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HAIR ELEMENTAL CONTENT OF TEENAGERS: INFLUENCE OF  
PHYSIOLOGICAL AND ECOLOGICAL FACTORS

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**SUMMARY:** Hair samples of 3980 relatively healthy teenagers (1676 boys, 2212 girls) of 10–14 years old, residing in different regions of Russia, were analyzed by ICP-AES method. Concentration of Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Si, Sn, Ti, V, Zn was determined. Girls were found to have higher level of Ca, Cu, Mg, Mn, Ni, Si, Zn and lower one of Cd, Cr, Fe, Hg, K, Li, Na, P, Pb, Ti than boys. The most distinct sex dependent differences are characteristic for major elements. Dependence of element level on age were found for all investigated elements except Co, Se, As, Sn, V. No considerable systematic effect of megalopolis conditions on elemental status of teenagers was detected. Boys were found to be more subject to elemental disorders than girls.

### Introduction

It is well-established that major and trace elements play an important role in human organism, participating directly or indirectly in regulation of virtually all vital functions and processes of organism's growth and development. Deviations in elemental balance may cause different disturbances of physiological processes. It is extremely important for such group of people as teenagers, because sexual maturation is connected with intensive deep changes in the organism while the course of these processes in a great measure determinates future reproductive health of the individual and, as a result, reproductive health of population. So, unveiling of principles determining formation of elemental status in this age seems an important problem. As it was established (Anke, Risch, 1979; Kollmer, 1983; Haaranalyse..., 1987; Skalny, 2000), hair elemental content reflects elemental status of the whole organism adequately enough and may be used for screening investigations and pre-nosological diagnostics of elemental disturbances and element-related diseases. In the present work we investigated possible connection of sex and age with content of major and trace elements in hair of patients, as well as general influence of ecological conditions.

### Materials and Methods

Hair samples collected during the years 1997–2002 from 3980 relatively healthy persons (1676 males, 2212 females) of 10–14 years old (Table 1), residing in different regions of Russia, were investigated. Among these persons several groups of people residing in some large industrial Russian cities (Moscow, St. Petersburg, Novosibirsk, Irkutsk, Tula) and a control group of people living in rural areas of Moscow Region were additionally separated in order to estimate an influence of ecological factors on hair mineral content.

In all cases concentration of the following 24 chemical elements in the samples was determined: Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Si, Sn, Ti, V, Zn.

**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 ICAP-9000 (Thermo Jarrell Ash, USA) and Optima 2000 DV (Perkin Elmer, USA) spectrometers.

Hair analyses were carried out in accordance with IAEA recommendations and methodical guidelines of Ministry of Health of Russian Federation. For the check-up our laboratory data the

Table 1. Distribution of the investigated persons along age and sex.

Sex \ Age	10 y.o.	11 y.o.	12 y.o.	13 y.o.	14 y.o.
Females	534	486	392	394	406
Males	384	376	312	297	307

Table 2. Average concentration of some chemical elements in hair of teenagers aged of 10–14 years depending on sex.

Chemical element	Girls (n = 2212), mg/kg (M±m)	Boys (n = 1676), mg/kg (M±m)	Significance of difference
Al	21.5 ± 0.36	21.95 ± 0.39	Not significant
As	0.293 ± 0.024	0.292 ± 0.01	Not significant
Be	0.008 ± 0.001	0.008 ± 0.001	Not significant
Ca	924.1 ± 16.5	521.6 ± 11.1	p <0.001
Cd	0.165 ± 0.008	0.191 ± 0.006	p <0.05
Co	0.166 ± 0.004	0.176 ± 0.007	Not significant
Cr	0.786 ± 0.019	0.861 ± 0.02	p <0.05
Cu	11.81 ± 0.17	11.26 ± 0.34	p <0.05
Fe	21.96 ± 0.43	24.68 ± 0.52	p <0.01
Hg	0.202 ± 0.012	0.283 ± 0.029	p <0.05
K	185.4 ± 8.7	414.2 ± 14.4	p <0.001
Li	0.052 ± 0.002	0.07 ± 0.005	p <0.05
Mg	74.09 ± 1.8	42.57 ± 1.4	p <0.001
Mn	1.132 ± 0.039	0.889 ± 0.023	p <0.01
Na	284 ± 9.5	608.9 ± 21.1	p <0.001
Ni	0.624 ± 0.034	0.461 ± 0.019	p <0.01
P	152.7 ± 0.9	158.9 ± 1.2	p <0.05
Pb	1.162 ± 0.079	2.279 ± 0.096	p <0.01
Se	1.396 ± 0.029	1.375 ± 0.035	Not significant
Si	27.96 ± 0.76	23.86 ± 0.68	p <0.01
Sn	1.079 ± 0.023	1.105 ± 0.028	Not significant
Ti	0.501 ± 0.013	0.569 ± 0.016	p <0.05
V	0.136 ± 0.006	0.152 ± 0.008	Not significant
Zn	189.5 ± 1.2	167.0 ± 1.2	p <0.001

