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THE SEXUAL DIFFERENCES IN 1–6 YEARS OLD CHILDREN MULTIELEMENT HAIR ANALYSIS

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ABSTRACT: The multielement hair analysis of relatively healthy 1–6 years old children (1986 males, 1994 females), living in different climato-geographical regions of Russia and CIS during the years 1997–2001 was made using ICP-AES method. Gradual decrease of hair P, Ca, K levels with age was observed. The hair Zn level in both boys and girls was found to be minimal in period from 2 till 5 years. 2–3 years old females demonstrated more profound decrease of hair Zn. Males had significantly higher K, Na, P, Pb, Sn concentrations in hair, females – higher concentration of Al, Fe, Ni. From age of 4 years girls had higher hair Ca, Mg levels. Both male and female groups demonstrated significant elevation of average Mn hair concentration in 3–4 year age. Male groups are generally characterized by higher concentration of toxic elements. Age-specific changes in hair elemental content of boys were found to be more significant as compared to girls.

Introduction

Major and trace elements play an important role in human nutrition, especially in childhood. Now it is undoubted that concentrations of chemical elements in human hair reflects condition of metabolic processes in the organism adequately enough. Methods for diagnostics of metabolic processes, based on analysis of hair elemental content, are developed and successfully applied. However, the dependence of elemental hair content on sex, determined by natural age- and sex-related differences in metabolism, is still insufficiently explored (Skalny, Skalnaya, 1999; Skalny, 2001).

Materials and Methods

Hair samples of 3980 relatively healthy children (1986 males, 1994 females) 1–6 years old were investigated. Concentration of the following 20 chemical elements in the samples was determined: Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Si, Sn, Ti, Zn.

Sampling. Hair samples were taken from occipital zone of scalps. Titanium nitride-coated scissors were employed throughout the campaign to minimize any possible release of contaminations elements. 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 labelled 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 3–4 cm, washed with a mixture of ethyl ether and acetone (3:1 v/v) under continuous stirring for 10 min, then dried at 85°C for 1 hour. After that the samples were treated with a diluted (5%) aqueous solution of EDTA for 1 hour, repeatedly rinsed with double distilled water, and finally dried at 85°C for 12 hour in an oven to determinate the sample dry weight just before the subsequent step is started. Hair digestion has been carried out in a microwave using wet ashing (HNO_3 and H_2O_2 as 3:1) procedure (Caroli et al., 1992).

Analytical determination has been carried out using inductively coupled argon plasma atomic emission spectrometry (ICP-AES) method because of its suitability for this kind of investigation (multielement capability, wide dynamic range, adequate detection possibility and relative independence from matrix interference etc.). "Thermo Jarrell Ash" ICAP-9000 spectrometer was used.

For the check-up our laboratory data the certified reference material of human hairs obtained from Shanghai Institute of Nuclear Research was analyzed (Table1).

TABLE 1. CONCENTRATION OF CHEMICAL ELEMENTS IN HAIR REFERENCE MATERIAL AS DETERMINED IN ANO CBM IN COMPARISON WITH THE REFERENCE DATA, MG/KG.

Element	Reference data	CBM data	Element	Reference data	CBM data
1.Ca	1162	1165	10.Se	0.6	1.0
2.Mg	100	82	11.Co	0.13	0.13
3.P	184	162	12.Cr	3.4	2.12
4.K	11.8	11.9	13.V	0.07	0.077
5.Na	266	269	14.Ni	1.7	1.5
6.Fe	64.6	64.9	15.Al	15.6	16.3
7.Zn	181	180	16.Cd	0.1	0.12
8.Cu	21.6	18.7	17.As	0.6	0.86
9.Mn	2.74	2.30	18.Pb	6.5	6.48

Table 2. Concentration of some chemical elements in hair of female children 1–6 years old, mg/kg (M±m).

