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THE MULTIELEMENT HAIR ANALYSIS AS A TOOL FOR PRELIMINARY EVALUATION OF SEVERE TECHNOGENIC POLLUTION EFFECTS ON THE CHILDREN'S HEALTH

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ABSTRACT: Presented hair samples, collected in children, living in town of Veles, contain significantly elevated concentration of Pb, Hg, Ni, Cd, Sn, As, Na, Se and decreased concentration of Mg, Mn, Cr and Li in comparison to local control (Ivankovci). The average concentration of heavy metals (Pb, Ni, Cu) are higher than corresponding data from children, living in Russian Federation (external control). The increased hair content of Pb (43% of cases), Cd (21%), Cu (16%), Ni (14%), decreased hair Mg (in 51% of all cases) are typical for children, living in Veles. There are closed correspondence between elevated hair toxic metals levels and CNS diseases, immunodeficiency, anemia, bronchopneumonia, chronic bronchitis and scoliosis in children. All obtained data suggest the influence of heavy metal (Cd, Pb, Ni, Sn, Hg, Cu) pollution of environment in town Veles, Macedonia on the morbidity in children, especially, rate of neurologic, immunodeficient and bronchopulmonar diseases, alopecia, anemia.

The further clinical and laboratory investigation, social, technological and medical actions are critically needed.

Introduction

The lead-zinc smelter "Zletovo" was built 30 years ago. The average year atmospheric emission of metals is 2070 tons (Pb), 49 tons (Cd) and 11290 tons of SO_2. Every year smelter used 71380 tons of Zn, 36320 tons of Pb, 50820 tons of S, 9828 tons of Cu and 72 tons of As. The metal pollution caused lot of health problems in population of Veles (44000 inhabitants), especially in workers of smelter and children (Rishtova, Petrova, 2002). The estimation of real influence of toxic metals pollution on the children morbidity was the main task of this investigation.

Material and methods

During the year 2003 hair samples of 80 children from Macedonia were investigated.

Hair and nail samples according to IAEA and Russian Ministry of Public health were collected (Skalny, 2000, Methodical recommendations, established by Federal Center of sanitary-epidemiological service of Ministry of Public Health of Russian Federation 29/01/2003).

Totally, there were 70 4–10 y.o. children, living in town Veles, Macedonia (polluted region) and 10 ones from "ecologicaly pure" village Ivankovci investigated. Obtained data were compared with Russian reference data using standard statistical methods.

Sampling. Hair samples were taken from 3–5 places of scalp occipital zone. Proximal parts of hair strands 3-4 cm long were used for analysis. Hair (0.2–0.5 g) thus cut was immediately placed in special bags, which were then accurately sealed and labeled with a group number, the subject name, and the date.

All specimens were stored in dry, cool and ventilated environment until delivery to the laboratory and then kept in desiccators until analysis.

Sample treatment. Hair samples were cut in pieces no longer than 1 cm, processed by acetone (ex.p.) in 10–15 minutes, and then washed thrice by double distilled water. After that they were dried at 60°C till air-dry condition (Caroli et al., 1992). Then 0.1 g of the dried hair was used for analysis. Hair digestion has been carried out in plastic test-tubes by wet ashing with nitric acid on a balneum within 1 hour (Skalny et al., 2001).

Analytical determination has been carried out by atomic emission spectrometry with inductively coupled argon plasma (ICP-AES) method using Optima 2000 DV (Perkin Elmer, USA) spectrometer.

For the check-up our laboratory data the certified reference material of human hair, obtained from Shanghai Institute of Nuclear Research, was used.

Results

The evaluated analytical data, presented in Table 1, demonstrated significant difference in hair elemental content of children from Veles and control group.

Table 1. Major and trace elements concentration in children's hair in Macedonia in comparison to Moscow and Russian Federation.

