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PRACA ORYGINALNA ORIGINAL PAPER

Participation of migration paths of selected metals in bone intoxication of Upper Silesia inhabitants

Udział dróg migracji wybranych metali w intoksykacji kości osób zamieszkujących region Górnego Śląska

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ABSTRACT

INTRODUCTION: The aim of the paper was to analyze the content of cadmium, manganese, chromium, lead, zinc and copper in the bone tissue of people living in cities in the Upper Silesia Industrial District (Bytom, Katowice, Chorzów, Siemianowice Śląskie, Świętochłowice). It also specifies the relationship between the content of selected metals in the environment and in bone tissue.

MATERIAL AND METHODS: The sample material was collected at the Municipal Hospital in Siemianowice Ślaskie. The study group amounted to 53 heads of femur, including 43 from women and 10 from men. The studied tissues were taken intraoperatively during hip replacement procedures (endoprosthetics). The content of cadmium, manganese, chromium, lead, zinc and copper was determined by atomic absorption spectrophotometry using a Pye Unicam SP-9 apparatus.

RESULTS: The average content of elements in the femoral heads in an increasing series is as follows: Cd 0.16 < Ni = 0.85 < Mn = 0.87 < Cu = 3.77 < Cr = 5.37 < Zn = 82.42 (µg/g).

CONCLUSIONS: The metal intoxication of bones sourced in suspended particulates and dust emitted from soil into the air mainly concerned the residents of Katowice. Referring this information to the obtained results, the highest contents of cadmium, copper, and chromium in the bone tissue of the inhabitants of this city can be confirmed.

KEY WORDS bone, AAS, metal migration

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STRESZCZENIE

WSTĘP: Celem pracy była analiza zawartości kadmu, manganu, chromu, ołowiu, cynku i miedzi w tkance kostnej osób zamieszkujących miasta na terenie Górnego Śląska (Bytom, Katowice, Chorzów, Siemianowice Śląskie, Świętochłowice). Określono również ponadto zależność między zawartością wybranych metali w środowisku i w tkance kostnej.

MATERIAŁ I METODY: Materiał pobierano w Szpitalu Miejskim w Siemianowicach Śląskich. W grupie badanej poddano analizie 53 głowy kości udowej, w tym 43 od kobiet i 10 od mężczyzn. Próbki tkanki kostnej zostały pobrane w trakcie endoprotezoplastyki stawu biodrowego. Badane tkanki pozyskiwane były śródoperacyjnie w trakcie zabiegów endoprotezoplastyki stawu biodrowego. Zawartość kadmu, manganu, chromu, ołowiu, cynku i miedzi oznaczano za pomocą metody atomowej spektrofotometrii absorpcyjnej za pomocą aparatu Pye Unicam SP-9.

WYNIKI: Średnia zawartość pierwiastków w tkankach głowy kości udowej przedstawiała się następująco: Cd 0,16 < Ni0,85 < Mn 0,87 < Cu 3,77 < Cr 5,37 < Zn 82,42 (µg/g).

WNIOSKI: Intoksykacja kości metalami z pyłu zawieszonego oraz pyłu wyemitowanego z gleby do powietrza dotyczy głównie mieszkańców Katowic. Porównując te informacje z uzyskanymi wynikami potwierdza się największą zawartość takich metali, jak kadm, miedź, chrom, w tkance kostnej mieszkańców tego miasta.

SŁOWA KLUCZOWE kości, AAS, migracja metali

INTRODUCTION

The intensive development of civilization associated with the development of industry and agriculture often causes increased emissions of metals into the environment, which become a source of human exposure. Contaminants get inside the human body in different ways. All the elements of the environment are interconnected and if any of them is contaminated, it affects human health. Changes in the chemical composition of water, soil and air can lead to excessive concentrations of toxic substances in food and drinking water. Gases, particulates, and many dangerous substances such as lead, cadmium and mercury are absorbed along with air [1]. Chemical elements, both those essential and toxic, are absorbed by the human body mainly from food or drinking water [2]. They undergo many changes and are then excreted from the body. Often at high exposure levels elements accumulate, resulting in a significant increase in their concentration in different organs and tissues, which can lead to various pathological changes [3,4,5]. Toxic elements may affect the ratio between the contents of trace elements, which is why it is important to assess the effect of contamination sources on the health of the population, accumulation of elements, and the interrelations between their concentrations. Bones are especially susceptible to the accumulation of metals because due to their long-time of renewal, they constitute a reserve of free exchange of elements in the body. Therefore, determining the levels of toxic metals in bone tissue may reflect their total amount in the body [3,4].

