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EPIDEMIOLOGICAL SIGNIFICANCE OF DETERMINATION OF LEAD, CADMIUM, COPPER AND ZINC IN HAIR AND PERMANENT TEETH, IN PERSONS LIVING IN THE VICINITY OF A LEAD SMELTERY

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In this paper the content of lead, cadmium, copper and zinc was analysed by atomic absorption spectrophotometry (model Unicam SP 90), in the hair of 200 persons residing in the immediate vicinity (within a distance of 5 km) of a lead smeltery and in a control group of 200 persons living at a distance greater than 10 km from the main air pollution source. Statistically significant differences in the content of the metals were found, the probability range being 0.05—0.01.

The concentration of lead, cadmium, copper and zinc in permanent teeth was also analysed in relation to the distance of the residence from the lead smeltery in a group of 111 persons living 1—5 km from it and in 23 persons living in the area 20 to 30 km away. The established differences were statistically significant for all analysed metals with the exception of zinc.

Within the project »Lead as an Environmental Pollutant« (1, 2), the air and soil pollution and crop contamination were investigated in the nearer and greater vicinity of a lead smeltery.

Samples of 1 kg of foodstuffs and grain were collected and placed in special glass containers. An equal number of samples taken in the same manner 20 km or more away from the smeltery was used as control.

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The samples were tested for their content of lead, cadmium and manganese. The results of food contamination are presented in Table 1.

Significantly higher values of lead, cadmium and manganese were found in the air samples taken in the 5 km area surrounding the main air pollution source. Control samples taken 10 km from the air pollution source revealed no increase of the metal content in the air, soil, grain, fruit or vegetables.

In the soil samples taken within a 5 km area lead content amounted to 18 mg/kg, manganese up to 34.5 mg/kg and cadmium up to 1.13 mg/kg.

The studies were extended by measurements of lead, zinc, cadmium and copper in the hair and teeth of the people living in the vicinity of the smelting plant and in control subjects.

MATERIAL AND METHODS

The hair samples of 400 residents, of both sexes and different age who live in the vicinity of the industrial area from which lead, zinc, cadmium and copper are released into the air, were tested for the content of these metals. The first group consisted of 100 women and 100 men aged from 8 to 74 years, living within a 5 km area from the smeltery's main chimney. The control group consisted of an equal number of subjects of the same age living at a distance of 10 km and more from the smeltery. No subject was ever employed in the smeltery, nor at any workplace exposed to dust or vapours of lead, cadmium, copper or zinc.

A gram of hair was taken for analysis from persons of different age, both sexes and with different places of residence. The samples of hair, dissolved in nitric acid, were analysed for cadmium, copper, lead and zinc content by the method of atomic absorption spectrophotometry using the model Unicam SP 90 in the Toxicology Laboratory of the Military Medical Academy in Beograd.

The four metals were also quantitatively analysed in the permanent teeth of 111 residents living within a 5 km area from the lead smeltery, by means of the same equipment. The samples of the teeth of 23 subjects residing further than 20 km from the smelting works were taken as the control group. They were collected during a period of six months in a nearby dental clinic. The extraction was undertaken for well developed caries. Only the teeth of male residents aged 18—50 years were taken and divided according to the place of residence into two groups.

The analyses of metals in the hair and permanent teeth were carried out under the conditions prescribed in the Manual for the operation of the atomic absorption spectrophotometer and according to the instructions in the literature (3).

Table 1.

*Lead, cadmium and manganese content (range, in mg/kg) in soil and crops**

	No of sample		Lead		Cadmium		Manganese	
	Smelter area	Control area	Smelter area	Control area	Smelter area	Control area	Smelter area	Control area
Soil	8	8	0.1— 5.8	0.1 —0.5	0.001—0.063	0.001—0.002	0.68— 1.24	0.1 —0.7
Wheat	6	6	0.1—18.0	0.05—1.2	0.010—0.063	0.005—0.008	5.75—34.50	1.2 —3.6
Corn	3	3	1.5—16.0	0.3 —1.4	0.010—0.070	0.005—0.010	4.75— 9.00	1.6 —3.0
Apple	7	7	0.3— 3.7	0.03—0.1	0.003—0.010	0.001—0.004	0.25— 0.50	0.01—0.03
Pear	3	3	4.5— 6.8	0.2 —1.4	0.003—0.018	0.001—0.004	0.50— 0.80	0.01—0.09
Potato	9	9	0.1— 0.3	0.01—0.08	0.010—1.130	0.002—0.003	0.65— 1.30	0.04—0.09

* Results taken from the official records of the Municipal Assembly of Kosovska Mitrovica.[1, 2]

Table 2.