certified reference material of human hair GBW09101, obtained from Shanghai Institute of Nuclear Research, was used.

Statistical calculations were made using Microsoft Excel XP application package. Data were compared using Student's t-test.

## Results and Discussion

The obtained results of multielement hair analysis (Table 2) showed that hair elemental content in teenagers of each sex considerably differs. Thus, girls as a whole are characterized by higher concentration of Ca, Cu, Mg, Mn, Ni, Si, Zn and lower concentration of Cd, Cr, Fe, Hg, K, Li, Na, P, Pb, Ti as compared with boys.

The most distinct sex-dependent differences are observed in concentration of major elements. Relative excess of Ca, Mg in girls as compared to boys is found to be 1.77 and 1.74 fold respectively. This proportion is observed through all the age range from 10 to 14 years, and so is the Ca/Mg ratio, which is practically stable and equal in both sexes through years, being about 12:1 (Fig. 1a). At the same time, Ca/P ratio is

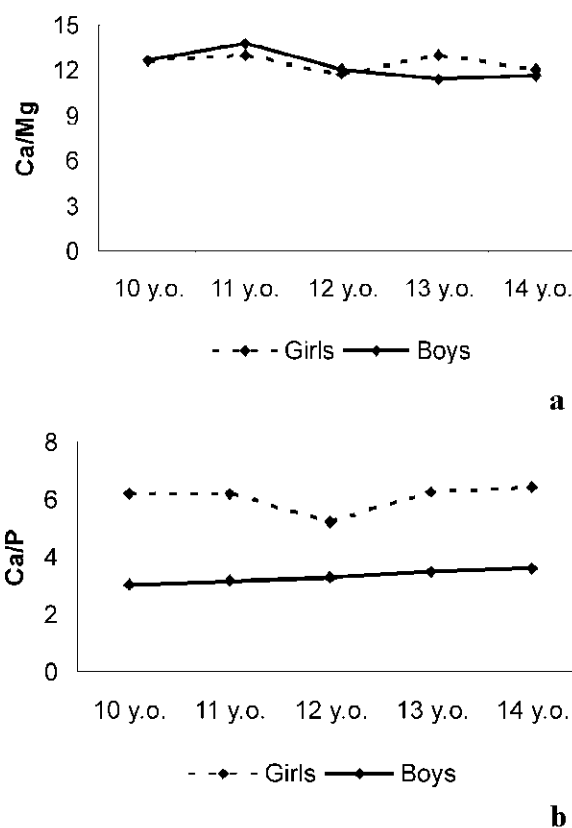


Fig. 1. Change of Ca, Mg and P rate in hair of teenagers depending on sex and age.

found to be very different in different sexes: 6:1 in girls and about 3:1 in boys (Fig. 1b).

Such a high level of phosphorus may be due to potentially more intensive energy exchange in boys, connected with use of energetic phosphates like ATP or GTP. It is also known that in processes of absorption phosphate is closely connected with sodium (Reichl, 2000), which is more abundant in boys. Age dependent dynamics of phosphorus level is poorly expressed. But there is a tendency towards increase of hair P concentration with age with statistically significant ( $p < 0.001$ ) peaks in girls of 12 y.o. and boys of 14 y.o. that possibly coincides with the end of growth spurt in corresponding sex. Absolute values of Ca, Mg concentrations increases with age in both girls and boys with the changes being more profound in boys (Fig. 2).

