by the Tessier *(23)* method is basic in the evaluation of the ecological evaluation of the region studied. In the case of the Zwardoń area the greatest fraction of metals like Pb, Zn, Co, and Cu in the soil occurs in the residual part (HF, $HClO₄$). Similar results were received by Glażewski and suggested that residual fraction in the soil was derived from emission sources *(34). A* considerable amount of metals is in the Mn-Fe and Mn oxide fractions. Cr is also found in considerable amounts in organic and exchangeable forms. The concentrations of particular metal fractions in the studied areas are collected for example in Figs. 4 and 5. As is seen, for example, in the soil in Zwardon-Sól (near the railroad), the distribution of $C\overline{d}$ is rather uniform in particular fractions, but Mn and Zn are diverse, as is shown in Figs. 4 and 5. We can observe different levels of heavy metals and changes of metal species in summer and in autumn, which many authors explain by the presence of plant vegetation *(35).* Since we sampled soil for different parts of Zwardoń, we used analyses of variance for comparable concentrations of metals for all fraction. We did not receive essential differences between each part of sampling for each metal and for each fraction. Only for Mn was the variance for different investigated parts of Zwardoń statistically essential ($p < 0.05$).

In summary we calculated Pearson's product correlation in soil (total and each chemical form) in hair and in teeth to investigate bioavailability of heavy metals in the human organism. Essential correlations between heavy metals in soil (total and each chemical form F1, F2, F3, F4, F5, and F6) in hair and in teeth are shown in Table 6. We received essential correlations simultaneously between:

- 1. Pb vs Mn in an exchangeable form of metal in soil, in teeth, and in soil (total).
- 2. Cd vs Zn and Mn vs Co in an organically bound form in soil and in teeth and soil (total), and Cu vs. Zn in all investigated samples (teeth, hair, soil total, and organically bound form in soil).
- 3. Mn vs Co and Cr vs Mn in residual form in soil, in teeth and in soil (total) and between Co vs Ni for hair, soil (total), and residual form in soil.

Summing up, we received essential correlations for every investigated sample (teeth, hair, soil [total]) between Cu vs Zn for organically bound fraction in soil.

We received essential correlations between pairs of metals that are antagonists (Pb-Mn, Cd-Zn, Cu-Zn, Mn-Co, Cr-Mn, Co-Mn) or antagonism is possible (Co-Ni) *(32).* These results can be useful in explaining

Fig. 4. Chemical form of metals in the soil $(\mu g/g)$ (summer Sol PKP). F1, exchangeable; F2, carbonates; F3, Mn-oxides; F4, Mn-Fe oxides; FS, organic; F6, residual.

Fig. 5. Chemical form of metals in the soil $(\mu g/g)$ (autumn Sol PKP). F1, exchangeable; F2, carbonates; F3, Mn-oxides; F4, Mn-Fe oxides; F5, organic; F6, residual.

Chemical form of metal in soil n*=8	Essential correlation's between metals p<0.05	teeth $n=61$	hair n=40	soil (total) $n = 52$
$F(1)$ -Exchangeable	Pb versus Mn	$\ddot{}$		$\ddot{}$
	Zn versus Cr			$\ddot{}$
F(2)-Carbonates	Pb versus Cd	\blacksquare	٠	٠
$F(3)$ -Mn oxides		٠	ü	
F(4)-Mn-Fe oxides	Pb versus Zn	٠		$+$
F(5)-organically bound	Pb versus Zn			$\ddot{}$
	Cd versus Zn	$\ddot{}$		
	Cu versus Pb			
	Cu versus Zn	$\ddot{}$	$\ddot{}$	+
	Mn versus Co	$\ddot{}$		$\ddot{}$
F(6)-residual	Co versus Ni		$\ddot{+}$	\div
	Co versus Zn			
	Cu versus Ni			
	Cu versus Co			
	Mn versus Co			+
	Mn versus Cu			
	Cr versus Ni			\ddag
	Cr versus Co			$\ddot{}$
	Cr versus Cu	+		
	Cr versus Mn			$\pmb{+}$

Table 6 Essential Correlations Between Heavy Metals in Soil (Total and Chemical Form) in Hair and in Teeth

*n—samples, + occurrence essential correlations ($p < 0.05$), - no occurrence essential correlations.

nism is possible (Co-Ni) *(32).* These results can be useful in explaining the influence of environment on body burden of heavy metals.

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