Cadmium, copper, lead and zinc concentrations in human hair in relation to age, sex and vicinity of a lead smeltery (mean ± S. D. in μg/g)

Age	Sex	No samples	Cadmium		Copper		Lead		Zinc	
			Control area	Smeltery area	Control area	Smeltery area	Control area	Smeltery area	Control area	Smeltery area
8—14	M	40	1.6±8.0	2.9±1.2	13.7± 1.2	22.0±3.0	68.8± 8.67	167.1± 18.06	248.5± 24.9	419.0±216.8
	F	40	1.3±0.6	2.3±1.3	7.9± 2.3	11.2±2.3	55.4±38.8	134.3± 65.9	241.6± 66.0	386.5±106.0
15—29	M	40	2.1±1.3	2.4±1.3	11.9± 5.8	12.1±6.6	182.7±29.3	277.3± 28.5	371.1± 26.4	365.6±114.5
	F	40	3.4±1.9	2.2±1.3	10.4± 3.1	22.3±2.71	86.7±11.35	160.1±113.5	242.5± 95.8	383.7±175.8
30—44	M	40	2.6±0.9	2.0±1.1	11.8± 3.4	11.8±3.5	53.8±36.3	88.4± 44.8	331.3± 79.7	390.0± 17.5
	F	40	1.4±1.2	2.6±1.0	16.6±13.5	13.2±2.9	70.1±38.9	172.6± 84.1	287.7±105.3	550.6±364.9
45—59	M	40	1.5±0.4	3.3±1.5	11.2± 1.5	16.3±5.9	70.8±13.0	615.4±246.7	280.3± 28.7	299.0± 31.1
	F	40	0.7±0.4	2.2±1.9	10.9± 1.2	11.2±5.3	39.3±13.7	118.1± 55.6	280.3± 18.6	413.3± 30.3
60—74	M	40	2.0±1.1	3.1±1.9	10.9± 2.4	13.5±1.8	39.6±14.6	552.1± 61.4	285.9±108.0	451.5±180.8
	F	40	1.6±0.7	2.4±2.1	12.5± 3.2	12.3±5.6	25.7± 5.5	148.1± 39.9	315.1± 84.0	484.8±329.0
Total	M	200	1.9±1.3	2.7±1.5	11.9± 4.3	15.6±1.67	80.1±15.1	312.4± 36.5	300.7±136.8	385.6±168.2
	F	200	1.7±1.4	2.3±1.5	10.8± 6.4	15.5±1.7	56.0±49.1	148.6± 93.4	266.6± 86.9	430.6±262.3

Table 3

T values — obtained by Student's t-test from differences in metal content in hair samples for various age and sex groups — control and experimental

Metal	Age (years)	Pairs***			
		1	2	3	4
Cadmium	8—14	1.88	2.14*	5.65**	4.35**
	15—29	3.61**	0.71	1.03	3.33**
	30—44	5.10**	2.63**	2.73**	4.80**
	45—59	0.90	2.82**	7.20**	5.00**
	60—74	2.00*	1.55	3.14**	2.28*
	Total	1.54	2.67**	5.71**	4.28**
Copper	8—14	6.44**	19.30**	8.75**	6.60**
	15—29	1.44	9.00**	0.14	18.30**
	30—44	2.18*	1.94	0.00	1.56
	45—59	1.00	4.08**	5.30**	0.34
	60—74	2.66**	1.29	5.55**	0.20
	Total	2.04*	0.50	11.56**	3.86**
Lead	8—14	2.13*	3.81**	30.70**	6.52**
	15—29	19.20**	6.33**	14.55**	4.10**
	30—44	1.94	5.58**	3.78**	7.02**
	45—59	10.50**	12.42**	13.60**	8.75**
	60—74	5.56**	34.89**	51.25**	19.13**
	Total	6.64**	23.00**	7.70**	12.41**
Zinc	8—14	0.62	0.83	4.93**	7.34**
	15—29	2.89**	0.54	0.12	4.46**
	30—44	2.09*	2.51*	1.93	4.38**
	45—59	0.33	2.37*	2.79**	2.80**
	60—74	1.35	0.56	5.14**	3.16**
	Total	2.91**	2.05*	5.54**	8.40**