Quite another determinations were observed for sodium and potassium. Hair concentrations of K, Na were found to decrease with age. The decrease is more significant in girls, where level of these electrolytes turns nearly halved along the period from 10 to 14 y.o. (Fig. 3). On the contrary to Ca, Mg, boys have about two-fold more Na, K than girls. This proportion is also observed in all the age range, though not so strict as in case of Ca, Mg: it varies from 1.8 to 2.4 for sodium and from 1.8 to 2.6 for potassium. The K/Na balance is also very similar in both sexes, but unlike Ca/Mg it is not constant in time. There is a gradual change of K/Na

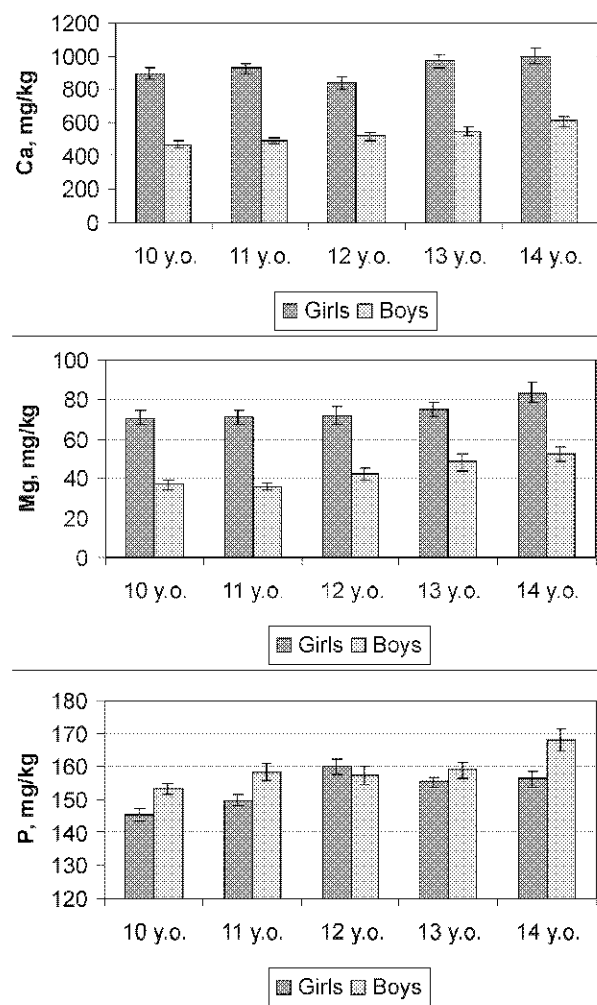


Fig. 2. Change of Ca, Mg and P concentration in hair of teenagers depending on sex and age.

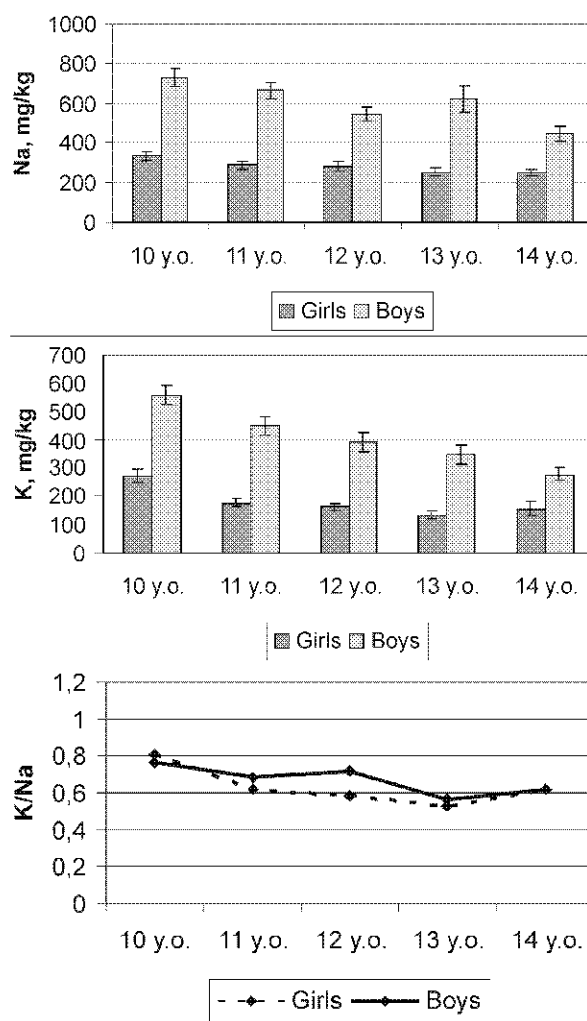


Fig. 3. Change of Na, K concentration in hair of teenagers depending on sex and age.