Element	Veles, n = 59	Ivankovci, n = 10	Moscow, n = 1185	Russia, n = 2181
Al	*11.95±1.65*	*13.78±1.96*	24.07±0.42	24.39±0.31
As	***0.16±0.03***	0.1±0.01	0.29±0.01	0.27±0.01
Be	0±0	0±0	0.01±0	0.01±0
Ca	321.58±38.34	333.06±56.84	424.04±10.46	487.5±9.42
Cd	**0.25±0.05**	0.12±0.03	0.24±0.03	0.27±0.01
Co	0.02±0	0.02±0	0.2±0.01	0.2±0
Cr	0.6±0.05	0.92±0.07	0.95±0.03	1±0.02
Cu	*12.47±0.81*	10.11±0.28	10.74±0.21	10.13±0.11
Fe	23.25±2.78	22.39±2.51	22.98±0.52	25.15±0.38
Hg	0.21±0.06	0.06±0.01	–	–
K	*437.65±86.17*	*336.04±151.76*	843.04±29.8	825.99±19.64
Li	*0.03±0*	0.05±0.01	0.08±0.01	0.08±0
Mg	31.55±6.15	44.23±7.41	35.84±1.76	40.45±1.24
Mn	*0.58±0.1*	0.93±0.16	0.75±0.05	0.93±0.04
Na	*341.72±85.66*	*196.05±59.89*	731.72±29.72	755.17±19.6
Ni	***0.95±0.32***	0.44±0.1	0.5±0.01.393	0.55±0.02
P	156.09±4.96	148.48±4.15	147.87±1.11	152.53±0.97
Pb	***5.62±0.84***	1.49±0.43	1.8±0.1	2.34±0.09
Se	0.39±0.02	*0.24±0.03*	0.41±0.03	0.38±0.02
Si	26.66±2.51	23.33±4.25	17.77±0.53	19.15±0.38
Sn	*0.14±0.02*	*0.08±0.01*	0.39±0.03	0.45±0.03
Ti	*1.17±0.08*	1.09±0.26	0.45±0.02	0.49±0.01
V	*0.08±0.01*	*0.09±0.01*	0.17±0.01	0.17±0.01
Zn	*179.11±9.3*	*171.08±29.51*	119.83±2	121.11±1.3

Bold — significant difference between Veles and Ivankovci; *italics* — significant difference in comparison to Russia and Moscow.

Firstly, the Pb hair level in group from Veles (group 1) was 3.8 times higher, than in control group (Ivankovci, group 2). Also, it was 3.1 and 2.4 times higher, than in Moscow (group 3) and Russian (group 4) children, respectively.

Also, there was increased Ni hair level (0.95±0.32 ppm in group 1 vs. 0.44±0.1 in group 2 and 0.5±0.01 in group 3, 0.55±0.02 in group 4), i.e. approximately 2 times higher in Veles children as compared to another groups. Group 1 in comparison to group 2 had the exceeded Hg (3.5 times), Cd (2.1 times), Sn (1.8 times), As (1.6 times), Se (1.6 times), Na (1.7 times), Cu (1.2 times) hair levels. Simultaneously, the investigated Veles children demonstrated decreased hair concentrations of some essential elements such as Cr (1.5 times), Mg (1.4 times), Mn (1.6 times), Li (1.7 times) as compared to local control.

Data, presented in table 2, suggest above analytical results. The elevated hair levels (more than 5 ppm) were observed in 42.5% of all investigated Veles children (0% on local control). Exceeding of relative biologically allowable levels (BAL) for Ni were found in 13.8% of cases in Veles, Cu — in 16%, Cd — in 21% (in comparison to 0% in local control).

Low hair Mg in 51%, Mn in 46%, Fe in 19%, P in 46%, Zn in 38% in group 1 and in 0%, 20%, 10%, 0% and 20% in group 2, respectively, were found.

So, the maximal difference in hypoelementosis frequency in Veles and control in case of Mg (51%) was estimated. Risk of hyper- and hypoelementoses, evaluated on the basis of children hair analysis is presented in Figure 1. So, there are the evident difference in lot of elements in group 1 and group 2 and it suggest the elevated risk of heavy metal related diseases (such as immunodeficiency, anemia, allergic diseases, CNS disturbances including mental disorders, alopecia etc.) in children, living in town of Veles.