Metals and their compounds affect the skeletal system, which is particularly negatively affected by cadmium, lead, and strontium. They may replace other metals by changing the course of a series of biochemical reactions, and act as inhibitors, typically due to the formation of complex compounds with sulfhydryl groups of proteins [6]. The influence of environmental pollution on bone tissue has been repeatedly described in literature [7,8,9,10,11,12,13,14,15,16].

Human activities such as the production of cables, wires, bearings, dyes, batteries, plastics, and insecticides are sources of lead, cadmium and mercury in the environment. It is estimated that in 2007 the anthropogenic atmospheric emissions of lead and cadmium from the Baltic countries amounted to 1142 and 106 tonnes, and Poland emitted into the atmosphere 49% and 38% of the total amount, respectively [17,18]. Until recently, vast amounts of Pb were introduced into the environment by cars driven by leaded petrol. In Poland lead compounds have not been used as an additive to gasoline since 2005, however, it is still a component of jet fuel. Intensified development of the motorization industry has resulted in an increase in the amount of cadmium in road and aviation particulate matter due to the wearing of tyres where cadmium is used as a hardening agent [19].

The aim of the paper was to determine the participation of migration paths of selected metals: Cr, Cu, Ni, Mn, Cd, Zn in bone intoxication of people living in the region of Upper Silesia. The contents of cadmium, manganese, chromium, lead, zinc, and copper in the bone tissue of residents of the Upper Silesia Industrial District was determined as well.



MATERIALS AND METHOD

The subject of the research was samples of femur heads taken from persons residing in cities in the Upper Silesian Industrial District: Bytom, Chorzów, Katowice, Siemianowice Śląskie, Świętochłowice. The samples were obtained intraoperatively during Total Hip Replacement procedures performed in the Community Hospital in Siemianowice Śląskie. In total, samples from 58 patients (47 females and 11 males) were collected. The average age of patients in the study group was 66.12 years (67.57 years for women and 60.27 for men). The subject population consisted of smokers (n = 14) and non-smokers (n = 44). The study was approved by the local Ethics Committee (decision no. NN-6501-160/I/06).

The femur heads were divided into articular cartilage, cortical bone and trabecular bone samples. The samples were initially dried at a temperature of $100 \pm 2^{\circ}$ C and then incinerated at a temperature of $420 \pm 2^{\circ}$ C in a hermetic muffle oven. A known mass of ash was solubilized with 5 ml of Supra pure 65% HNO₃ (V) (Merck, Germany). The resulting solution was transferred into a 25 ml volumetric flask and filled up to the 25 ml mark with double distilled water.

The contents of the following elements: Cr, Cu, Ni, Mn, Cd, Zn in the femur heads were determined by the method of atomic absorption spectrophotometry (AAS) using a Pye Unicam SP-9 apparatus in an ace-tylene-air flame.

The statistical analysis of the gathered data was performed with Statistica PL v. 7.1 software.

To conduct statistical analysis of the occurrence of Cr, Cu, Ni, Mn, Cd, Zn in the femoral head tissues of patients living in different cities of the Upper Silesia Industrial District, the non-parametric Kruskal-Wallis ANOVA by Ranks test (p < 0.05) was used.

The participation of migration paths of cadmium, manganese, chromium, lead, zinc, copper and nickel to the bones of inhabitants of individual cities of the Upper Silesia Industrial District (Bytom, Katowice, Chorzów, Siemianowice Śląskie, Świętochłowice) was estimated on the basis of the following dependence:

where:

 $\mathbf{C}_{z} = \mathbf{K}_{p}\mathbf{C}_{p} + \mathbf{K}_{g}\mathbf{C}_{g},$

 C_z – concentration of the element in bone C_p – concentration of the element in particulate matter C_g – concentration of the element in soil

Coefficients K_p and K_g are a measure of a given method of penetration of the element into bone.

This equation can be summarized as follows:

$$\frac{C_Z}{C_g} = \int \left(\frac{C_p}{C_g}\right) [20, 21].$$

Information on the concentration of elements in particulate matter and in soil was obtained from the data available in literature [22,23].

