

# METAL IONS

## MEN'S AND WOMEN'S HAIR TRACE ELEMENT CONCENTRATIONS IN MOSCOW REGION

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**ABSTRACT:** The analysis of 1206 20–40 years old human's hair samples, collected in Moscow Region (excluding the Moscow city) by ICP-AES shows, that in comparison to average data, obtained in our laboratory for European part of Russia and Moscow city, the lower hair As and higher Mg, Mn, Ca and Fe concentrations in Moscow Region men and women were observed. Comparison to Moscow city shows increased hair Cd level in men and women and Pb, Sn levels — only in men. Significant differences between rural and urban hair concentrations (higher Zn, P in women, living in rural part; lower Sn and higher Cu, Fe in men, living in rural part of Moscow Region) was established. There is an evident correlation between distance from Moscow city and elemental hair composition, more significant in men as compared to women. There is significant variability in men hair concentrations of some important trace elements: Ca, Mg, Na, Pb, Fe, Cu, Mn concentration was increased in middle and far zone in comparison with the nearest to Moscow city part of region; concentration of As and Se in far and middle zone was lower. In hair of women, living in far zone of Moscow Region, higher concentration of Sn and lower concentration of Si in comparison with the nearest and middle zone were detected. Also, the dependence of hair elemental content on geographical direction was established. Hair Na, P, Fe, Pb, Cd concentration was significantly higher in men, living on south direction. Estimation of women's hair elemental content didn't show significant differences between inhabitants of different geographical directions.

### Introduction

The influence of unfavorable social, economical and ecological factors on humans is one of the reasons of public health worsening in many regions of Russia. The decline of demographic data is firstly due to dangerous for health chemical and physical factors of anthropogenic origin (heavy metals and organic compounds pollution, radiation, electromagnetic fields etc.). On the other hand, today the deficiencies and excesses of trace elements of natural origin in some Russian regions are very widespread (Veldanova, Skalny, 2001). By the by, there are a few representative analytical data (Skalny, 2000) concerning epidemiology of elementoses in different regions including Moscow Region. The aim of the

present study is evaluation of elemental homeostasis and adequate provision of adult inhabitants of Moscow Region with major and trace elements on the base of multielement hair analysis.

### Material and Methods

There are 6580 thousands of inhabitants in Moscow Region (except Moscow city). The birth rate is lower than average in Russian Federation (–6.7‰ vs. 8.6‰) and mortality is relatively high (15.1‰ vs. 13.8‰). The children morbidity is also worse, than in whole Russia (1629.4‰). There is relatively high incidence of infectious diseases (114.4‰ vs. 102.7‰), broncho-pulmonary diseases (985‰ as compared to 790.9‰ in Russia).

Totally, 1206 relatively healthy men and women 20–40 y.o., living in Moscow region were observed and their hair samples, collected during 1997–2001, were investigated.

**Sampling.** During the physicians' examinations the special medical documentation, including questionnaire, were filled and scalp hair (occipital part) samples were collected.

Titanium nitride-coated scissors were employed throughout the campaign to minimize any possible release of contaminations elements. 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.** Washing of 0.2–0.5 g of hair (see Caroli et al., 1992), cut in pieces no longer than 3–4 cm, with a mixture of ethyl ether and acetone (3+1 v/v) under continuous stirring for 10 min, drying at 85°C for 1 hour, treatment with a diluted (5%) aqueous solution of EDTA for 1 hour, repeating rinsing with double distilled water, and finally drying at 85°C for 12 hour in an oven to determinate the sample dry weight just before the subsequent step is started. Hair microwave digestion has been carried out using wet ashing (HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> as 3:1) procedure.

**Analytical determination** has been carried out using inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) because of its suitability for this kind of investigation (multielement capability, wide dynamic range,

TABLE 1. CONCENTRATION OF CHEMICAL ELEMENTS IN HAIR OF INHABITANTS (20–40 y.o) OF MOSCOW REGION, MOSCOW CITY AND WHOLE RUSSIA.