Element	Age of girls				
	1–2 years (n = 319)	2–3 years (n = 410)	3–4 years (n = 414)	4–5 years (n = 387)	5–6 years (n = 464)
Al	23.94±0.71	**25.2±0.78**	25.42±0.77	23.33±0.7	22.94±0.75
As	0.26±0.02	0.24±0.02	0.22±0.02	0.24±0.01	**0.33±0.02**
Ca	462.41±23.19	452.97±20.21	466±21.15	460.23±23.4	**494.37±22.99**
Cd	**0.32±0.02**	0.36±0.04	0.42±0.1	0.26±0.02	**0.2±0.01**
Co	0.19±0.01	0.19±0.01	**0.2±0.01**	0.23±0.01	**0.16±0.01**
Cr	0.92±0.04	0.95±0.03	0.9±0.04	0.96±0.07	0.91±0.06
Cu	13.53±0.32	13.42±0.36	13.06±0.24	**13.66±0.44**	13.19±0.3
Fe	25.47±0.88	**24.89±0.81**	24.68±0.85	25.51±0.83	24.06±0.65
K	1183.76±76.84	1096.18±61.19	**1038.55±57.77**	938.55±56.98	**700.83±43.03**
Mg	33.42±2.78	35.61±2.68	35.73±2.61	**44.14±3.69**	**43.01±3.19**
Mn	0.91±0.1	0.88±0.06	1.14±0.21	0.89±0.07	0.81±0.04
Na	**643±47.98**	853.56±57.38	**787.41±44.88**	765.04±51.43	**565.33±34.92**
Ni	0.59±0.04	0.57±0.05	**0.71±0.11**	**0.73±0.07**	**0.85±0.1**
P	**147.78±1.65**	**141.58±1.55**	143.87±2.04	146.5±2.13	**140.09±1.76**
Pb	2.83±0.18	3.32±0.27	2.67±0.33	**2.13±0.15**	**1.94±0.1**
Se	1.02±0.08	0.86±0.04	0.99±0.07	**1.10±0.06**	0.94±0.05
Si	18.44±0.84	16.88±0.82	16.49±0.73	16.77±0.91	**16.96±0.88**
Sn	1.46±0.06	1.56±0.08	1.58±0.07	1.47±0.06	**1.37±0.06**
Ti	0.49±0.05	0.51±0.03	0.5±0.03	0.45±0.03	**0.46±0.03**
Zn	114.16±5.99	**93.56±4**	98.94±3.57	103.96±3.72	114.64±2.72

Bold font — significant ($p<0.05$) difference from boys of the corresponding age.

Results and Discussion

The obtained results of multielement hair analysis (Tables 2, 3) show that children's hair elemental content has the special features, depended on sex.

The boys of all investigated age groups differ from girls by higher P, K, Na and lower Ca, Mg hair content. The latter is more distinct after 4 years of age. In boys P, Ca concentration decreases as the age grows, and the K one decreases in the both sexes but more profoundly in girls. At the same time, Na hair concentration has a peak in both girls and boys in the age of 2 and 3 years respectively. Both male and female groups demonstrated the significant elevation of average Mn hair concentration in 3–4 year age.

In boys, growth is accompanied with gradual decrease of Cu hair content while the Zn concentration has a minimum in the age of 2–5 years. Girls are characterized by the similar dynamics of the Zn level with slightly more profound decrease in 2–3 years age, but Cu/Zn balance in this sex is more stable due to not such even decrease of Cu level as in boys. In females 1–5 years old higher hair concentration of Co, Cr and Fe is observed. However, after 5 years the situation is reversed.

A notable peculiarity of boys is higher hair concentration of toxic elements: Cd, Pb, Sn, As (see also Skalny, 2000), which is especially distinct in the age of 1–2 years. Such an early age of patients allows to suppose that this phenomenon is due to some endogenous (metabolic) reasons, not exogenous i.e. connected with differences in behavior of the sexes in the environment.