RESULTS

The average contents of the following elements: Cd, Cr, Cu Mn, Ni and Zn in patients living in cities of the Upper Silesia Industrial District are presented in Table I.

Table I. Statistical characteristics of occurrence of following metals: Cd, Cr, Cu, Mn, Ni, Zn in femur heads in inhabitants of various cities of Upper Silesia Province $[\mu g/g]$

Tabela I. Charakterystyka statystyczna występowania metali: Cd, Cr, Cu, Mn, Ni, Zn w głowie kości udowej u mieszkańców miast Górnego Śląska [µg/g]

Element	Arithmetic mean	Median	Range	Percentyl	
Element	Anumeuc mean	weulan	Kange	10	95
Cd	0.16	0.12	0.01–1.71	0.03	0.41
Cr	5.37	3.51	0.05–89.14	0.33	12.72
Cu	3.77	2.93	0.21–59.65	1.21	6.00
Mn	0.87	0.56	0.03–7.57	0.10	2.94
Ni	0.85	0.49	0.06–13.41	0.10	3.01
Zn	82.42	63.51	6.95–309.52	18.75	196.91

The average cadmium content ranged from 0.13- $-0.18 \mu g/g$, and there were no statistically significant differences in the cadmium content among people living in different cities in the Upper Silesia Industrial District (Tab. II). The average chrome content ranged from 4.55 up to 7.30 μ g/g, and statistically significant differences occurred between those living in Katowice, Bytom and other cities of Silesia. The largest chromium content was present in the residents of Katowice (7.30 μ g/g) and Bytom (6.07 μ g/g). The copper content ranged from 2.92–5.60 μ g/g, and statistically significant differences in the content of copper occurred between the residents of Katowice and other towns. In the residents of Katowice the average copper content in bones was 5.60 μ g/g, while in the residents of Świetochłowice it amounted to 2.92 µg/g. The average manganese content varied in the range 0.64- $-1.02 \mu g/g$, and statistically significant differences did not occur. Similarly for nickel there were no statistically significant differences, and the average content in the bones of inhabitants of particular cities ranged from 0.53 up to 1.09 μ g/g. Although the average zinc contents in the selected Silesian towns were at a similar level, ranging from 71.21 up to 92.48 µg/g, statistically significant differences did not occur - Table II. There were no statistically significant differences in the presence of Cr, Cu, Ni, Mn, Cd and Zn in the femur head tissues of patients living in different cities of the Upper Silesia Industrial District (Kruskal-Wallis ANOVA Test by Ranks -p > 0.05).



Table II. Statistical characteristics of occurrence of following metals: Cd, Cr, Cu, Mn, Ni, Zn in femur heads in inhabitants of various cities of Upper Silesia Province [µg/g]

Tabela II. Charakterystyka statystyczna występowania następujących metali: Cd, Cr, Cu, Mn, Ni, Zn w głowie kości udowej u mieszkańców miast Gómego Śląska [µg/g]

		Cd	Cr	Cu	Mn	Ni	Zn
Bytom	AM±SD	0.13 ± 0.11	6.07 ± 6.03	3.41 ± 2.22	0.81 ± 1.27	0.81 ± 1.49	92.48 ± 78.86
	RANGE	0.02-0.38	0.14-23.02	0.34-9.93	0.03-5.83	0.08-6.91	6.95–309.52
Chorzów	$AM \pm SD$	0.14 ± 0.12	4.73 ± 4.43	3.16 ± 1.77	1.02 ± 1.28	0.53 ± 0.48	83.02 ± 57.17
	RANGE	0.01–0.45	0.05-12.14	0.46-7.45	0.03-4.15	0.09–2.24	15.33–196.91
Katowice	$AM \pm SD$	0.18 ± 0.22	7.30 ± 13.70	5.60 ± 9.77	0.92 ± 1.24	0.80 ± 1.16	84.28 ± 66.09
	RANGE	0.01–1.23	0.15-89.14	1.39–59.65	0.03–7.57	0.08–6.15	13.56–269.22
Siemianowice	$AM \pm SD$	0.18 ± 0.22	4.55 ± 4.36	3.20 ± 1.73	0.88 ± 1.00	1.09 ± 2.17	80.64 ± 65.46
	RANGE	0.01-1.71	0.10-12.82	0.21-7.10	0.03-5.00	0.06-13.41	8.26-292.56
Świętochłowice	$AM \pm SD$	0.14 ± 0.09	4.89 ± 4.46	2.92 ± 1.55	0.64 ± 0.76	0.66 ± 0.75	71.21 ± 57.78
	RANGE	0.01–0.33	0.05-12.44	0.66–5.78	0.03–3.31	0.09–2.65	7.95–190.47

AM - arithmetic mean, SD - standard deviation

The role of the major sources of strain on the body with copper, manganese, nickel, zinc, cadmium, and chromium are shown in Figs 1–6.