The possible relations between children's health conditions and hair elemental content were also inves-

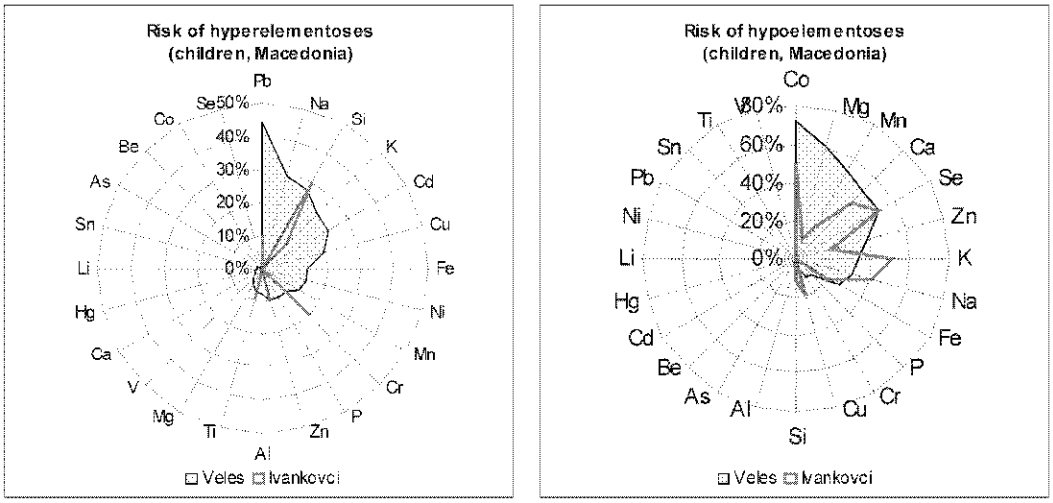

Figure 1. Frequency of mineral imbalances in children's hair (Macedonia).

Table 2.

Element	Veles					Ivankovci					Limits (ppm)	
	Upper limit	Lower limit	Norm	Increased	Decreased	Upper limit	Lower limit	Norm	Increased	Decreased	Lower	Upper
Al	1.25%	1.25%	90.00%	6.25%	1.25%	0.00%	0.00%	100.00%	0.00%	0.00%	2	35
As	0.00%	0.00%	100.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	2
Be	0.00%	0.00%	100.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	1
Ca	0.00%	18.75%	47.50%	2.50%	31.25%	0.00%	0.00%	60.00%	0.00%	40.00%	260	660
Cd	1.25%	0.00%	77.50%	21.25%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	0.5
Co	0.00%	8.75%	28.75%	0.00%	62.50%	0.00%	0.00%	50.00%	0.00%	50.00%	0.02	1
Cr	1.25%	3.75%	80.00%	8.75%	6.25%	0.00%	0.00%	80.00%	20.00%	0.00%	0.25	0.5
Cu	2.50%	2.50%	77.50%	16.25%	1.25%	0.00%	10.00%	80.00%	0.00%	10.00%	10	15
Fe	1.25%	7.50%	60.00%	12.50%	18.75%	0.00%	10.00%	80.00%	0.00%	10.00%	10	25
Hg	0.00%	0.00%	97.50%	2.50%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	2
K	1.25%	8.75%	43.75%	22.50%	23.75%	10.00%	30.00%	40.00%	0.00%	20.00%	30	400
Li	0.00%	0.00%	98.75%	1.25%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	0.5
Mg	0.00%	8.75%	35.00%	5.00%	51.25%	0.00%	10.00%	90.00%	0.00%	0.00%	25	70
Mn	0.00%	6.25%	35.00%	12.50%	46.25%	0.00%	0.00%	80.00%	0.00%	20.00%	0.25	1
Na	1.25%	10.00%	41.25%	27.50%	20.00%	0.00%	0.00%	60.00%	0.00%	40.00%	50	300
Ni	0.00%	0.00%	86.25%	13.75%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	2
P	0.00%	6.25%	77.50%	10.00%	6.25%	0.00%	0.00%	100.00%	0.00%	0.00%	120	150
Pb	1.25%	0.00%	56.25%	42.50%	0.00%	10.00%	0.00%	90.00%	0.00%	0.00%	0	5
Se	0.00%	16.25%	50.00%	0.00%	33.75%	0.00%	10.00%	50.00%	0.00%	40.00%	0.25	1.5
Si	3.75%	0.00%	68.75%	23.75%	3.75%	0.00%	0.00%	60.00%	30.00%	10.00%	10	30
Sn	0.00%	0.00%	98.75%	1.25%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	3
Ti	3.75%	0.00%	92.50%	3.75%	0.00%	0.00%	0.00%	90.00%	10.00%	0.00%	0	3
V	1.25%	0.00%	96.25%	2.50%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%	0	0.5
Zn	2.50%	0.00%	52.50%	7.50%	37.50%	0.00%	0.00%	70.00%	10.00%	20.00%	140	200