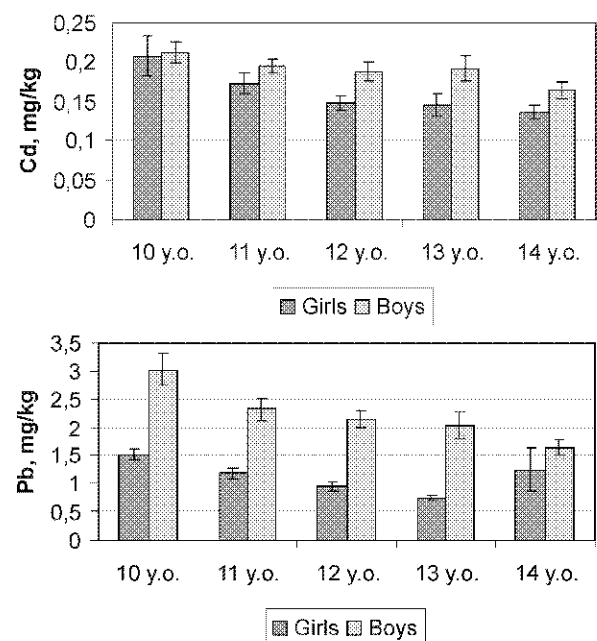


Fig. 4. Change of Cd, Pb and Hg concentration in hair of teenagers depending on sex and age.