 C_z – concentration of the element in bone; C_p – concentration of the element in particulate matter; C_g – concentration of the element in soil













Fig. 3. Participation of chromium migration in bone intoxication. Ryc. 3. Udział migracji chromu w intoksykacji kości.



 C_z – concentration of the element in bone; C_p – concentration of the element in particulate matter; C_g – concentration of the element in soil

Fig. 4. Participation of zinc migration in bone intoxication. Ryc. 4. Udział migracji cynku w intoksykacji kości.



 C_z – concentration of the element in bone; C_p – concentration of the element in particulate matter; C_g – concentration of the element in soil

Fig. 5. Participation of copper migration in bone intoxication. Ryc. 5. Udział migracji miedzi w intoksykacji kości.





Fig. 6. Participation of nickel migration in bone intoxication. Ryc. 6. Udział migracji niklu w intoksykacji kości.

The equations that describe the participation of migration of the analysed elements from strain sources such as suspended particulates from long-range and local emissions, and dust emitted into the air layer, are as follows:

 $\begin{array}{l} Cu_z = 0.059 \ Cu_p + 0.155 \ Cu_g \\ Mn_z = 0.005 \ Mn_p + 0.019 \ Mn_g \\ Ni_z = 0.031 \ Ni_p + 0.0008 \ Ni_g \\ Zn_z = 0.012 \ Zn_p + 0.076 \ Zn_g \\ Cd_z = 0.005 \ Cd_p + 0.019 \ Cd_g \\ Cr_z = 0.013 \ Cr_p + 0.362 \ Cr_g \end{array}$

A comparison of the coefficients that characterize the participation of environmental sources suggests that the role of suspended particulate matter is the highest for copper and nickel, and the lowest for manganese and cadmium. As for the role of dust emitted from the soil into the air, a comparison of the coefficients allows one to notice the greatest importance of chromium and copper, and the lowest of nickel.

DISCUSSION

The Silesian Province is one of the smallest provinces in the country. The exploitation of mineral resources located in this area and the associated industrialization, as well as the very high concentration of people has resulted in a situation where the Silesian Province has the most degraded environment. The Upper Silesian Industrial District (GOP) is situated in the central part of Silesia, and it is an area with the highest concentration of industrial plants in Poland. The main source of air pollution is anthropogenic emissions from energy, industry, public utilities and transport [22].

Bone tissue is a specialized tissue in our body serving many functions, primarily, it is a structural element of the body and storage for elements that can be released in urgent circumstances, e.g. Pb [24]. Man is exposed to toxic substances which may accumulate in the body, and as a result of a significant increase in their concentration, they can lead to a variety of pathological changes in tissues. Bones are tissues susceptible to the accumulation of metal due to the long recovery time, which is why they often reflect the overall level of toxic metals in our body [24,25].

The occurrence of the elements in the femur head tissues were as follows: cadmium > nickel > manganese > copper > chromium > zinc. The highest cadmium content was detected in the heads of femur in the residents of Katowice and Siemianowice (0.18 $\mu g/g$), and the lowest in the patients from Bytom (0.13 μ g/g). For manganese the highest content was reported in people living in the area of Chorzów (1.02 μ g/g), and the lowest – Świętochłowice (0.64 μ g/g). For nickel the content was as follows: the highest 1.09 μ g/g – Siemianowice, the lowest 0.53 µg/g - Chorzów. Accordingly, for copper the highest amount was reported in the patients from Katowice (5.6 μ g/g), and the lowest from Swietochłowice (2.92 μ g/g). Also for chromium it was the highest in the residents of Katowice (7.30 μ g/g), and the lowest in the residents of Siemianowice (4.55 μ g/g). The zinc content was 92.48 μ g/g in the inhabitants of Bytom, and it was the greatest value, and the lowest was 71.21 μ g/g in the residents of Świetochłowice. There were no statistically significant differences in the presence of cadmium, nickel, manganese, copper, chromium, and zinc in femur head tissues in patients living in different cities of the Upper Silesia Province (Kruskal-Wallis ANOVA Test by Ranks p > 0.05).