* — Statistically significant, $p<0.05$
** — Statistically significant, $p<0.01$
*** — Pairs: 1. Men — women in control group
2. Men — women in experimental group
3. Men in control and experimental group
4. Women in control and experimental group

Table 4

Cadmium, copper, lead and zinc concentrations (mean ± S. D.) in permanent human teeth in relation to the distance from the lead smeltery

Groups	No of samples	Cadmium	Copper	Lead	Zinc
Control	23	1.02±0.6	4.2±1.4	18.6±6.2	267.5±252.0
Exposed	111	1.9 ±0.4	5.4±1.9	30.2±3.5	307.5±274.0
Student's test		t — 5.18 p<0.01	t = 2.07 p<0.05	t = 8.57 p<0.01	t = 0.64 p<0.05

RESULTS

Cadmium content in the hair was measured in two groups of subjects, each consisting of 40 boys and 40 girls, aged 8—12 years. The results are presented in Table 2. Statistically significant differences were found in the probability range of $P<0.05$ and $P<0.01$ by the Student's t-test (Table 3). Differences were also established when experimental groups of boys and girls were compared to their control groups. However, the test showed no difference in the hair cadmium content in the control groups.

The content of copper, lead and zinc was investigated in the same age groups and statistically significant differences were found in all the combinations of the test (see legend in Table 3), except for zinc. A significant difference in the content of the metals in the hair was found in all other age groups, especially for cadmium and lead.

The analysis of the cadmium, copper, lead and zinc concentrations in the dentine of the permanent teeth indicates statistically significant differences between the control and test groups, especially for cadmium and lead in the probability range of $P<0.01$ ($P<0.05$ for copper). Differences in the zinc content were not statistically significant (Table 4).

DISCUSSION

Air pollution, a consequence of a highly developed industry and traffic, is a great problem of modern civilisation. Large amounts of lead are found in the air of urban environments. The mean atmospheric lead concentrations vary from 0.0010 mg/m^3 over the Pacific ocean, 2.6 mg/m^3 above Milano, 3.2 mg/m^3 above London up to 7.6 mg/m^3 above Los Angeles (2).

Air pollution in the study area during 1973/74 significantly exceeded the MAC values for urban areas (1). In 88 samples out of 117 lead in air concentrations were above the MAC values. The mean monthly lead concentrations ranged from 0.9 to 23.8 mg/m^3. With the industrial development air pollution appears to produce a progressively harmful effect on farming and cattle breeding. In the tissue samples taken from dead horses and other domestic animals, lead concentrations amounted from 5 to 14 mg/kg. Lead content in cattle feed dry material in this area reached 87 mg/kg (4).

Our data show that high concentrations of lead, and other pollutants in the air have resulted in their high deposition in the soil, vegetables and fruit (Table 1).

Statistically significant differences with the probability range of $P<0.05$ and $P<0.01$ (Table 3) were discovered when the contents of cadmium, copper, lead and zinc were measured in the hair of the population in the vicinity of the lead smeltery (up to 5 km) and of those residing at a distance of 10 km and further. The hair content of cadmium, copper, lead and zinc in all age groups obtained by the Student's t-test shows statistically significant differences for all metals and all pairs of groups with the exception of the cadmium content in the control group of women and men and the copper content in the experimental group.

The significantly higher copper, lead and zinc content in the hair of the control group of men may be explained by their more frequent visits to the town where they were occasionally exposed to the polluted air. The statistically significant lower cadmium, lead and zinc concentrations in the hair in the exposed group of women are probably a consequence of their spending more time indoors, as they mostly belong to the Moslem population. In Tables 2 and 3 the mean values, standard deviations and the values of the Student's t-test are given for all age groups.

On the basis of a separate analysis of all the metals according to their content in the hair, and an analysis according to age and sex it may be concluded that the content of cadmium and lead directly depends on air pollution, while the levels of zinc and copper as intrinsic elements, show certain deviations.