tigated. All children were divided into 10 groups in accordance with its leading clinical diagnosis.

The maximal average Pb hair level (9.54±3.23 ppm) was established in children, suffering from different CNS diseases (table 3). The maximal Pb nails concentration (14.47±3.85 ppm) was found in alopecia patient. Also, high Pb hair levels corresponded with such diagnosis as scoliosis (7.34±5.08 ppm), immunodeficiency (7.02± 2.07 ppm), anemia (6.69±1.76 ppm), chronic bronchopneumonia (6.65±2.35 ppm) and chronic bronchitis (6.41±1.85 ppm). Children, suffering mainly by different allergic diseases, asthma bronchiale, cardio-vascular diseases have the moderate Pb hair concentrations data, but they were also higher then local controls data. The frequency of hyper and hypoelementoses at different diseases are presented in Figures 2–5.

As shown in Figures 2 and 3, 40–60% of patients, suffering from bronchopneumonia, chronic bronchitis, asthma, alopecia, anemia, immunodeficiency, allergies, CNS diseases have elevated hair Pb. Increased Cd hair data are typical for alopetic, asthmatic, immunodeficient and bronchitic patients; elevated hair Cu is typical also for the same groups of children. Elevated hair Ni was found in children with bronchitis, immunodeficiency, CNS diseases, asthma, alopecia. It was interesting that was detected significant risk of Si hyperelementosis in scoliosis patients.

The maximal influence of hypoelementoses was estimated in children, suffering from cardio-vascular diseases (K, Na, Mg, Fe, Se, Mn, Co), bronchopneumonia (Ca, Mg, Zn, Se, Co), asthma (Ca, Mg, Mn, Se, Co), allergies (Ca, Mg, Se, Mn, Co), anemia (Ca, Mg, Se, Co). Alopecia, usually, is due to Zn deficiency.

Conclusions

1. In hair of children, living in town of Veles, significantly elevated concentration of Pb, Hg, Ni, Cd, Sn, As,

Table 3. Average concentration of major and trace elements in hair of children suffering from different diseases (Macedonia).