Girls have the maximum hair level of heavy metals (Pb, Zn, Cd) in the age of 3–5 years while, unlike boys, by 6 years of age the concentration of these toxic elements decreases to the minimum for investigated age range. The same pattern is true for Al. At the same time, concentration of other toxic elements such as As and Ni in girls' hair increases with time, reaching the maximum by 6 years of age, when it rises even higher than in boys.

It is noteworthy that significance of differences between the sexes in elemental hair content gradually increases with age (see Tables 1,2), that is obvious to be connected with the course of sexual differentiation.

As a rule, the amplitude of age-dependent changes in hair concentration of observed chemical elements is higher in girls than in boys. However, boys are characterized by more cases of dramatic changes in elements

Table 3. Concentration of some chemical elements in hair of male children 1–6 years old, mg/kg (M±m).

Element	Age of boys				
	1–2 years (n = 319)	2–3 years (n = 410)	3–4 years (n = 414)	4–5 years (n = 387)	5–6 years (n = 464)
Al	24.26±0.77	**23.04±0.73**	23.84±0.75	22.4±0.71	22.53±0.78
As	0.25±0.02	0.27±0.02	0.26±0.02	0.28±0.02	**0.23±0.02**
Ca	456.43±17.25	447.62±18.15	430.55±17.85	406.64±18.06	**396.06±15.13**
Cd	**0.43±0.04**	0.33±0.02	0.31±0.02	0.31±0.03	**0.35±0.07**
Co	0.17±0.01	0.18±0.01	**0.17±0.01**	0.21±0.01	**0.2±0.01**
Cr	0.92±0.05	0.87±0.03	0.9±0.04	0.87±0.03	0.94±0.05
Cu	13.73±0.38	13.83±0.43	13.35±0.36	**12.69±0.21**	12.81±0.27
Fe	25.41±0.97	**22.53±0.64**	24.25±0.79	24.01±0.88	24.27±0.69
K	1294.55±71.25	1211.16±59.57	**1245.62±68.06**	1005.98±57.74	**940.57±51.81**
Mg	32.22±2.08	31.5±2.2	32.7±2.34	**29.54±1.98**	**34.48±2.46**
Mn	1.28±0.24	0.78±0.03	1.17±0.19	0.8±0.04	0.84±0.04
Na	**848.82±54.39**	942.42±60.72	**1041.99±61.12**	917.21±59.45	**792.66±46.57**
Ni	0.75±0.13	0.51±0.07	**0.44±0.03**	**0.54±0.05**	**0.56±0.04**
P	**153.34±2.24**	**148.93±2.3**	147.49±2.02	145.77±1.57	**147.66±1.75**
Pb	3.22±0.23	3.34±0.36	3.74±0.47	**2.7±0.15**	**2.85±0.16**
Se	0.85±0.05	0.99±0.06	0.92±0.05	**0.87±0.05**	0.94±0.05
Si	16.91±0.63	18.37±1.05	15.47±0.68	16.9±0.72	**20.97±1.16**
Sn	1.6±0.07	1.42±0.06	1.6±0.09	1.49±0.07	**1.59±0.07**
Ti	0.54±0.04	0.44±0.03	0.45±0.03	0.51±0.04	**0.56±0.03**
Zn	114.63±5.28	**104.7±3.57**	101.27±3.47	101.22±2.87	118.77±2.93

Bold font — significant ($p<0.05$) difference from girls of the corresponding age.

hair concentration in the course of growth. Thus, in this sex group change in concentration of six elements — Cd, Cu, K, Pb, Mn, Si — exceed 15% of corresponding normal range, being gradual enough, while in girls only Cd, K, Na and Pb concentrations changes in such manner.

Conclusions

1. Human hair elemental content has the special features, depending on sex, not only in pubertal or adult age, but from the first years of human being.

2. Generally boys are characterized by higher concentration of toxic elements in hair than girls.

3. Difference between the sexes in elemental hair content gradually increases with age.

4. Boys are characterized by more significant changes in hair elemental content in the course of growth (Cd, Cu, K, Pb, Mn, Si) as compared to girls (Cd, K, Na, Pb).

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