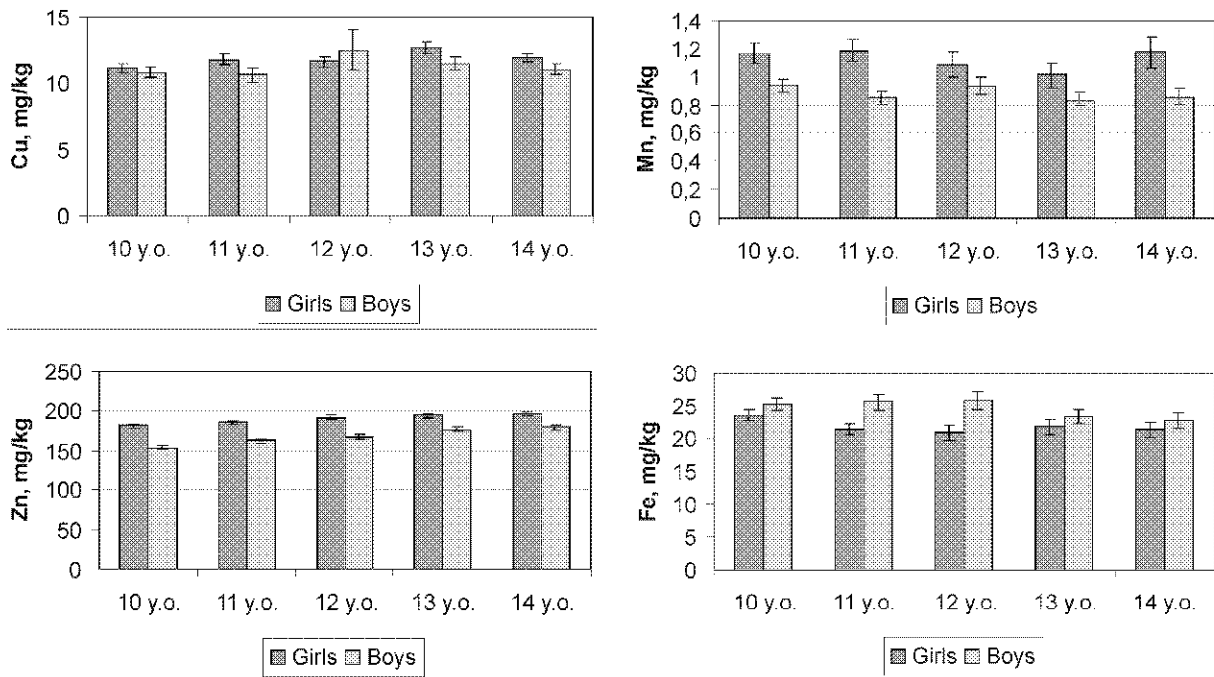


Fig. 5. Change of Cu, Zn, Mn and Fe concentration in hair of teenagers depending on sex and age.

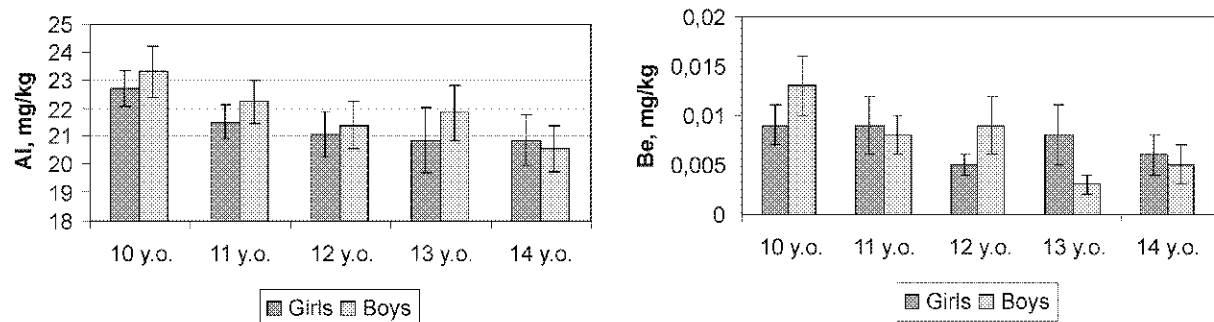


Fig. 6. Change of Al, Be concentration in hair of teenagers depending on sex and age.

ratio with age observed: its value decreases from 0.8 in the age of 10 years to 0.6 in 14 years. It is noteworthy that this decrease is observed not only in teenagers, but also in children of more early age, however in children of 1–6 years old concentration of K in hair exceeds that of Na (Skalnaya, Grabeklis, 2002) with the inversion happening in the age of 7 years.

Boys are characterized by higher concentration of toxic heavy metals: Cd, Pb, Hg (Fig. 4). It is especially distinct for Pb, where the difference is more than two-fold. This phenomenon was repeatedly pointed out earlier for different ages. The reasons of it are considered to be mainly of metabolic nature, because higher concentrations of toxic metals are observed in completely healthy persons living in non-polluted areas such as Caucasian villages (Gordon, 1985), and in infants where no sex dependent difference in environmental contacts supposed (Gordon, 1985; Skalny, 2000; Skalnaya, Grabeklis, 2002). Probably, the phenomenon may be connected with lower level of Ca, Mg and Zn, known as

antagonists of these metals, in boys. However, as young children as adult people have less difference in concentration of these metals in hair between sexes than teenagers. At the same time, absolute values of the Pb, Cd concentrations in young children are higher than those in teenagers while in adults they lower than in teenagers, becoming relatively stable after the age of 15–20 years at the low level. Considering the suggestions of essentiality of Pb for some vital functions (Anke, 1996) and relative essentiality of Pb, Cd, Hg as DNA protectors (Skalny, 2000), one may probably explain the increased gap in toxic metal levels between sexes by earlier physiological development of girls as compared with boys. More rapid development can result in earlier change of metabolism from “infant” pattern with high level of Pb, Cd, Hg to the “adult” one with low level of metals in girls while in boys the “infant” pattern keeps longer.

Higher levels of copper, manganese and zinc are observed in girls through all the investigated age period (Fig. 5). The only exception is the age group of 12 years

Table 3. Concentration of some chemical elements in hair of girls of 10–14 years old living in large cities in comparison with rural control area, (M±m).