Element	Immuno-deficiency n = 16	Allergies n = 14	CNS diseases n = 12	Bronchitis n = 17	Cardio-vascular diseases n = 8	Asthma bronchialis n = 6	Alopecia n = 8	Broncho-pneumonia chron. n = 6	Anemia n = 8	Scoliosis n = 4
Al	8.88±1.5	8.92±2.28	14.74±3.68	9.48±1.17	6.59±1.34	12.61±4.93	36.35±9.69	10.54±2.62	20.51±9.28	11.27±2.86
As	0.13±0.03	0.09±0.01	0.35±0.15	0.13±0.03	0.11±0.05	0.08±0.01	0.47±0.17	0.1±0.03	0.14±0.04	0.17±0.1
Be	0±0	0.01±0	0±0	0±0	0±0	0.01±0	0±0	0.01±0	0±0	0±0
Ca	360±98	383±102	311±49	272±41	419±178	317±93	1178±166	810±284	307±69	248±34
Cd	0.26±0.07	0.16±0.03	0.36±0.1	0.23±0.06	0.42±0.3	0.14±0.05	1±0.35	0.23±0.1	0.23±0.06	0.3±0.11
Co	0.02±0	0.02±0	0.03±0.01	0.02±0	0.02±0.01	0.02±0.01	0.08±0.02	0.03±0.01	0.04±0.02	0.02±0
Cr	0.5±0.05	0.7±0.15	0.58±0.08	0.57±0.05	0.51±0.09	0.91±0.33	0.86±0.2	0.58±0.1	0.6±0.16	0.52±0.08
Cu	11.24±0.51	12.18±1.04	11.98±0.64	12.13±0.91	11.73±0.45	18.39±7.41	10.23±1.57	18.91±7.32	11.95±0.7	11.3±1.02
Fe	15.64±1.7	21.14±3.86	26.47±7.04	19.05±1.8	14.3±1.14	25.12±8.31	91.65±21.62	22.62±2.34	33.12±16.01	20.41±3.19
Hg	0.09±0.02	0.12±0.03	0.29±0.18	0.09±0.02	0.09±0.02	0.27±0.19	0.05±0.01	0.26±0.19	0.48±0.37	0.05±0.01
K	435±199	334±142	516±230	401±170	305±236	327±89	1217±271	437±243	630±272	215±108
Li	0.03±0	0.03±0.01	0.04±0.01	0.03±0	0.02±0	0.05±0.01	0.1±0.02	0.03±0	0.05±0.02	0.03±0.01
Mg	46±21	32±8	24±5	27±5	33±14	30±8	180±58	100±54	28±9	24±7
Mn	0.47±0.1	0.45±0.13	0.75±0.28	0.44±0.07	0.25±0.03	0.67±0.28	3±0.79	0.68±0.2	0.96±0.52	0.6±0.14
Na	442±279	266±111	218±60	455±262	99±28	308±67	2646±718	435±242	479±230	357±268
Ni	0.51±0.09	2.05±1.33	0.76±0.2	1.76±1.1	0.67±0.42	0.44±0.09	3.81±1.11	0.7±0.15	0.52±0.18	0.66±0.38
P	143±3	163±9	166±18	146±8	145±8	154±7	419±50	162±9	168±16	146±4
Pb	7.02±2.07	3.83±0.81	9.54±3.23	6.41±1.85	2.28±0.64	3.77±1.08	14.47±3.85	6.65±2.35	6.69±1.76	7.34±5.08
Se	0.37±0.04	0.35±0.03	0.37±0.03	0.39±0.04	0.38±0.08	0.36±0.06	0.75±0.08	0.43±0.04	0.37±0.05	0.47±0.03
Si	32±8	27±5	25±3	22±4	29±5	23±6	23±4	44±17	21±6	38±6
Sn	0.13±0.05	0.1±0.02	0.23±0.06	0.14±0.04	0.09±0.05	0.15±0.03	0.22±0.04	0.16±0.07	0.15±0.07	0.09±0.02
Ti	1.06±0.08	1.33±0.28	0.97±0.1	1.06±0.09	0.87±0.07	1.74±0.62	1.89±0.45	1.47±0.17	1.29±0.18	1.08±0.11
V	0.08±0.01	0.07±0.01	0.09±0.02	0.08±0.01	0.05±0.01	0.1±0.02	0.19±0.04	0.09±0.01	0.11±0.03	0.07±0.01
Zn	173±21	204±18	169±23	178±24	197±27	179±17	146±6	242±48	171±18	172±42

Na, Se and decreased concentrations of Mg, Mn, Cr and Li in comparison to local control (Ivankovci) was found.