There are many literature works on the subject of the content of elements in bone tissue. The zinc content in a head of femur after a fracture of the femoral neck determined by Helliwell et al. [26] was 153.6 μ g/g, and was very high compared to the results obtained in the present study – 82.4 μ g/g.



Yoshinaga et al. [27] determined the content of copper, cadmium and zinc in the ribs of people living in Japan. The contents of cadmium (0.28 μ g/g) and zinc (149 μ g/g) were high compared to the results obtained in the present study, and for copper it was the other way round (0.19 μ g/g). What is more, the content of elements in ribs was also determined by Zaichick et al. [28], and the content of copper (1.35 μ g/g) was low compared to the results obtained in the present study, and the level of zinc was at a similar level (149 μ g/g). Budiš et al. [29] determined, among others, the content of manganese in heads of femur in patients living in northern Poland, which was in the range 0.12–0.21 mg/kg. In the present authors' research, the indicated manganese content was higher, averaging 0.87 μ g/g.

Uklejewski et al. [30] determined the content of elements in femoral heads in patients living in the Greater Poland Province in Poland. The zinc content was similar (72.09 mg/kg) to the present authors' results, and the same was for nickel 0.6 mg/kg. In contrast, lower levels of copper (0.91 mg/kg) and chromium (1.33 mg/kg) compared to the present authors' results were obtained.

The content of elements in intervertebral discs on the territory of Poland was determined by Kubaszewski et al [31]. Their work includes dozens of times higher contents of cadmium (8.6 mg/kg) and nickel (71.8 mg/kg) in relation to the results reported in this work. For copper and zinc, those contents were lower and are as follows: 2.0 and 39.9 mg/kg.

Kuo et al. [4] determined the content of elements in heads of femur in patients living in a highly contaminated area in Taiwan. Comparing the results with the present authors' research, the contents of manganese and copper were at a similar level and amounted to $Mn = 0.7 \ \mu g/g$ and $Cu = 3.6 \ \mu g/g$; the content of zinc was slightly higher. Several times higher values were recorded for Cd (1.2 $\ \mu g/g$), Ni (7 $\ \mu g/g$) and Cr (11.9 $\ \mu g/g$).

Garcia et al. [32] determined the elements in the bone tissue of people living in the region of Tarragona in Spain. The contents of cadmium, chromium, copper, manganese, and zinc were lower compared to the obtained results in the present study, and only for nickel was the content higher.

Making a comparison of the migration paths of metals in patients from various cities of the Upper Silesia Province, the following observations can be made:

- for zinc, copper, manganese, and cadmium, the migration from the emission sources is the highest in people living in Katowice
- for chromium the migration from the emission sources is the highest in people from Bytom
- the lowest coefficient values for nickel, copper, and chromium occurred in patients from Chorzów the lowest value of the coefficients for cadmium, manganese, and zinc were observed in people living in Bytom.

CONCLUSIONS

The concentrations of elements in femur head tissues were as follows: cadmium > nickel > manganese > copper > chromium > zinc. The metal intoxication of bones originating from suspended particulates and dust emitted from the soil into the air mainly concerned the residents of Katowice. Comparing this information to the obtained results, the highest contents of cadmium, copper, and chromium in the bone tissue of the inhabitants of this city can be confirmed. The contents of cadmium, chromium, and copper in femoral head tissues were also the highest in the patients from Katowice.

Participation of migration of cadmium in intoxication of bones.

Statistical characteristics of occurrence of following metals: Cd, Cr, Cu in femur heads in inhabitants of various cities of Upper Silesia Province.

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Author's contribution

Study design – B. Brodziak-Dopierała, J. Kwapuliński Data collection – K. Sobczyk Data interpretation – B. Brodziak-Dopierała, D. Wiechuła Statistical analysis – B. Brodziak-Dopierała, D. Wiechuła Data interpretation – B. Brodziak-Dopierała, D. Wiechuła, J. Kwapuliński Manuscript preparation – B. Brodziak-Dopierała Literature research – B. Brodziak-Dopierała



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