Element	Concentration, mg/kg (M±m)					
	Moscow Region (control) n = 43	Moscow City n = 913	St.Petersburg n = 57	Tula n = 59	Novosibirsk n = 304	Irkutsk n = 38
Al	21.79 ± 2.28	22.42 ± 0.61	20.08 ± 1.9	20.21 ± 2.42	22.35 ± 0.81	19.62 ± 1.62
As	0.251 ± 0.049	0.333 ± 0.056	0.341 ± 0.053	0.32 ± 0.041	0.303 ± 0.019	0.191 ± 0.039
Be	0.005 ± 0.003	0.007 ± 0.001	0.002 ± 0.001	0.002 ± 0.001	<b>0.012 ± 0.003**</b>	0.012 ± 0.007
Ca	700.2 ± 57.7	811.9 ± 21.4	<b>466.8 ± 41.8***</b>	<b>1116.9 ± 104.2***</b>	<b>1303.2 ± 51.4***</b>	<b>543.9 ± 60.4*</b>
Cd	0.122 ± 0.019	0.134 ± 0.007	0.114 ± 0.019	0.169 ± 0.019	<b>0.289 ± 0.042***</b>	0.12 ± 0.02
Co	0.219 ± 0.031	0.158 ± 0.005	<b>0.126 ± 0.016*</b>	0.154 ± 0.027	0.218 ± 0.012	0.176 ± 0.027
Cr	0.711 ± 0.074	0.82 ± 0.039	0.735 ± 0.064	0.719 ± 0.055	0.811 ± 0.027	0.806 ± 0.085
Cu	10.47 ± 0.58	<b>12.86 ± 0.31***</b>	11.86 ± 0.97	<b>12.31 ± 0.73*</b>	11.21 ± 0.5	8.43 ± 0.53
Fe	26.35 ± 4.37	19.26 ± 0.65	28.39 ± 3.18	29.52 ± 3.67	22.97 ± 0.89	25.29 ± 4.86
K	221.5 ± 51.6	180.3 ± 14.6	168.6 ± 37.7	313.5 ± 84.2	181.7 ± 27.5	144.7 ± 44.8
Li	0.076 ± 0.016	0.055 ± 0.004	<b>0.025 ± 0.004***</b>	0.056 ± 0.008	0.05 ± 0.004	0.044 ± 0.011
Mg	77.54 ± 10.08	71.39 ± 3.04	<b>47.48 ± 7.68**</b>	82.93 ± 15.82	76.08 ± 3.16	<b>40.59 ± 7.73**</b>
Mn	0.784 ± 0.114	0.703 ± 0.025	0.904 ± 0.099	1.231 ± 0.178	<b>1.596 ± 0.115***</b>	0.816 ± 0.133
Na	473 ± 143.7	271.2 ± 13.9	240.8 ± 41.6	491.1 ± 119.8	251.7 ± 28.8	239.5 ± 77.4
Ni	0.436 ± 0.068	0.497 ± 0.035	0.501 ± 0.11	1.221 ± 0.543	<b>0.599 ± 0.05*</b>	0.341 ± 0.06
P	151.2 ± 4	155.2 ± 1.3	152.4 ± 5	158.3 ± 4.2	<b>139.4 ± 2.4*</b>	147.9 ± 4.8
Pb	1.04 ± 0.192	0.825 ± 0.042	0.898 ± 0.147	1.474 ± 0.322	<b>1.707 ± 0.123**</b>	1.224 ± 0.311
Se	1.532 ± 0.27	1.384 ± 0.034	1.368 ± 0.17	1.112 ± 0.112	1.548 ± 0.084	1.148 ± 0.154
Si	23.44 ± 3.99	26.61 ± 1.12	35.16 ± 5.61	19.96 ± 3.24	29.64 ± 1.9	22.88 ± 4.31
Sn	1.307 ± 0.337	1.066 ± 0.033	1.113 ± 0.151	1.035 ± 0.126	1.237 ± 0.065	0.96 ± 0.128
Ti	0.438 ± 0.058	0.468 ± 0.019	0.55 ± 0.098	0.406 ± 0.054	0.518 ± 0.031	0.427 ± 0.066
V	0.123 ± 0.022	0.129 ± 0.005	0.131 ± 0.016	0.135 ± 0.017	0.127 ± 0.008	0.111 ± 0.021
Zn	190.4 ± 8.1	199.1 ± 2	<b>174.3 ± 5.8**</b>	<b>176.4 ± 6.6*</b>	<b>176.6 ± 3.2*</b>	<b>153.8 ± 9.9***</b>