2. The average concentration of heavy metals (Pb, Ni, Cu) are higher in comparison to external control (Russian Federation).

3. There are close correspondence between elevated hair toxic metals levels and CNS diseases, immunodeficiency, anemia, bronchopneumonia, chronic bronchitis and scoliosis in children.

4. The further clinical and laboratory investigation, social, technological and medical actions in town of Veles are critically needed.

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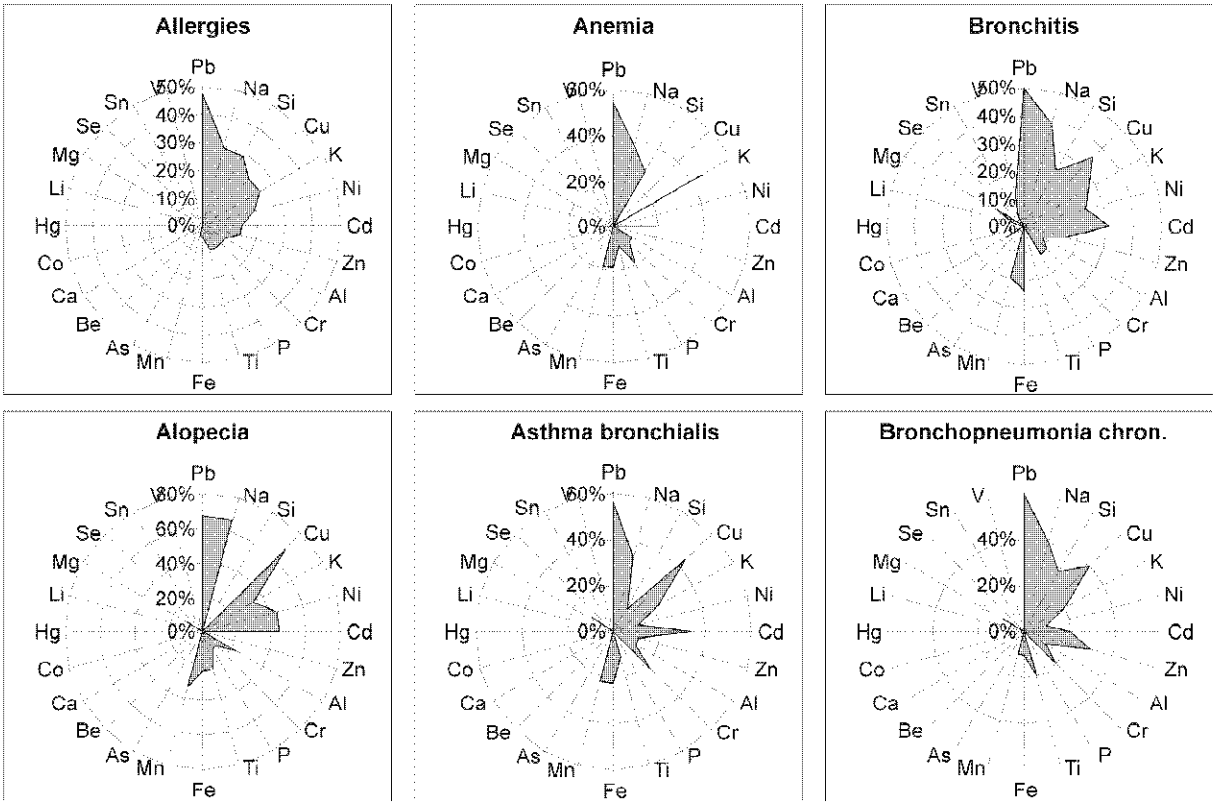

Figure 2. Risk of hyperelementoses (children, suffering from different diseases, Macedonia).