The content of metals under investigation in the hair of our subjects indicates that the lowest mean values of lead in the exposed groups were $\bar{x} = 88.4 \pm 44.8$ μg/g for men and $\bar{x} = 118.1 \pm 55.6$ μg/g for women. The highest values in the exposed group were $\bar{x} = 615.4 \pm 246.7$ μg/g for men and $\bar{x} = 172.6 \pm 84.1$ μg/g for women. These values were much higher than the data reported in domestic and foreign literature.

In a group of rural residents ($n = 30$) *Stanković* found the mean value of lead in the hair of 3.75 μg/g (5). In a group of 40 urban inhabitants this value amounted to 7.16 μg/g, and in a group of 50 people residing in the neighbourhood of the smeltery up to 33.13 μg/g. In exposed workers the mean value was $\bar{x} = 71.90$ μg/g (5).

The values of lead presently reported in foreign literature vary considerably according to the level of urbanisation and industrial development. The values reported in the US literature are 6.1 μg/g in towns without a lead industry and up to 22.3 μg/g in towns with a smeltery.

The content of cadmium found in the hair of our subjects corresponds to that reported in foreign literature (6), but the concentrations reported in some studies in this country vary considerably (5). Cadmium concentrations in the hair are generally found to be 0.2—2 μg/g. The cadmium concentration in the hair of inhabitants living in the neighbourhood of lead and zinc smelteries amounted to 2.0—3.5 μg/g. According to the authors from Finland 0.35 μg/g is considered as a normal value for cadmium in the hair (6).

The reported zinc concentrations in the hair are fairly high: 26—355 μg/g (7) in foreign and 137—158 μg/g in the Yugoslav literature (5).

The values obtained in our investigations are somewhat higher than the highest ones reported in foreign literature, especially in the people residing in areas directly exposed to pollution. The copper hair content in our investigations, like that of zinc, considerably exceeded the values reported in domestic (5) and foreign literature (7).

The mean lead and cadmium concentrations in the teeth of 111 persons exposed to air pollution give an insight into the total body burden of these metals.

The mean lead and cadmium content in exposed persons was almost two times higher than in the control group. The established differences were statistically significant, with the probability range of $P<0.01$, for copper only $P<0.05$. For zinc, however, the differences between the control and exposed groups were not significant.

In the literature greater attention has been paid to the dentine lead content than that of other elements. *Shapiro* and co-workers found significant differences in the dentine lead content in the residents of Philadelphia (183.3 ± 37.8 μg/g), Alaska (56.0 ± 30.1 μg/g), Mexico (Machu Pichu — 12th century) (13.6 ± 19.8 μg/g) and Egypt (the first and second millenium; 9.7 ± 10.7 μg/g).

This indicates a temporal difference (the present, 12th century, the first and second millenium), and a geographical difference caused by air pollution as a results of industrialisation (urban and rural environments).

The results of our investigations fully agree with the above in respect to geographical division (urban and rural regions) i. e. the concentrations of lead, cadmium and copper in the dentine of the population in urban environments with developed industries and consequent air pollution are significantly higher (Table 4).

Needman and co-workers (8) obtained similar results in a group of 40 children not exposed to lead in their environment (11.1 ± 14.8 μg/g), while in a group of 69 children living in a high risk area the dental lead content was 51.1 ± 10.9 μg/g.

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Sažetak

EPIDEMIOLOŠKI ZNAČAJ ODREĐIVANJA OLOVA, KADMIJA, BAKRA I CINKA U KOSI I TRAJNIM ZUBIMA OSOBA KOJE ŽIVE U BLIZINI TOPIONICE OLOVA

Autori iznose rezultate merenja sadržaja olova, kadmija, bakra i cinka u 200 uzoraka kose muškaraca i žena koji žive u blizini topionice olova i u uzorcima kose jednakog broja kontrolnih osoba koje žive daleko od topionice olova. Olovo, kadmij, bakar i cink određivani su atomskom apsorpcijskom spektrofotometrijom.

Nađene su značajne razlike u koncentraciji ispitivanih metala između eksponirane i kontrolne skupine ($p<0,05$ i $p<0,01$).

Koncentracije olova, kadmija, bakra i cinka merene su i u trajnim zubima 111 osoba koje žive u blizini topionice kao i u zubima 23 kontrolne osobe koje žive daleko od topionice. I u ovim su uzorcima utvrđene statistički značajne razlike u koncentracijama svih metala osim cinka između dviju ispitivanih grupa.

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