Note: Bold font indicates significant difference with control: \* – p < 0.05; \*\* – p < 0.01; \*\*\* – p < 0.001.

where mean concentration of copper in boys exceeds that of girls, however extremely high dispersion of copper concentration values in this group of boys makes the difference insignificant. Such an increased level of these trace elements can be partly due to biochemical interaction with lead and cadmium, which are known to be antagonists of zinc and copper. Besides this, Zn is intensively used during processes of body growth, especially of skeletal mass increase, and directly participate in male sexual function. These factors can also cause decrease of zinc mobile pool in boys, resulting in low hair concentration of the element. Investigation of infants' hair (Skalnaya, Grabeklis, 2002) did not show significantly increased levels of Cu, Mn, Zn in females of 1–6 years old. Thus, increased levels of copper and manganese in females are seems also typical for humans after beginning of sexual maturation (Skalny, 2000) and can be connected with direct participation of these elements in metabolism of female sexual hormones.

Female teenagers are found to have 1.1–1.3 times lower concentration of iron than males (Fig. 5). The difference is the most significant in the age of 11–12 years coinciding with typical period of growth spurt in girls before menarche. It happens mostly due to decrease of iron level in girls on the background of practically stable level in boys. It is noticeable that after the age of 12 years the situation inverts: iron level declines in boys being about constant in girls. Considering the fact that age of 13–14 years is a typical period of intensive growth in boys, it can be supposed that iron level dynamics is connected with this processes possibly being due to changes in effective blood volume. In addition, regular menstrual blood loss in females after menarche and generally lower level of hemoglobin as compared to males may determine relatively low hair iron concentration in girls above 13 years of age.

There is no distinct sex dependent differences in level of Al, however a tendency to decrease of its hair concentration with age was detected. The same is also

Table 4. Concentration of some chemical elements in hair of boys of 10–14 years old living in large cities in comparison with rural control area, (M±m).