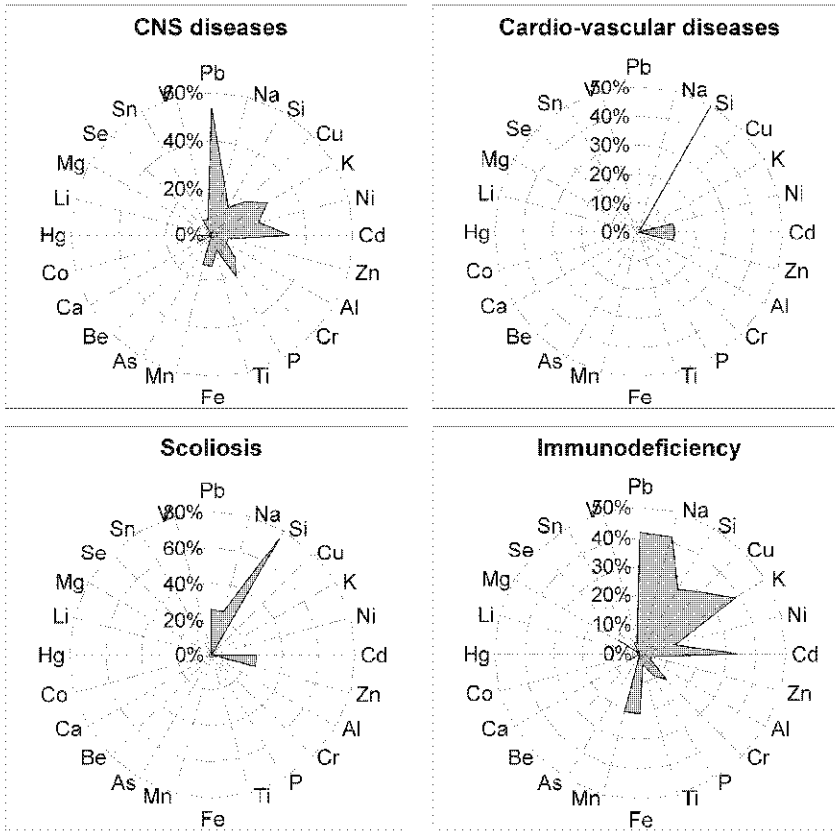

Figure 3. Risk of hyperelementoses (children, suffering from different diseases, Macedonia).

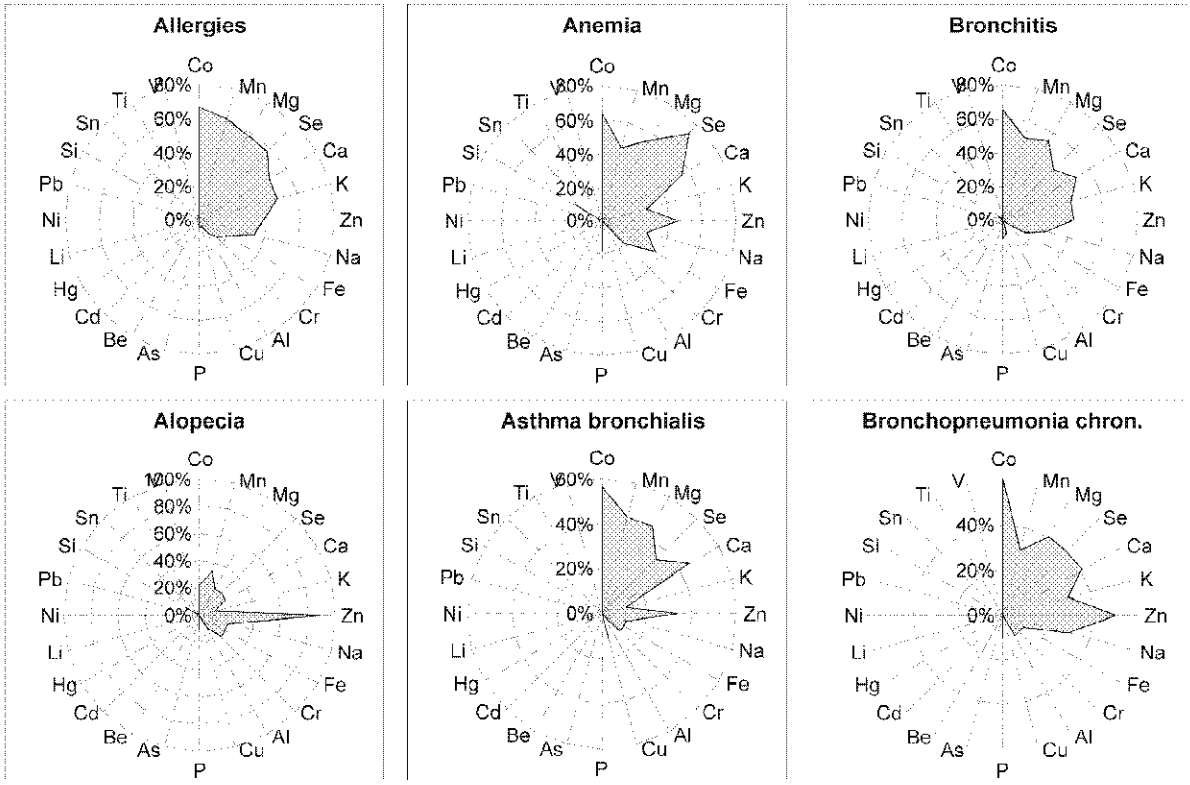

Figure 4. Risk of hypoelementoses (children, suffering from different diseases, Macedonia).

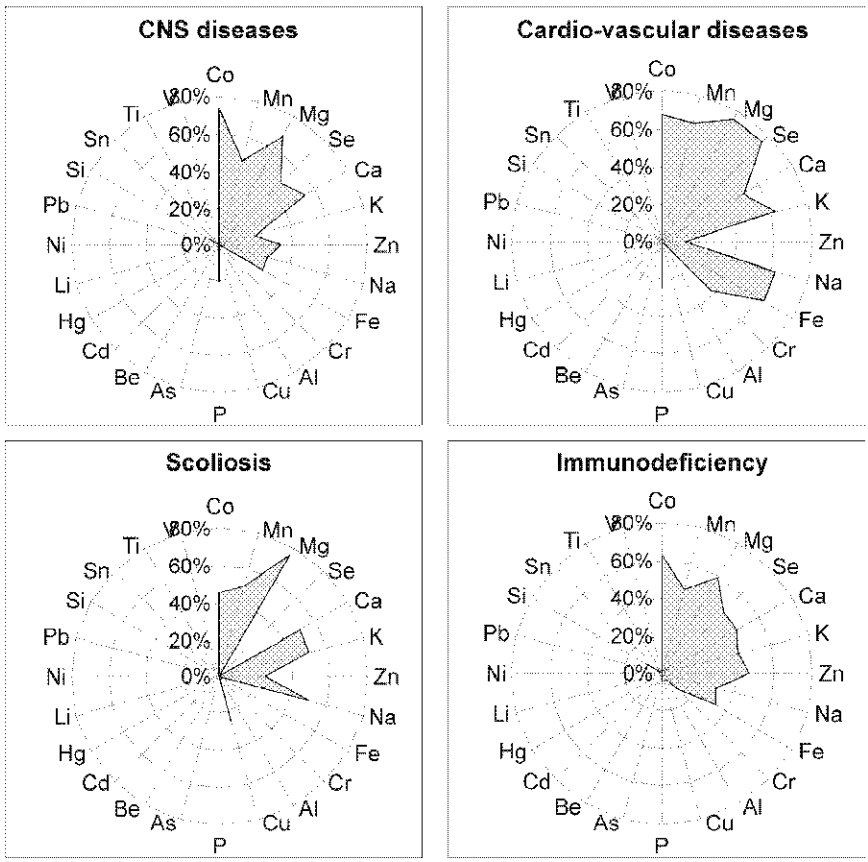

Figure 5. Risk of hypoelementoses (children, suffering from different diseases, Macedonia).