Element	Concentration, mg/kg (M±m)					
	Moscow Region (control) n = 40	Moscow City n = 708	St.Petersburg n = 36	Tula n = 40	Novosibirsk n = 251	Irkutsk n = 42
Al	32.81 ± 4.27	<b>21.47 ± 0.55*</b>	24.52 ± 2.72	23.94 ± 3.55	23.9 ± 1.05	23.02 ± 2.61
As	0.383 ± 0.111	0.299 ± 0.016	0.507 ± 0.099	0.314 ± 0.05	0.324 ± 0.023	<b>0.172 ± 0.052*</b>
Be	0.007 ± 0.004	0.009 ± 0.002	0.002 ± 0.001	0.016 ± 0.02	<b>0.009 ± 0.002*</b>	0.003 ± 0.002
Ca	728.3 ± 88.2	<b>524.9 ± 19.3*</b>	<b>326.6 ± 36.4***</b>	719.4 ± 128.7	<b>464.9 ± 16.7*</b>	<b>418.1 ± 35**</b>
Cd	0.261 ± 0.044	0.164 ± 0.008	0.136 ± 0.024	0.244 ± 0.044	0.259 ± 0.018	<b>0.131 ± 0.021*</b>
Co	0.225 ± 0.033	0.174 ± 0.015	0.106 ± 0.016	0.133 ± 0.025	0.205 ± 0.012	0.214 ± 0.026
Cr	1.35 ± 0.238	<b>0.781 ± 0.021*</b>	0.815 ± 0.102	0.906 ± 0.106	0.918 ± 0.044	1.204 ± 0.131
Cu	10.8 ± 0.87	12.99 ± 0.77	10.34 ± 1.1	10.17 ± 0.54	9.72 ± 0.23	<b>8.42 ± 0.4**</b>
Fe	45.53 ± 7.47	<b>20.97 ± 0.66*</b>	25.52 ± 2.09	25.76 ± 2.68	<b>24.25 ± 1.08*</b>	29.69 ± 5.06
K	746.5 ± 140.6	379.6 ± 21	343.2 ± 82.9	567.2 ± 103.4	501.1 ± 39.6	441.3 ± 92.1
Li	0.084 ± 0.013	0.057 ± 0.004	<b>0.04 ± 0.007**</b>	0.083 ± 0.013	0.057 ± 0.004	<b>0.047 ± 0.01*</b>
Mg	59.67 ± 8.11	44.86 ± 2.54	<b>24.1 ± 2.63***</b>	55.18 ± 14.83	<b>27.8 ± 1.24***</b>	<b>29.53 ± 3.66**</b>
Mn	1.542 ± 0.283	<b>0.704 ± 0.027*</b>	<b>0.645 ± 0.104*</b>	1.16 ± 0.191	0.902 ± 0.047	0.932 ± 0.164
Na	1227.9 ± 266.7	<b>535.7 ± 26.4*</b>	771.2 ± 216.8	1001.7 ± 334.5	<b>647.9 ± 45*</b>	<b>596.9 ± 128.3**</b>
Ni	1.004 ± 0.307	0.431 ± 0.035	0.36 ± 0.068	0.556 ± 0.122	<b>0.353 ± 0.028*</b>	<b>0.371 ± 0.06*</b>
P	194.4 ± 16.7	159.4 ± 1.8	154.4 ± 5.7	184.3 ± 12.4	<b>147.4 ± 1.7*</b>	<b>146.1 ± 3.8*</b>
Pb	2.193 ± 0.343	1.625 ± 0.116	1.736 ± 0.241	<b>4.38 ± 1.396*</b>	<b>2.851 ± 0.252*</b>	3.305 ± 0.959
Se	1.494 ± 0.333	1.468 ± 0.061	1.258 ± 0.19	1.163 ± 0.128	<b>1.471 ± 0.081***</b>	1.189 ± 0.173
Si	30.2 ± 3.93	24.59 ± 1.2	21.25 ± 3.66	22.04 ± 3.77	22.9 ± 1.6	<b>18.4 ± 2.05*</b>
Sn	1.309 ± 0.17	1.113 ± 0.05	0.916 ± 0.12	0.975 ± 0.108	1.151 ± 0.051	0.959 ± 0.152
Ti	0.84 ± 0.135	0.544 ± 0.025	0.781 ± 0.132	<b>0.404 ± 0.054*</b>	0.553 ± 0.028	0.712 ± 0.161
V	0.177 ± 0.029	0.146 ± 0.007	0.142 ± 0.036	0.161 ± 0.053	0.137 ± 0.008	0.144 ± 0.032
Zn	154.7 ± 8.3	172.2 ± 2	157.6 ± 7.9	153.1 ± 9.4	152.4 ± 3.2	152 ± 11.1

Note: Bold font indicates significant difference with control: \* —  $p < 0.05$ ; \*\* —  $p < 0.01$ ; \*\*\* —  $p < 0.001$ .

true for Be (Fig. 6). Neither age nor sex dependent differences were found for Co, Se, As, Sn, V.

Comparison of the data about elemental hair content of teenagers living in large cities with those of residents of rural areas of Moscow Region, having no considerable industry or energetic plants and known as unpolluted, did not reveal any systematic differences in elemental status of these categories of people including concentration of toxic metals. Only residents of Novosibirsk have significantly higher level of metal pollutants as lead, cadmium and beryllium with the difference being more distinct in girls ( $p < 0.01$ ). High concentration of Pb in hair is also observed in male residents of Tula, however it is not characteristic of female inhabitants. Among essential elements lower level of zinc in females is observed in all the investigated cities except Moscow. Notice may be also taken of difference in concentration of calcium, which differs from control in both boys and girls of virtually all cities, being usually lower than control. However, on the contrary,

girls of Tula and Novosibirsk has significantly higher Ca concentration as compared with Moscow Region.

Generally, number of elements, which level significantly differs from control, increases with distance from Moscow Region. It allows to suppose that biogeochemical and nutritional peculiarities have much more influence on elemental status of teenagers than technogenous load do. As it may be seen in Tables 3–4, boys are characterized by higher number of differences than girls. Besides other factors, it may be due to lower biochemical and physiological constancy, characteristic for male organism in comparison to the female one.

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