Element	Moscow		Russia		Moscow Region	
	Women	Men	Women	Men	Women	Men
	n = 2854	n = 1634	n = 2865	n = 2756	n = 862	n = 344
Al	20.24±0.25	22.56±0.38	22.14±0.27	22.86±0.3	20.86±0.59	23.37±0.93
As	0.35±0.03	0.34±0.01	0.24±0.03	0.31±0.01	<i>0.27±0.02</i>	<b>0.25±0.02</b>
Be	0.02±0	0.01±0	0.02±0	0.01±0	0.01±0	0.01±0
Ca	1094.07±16.75	757.89±14.63	1109.74±18.01	806.94±11.4	<b>1327.8±35.53</b>	<b>998.52±48.2</b>
Cd	0.18±0.01	0.21±0.02	0.19±0.01	0.23±0.01	0.18±0.01	0.25±0.02
Co	0.24±0	0.2±0.01	0.24±0	0.19±0.01	0.23±0.01	0.23±0.01
Cr	0.93±0.02	0.93±0.02	0.96±0.02	0.97±0.02	1±0.05	1.02±0.08
Cu	14.85±0.15	15.98±0.23	14.11±0.15	15.99±0.17	15.33±0.28	15.21±0.46
Fe	17.86±0.26	22.72±0.52	20.15±0.32	25.26±0.45	<b>24.77±0.67</b>	<b>32.71±1.72</b>
K	111.9±3.82	211.89±7.26	128.55±4.49	288.98±6.79	<i>144.96±10.24</i>	<i>260.33±19.59</i>
Li	0.07±0	0.08±0.01	0.09±0	0.09±0	0.08±0	0.13±0.02
Mg	89.07±1.93	59.23±1.56	97.81±2.19	61.05±1.27	<b>135.37±5.11</b>	<b>92.06±5.62</b>
Mn	0.9±0.02	0.83±0.05	1.28±0.04	0.92±0.03	<i>1.3±0.06</i>	<b>1.4±0.18</b>
Na	229.45±6.9	425.21±13.64	216.8±6.5	508.01±10.98	250.03±12.29	486.87±33.03
Ni	0.49±0.02	0.6±0.04	0.54±0.02	0.61±0.02	0.59±0.03	0.92±0.17
P	168.83±0.92	173.87±1.46	170.38±0.93	176.66±1.27	174.85±1.82	186.41±4.19
Pb	1.1±0.12	1.43±0.06	1.28±0.12	1.7±0.06	1.31±0.18	<b>2.55±0.27</b>
Se	1.22±0.03	1.08±0.03	1.3±0.03	1.06±0.03	1.17±0.06	0.99±0.09
Si	27.33±0.68	27.76±0.87	22.4±0.6	26.8±0.62	24.9±1.17	22.24±1.52
Sn	1.45±0.02	1.24±0.03	1.71±0.03	1.26±0.02	1.65±0.06	<b>1.64±0.1</b>
Ti	0.54±0.02	0.48±0.02	0.56±0.02	0.51±0.01	0.5±0.03	0.66±0.06
V	0.17±0.01	0.15±0.01	0.19±0.01	0.17±0.01	0.19±0.02	0.18±0.03
Zn	198.09±1.04	183.94±1.46	197.92±1.07	180.02±1.08	205.04±2.31	183.84±3.61

Bold font — significant difference from the data of Moscow and whole Russia.

Italic font — significant difference from the data of Moscow.

adequate detection possibility and relative independence from matrix interference, among others).

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

## Results and Discussion

The most salient characteristic of Moscow Region as a whole is considerably higher level of Ca, Mg, Fe, Mn and lower level of As in human hair, as compared to corresponding data from Moscow and average data from whole Russia (Table 1). Thus, Ca concentration in hair of women 20–40 years old is 1094.07±16.75 mg/kg, 1109.74±18.01 mg/kg and 1327.8±35.53 mg/kg, while that in men 20–40 years old is 757.89±14.63 mg/kg, 806.94±11.4 mg/kg and 998.52±48.2 mg/kg (Moscow, whole Russia and Moscow Region respectively). The Fe concentration in both women and men is also higher than

in Moscow city and whole Russia, while higher level of Mn as compared to average data from Moscow and whole Russia is detected only in men 20–40 years old (in women it is so only in comparison with Moscow). Lower As concentration in men as compared to those from Moscow and whole Russia (0.34±0.01, 0.31±0.01 and 0.25±0.02 mg/kg) is also noteworthy. At the same time, the difference in concentration for women is significant only between Moscow Region and Moscow (0.27±0.02 and 0.35±0.03 mg/kg, respectively,  $p<0.05$ ).

Higher concentration of K in hair of both men and women living in Moscow Region as compared to Moscow (260.33±19.59 and 211.89±7.26 mg/kg in men, 144.96±10.24 and 111.9±3.82 in women) may be also claimed as a special feature.

Men from Moscow Region are characterized by higher concentration of lead (2.55±0.27, 1.43±0.06, 1.7±0.06 mg/kg — Moscow Region, Moscow and whole Russia respectively,  $p<0.05$ ) and, in lesser degree, tin —

1.64±0.1 mg/kg in Moscow Region, 1.24±0.03 in Moscow and 1.26±0.02 in whole Russia ( $p<0.05$ ).

Generally, the obtained data allow to conclude that “elemental portrait” of men is the most original (there are significant differences in concentration of 10 and 8 chemical elements in comparison with the data from Moscow and whole Russia respectively). Women’s “elemental portrait” is mostly similar to that from whole Russia and Moscow, although has some differential peculiarities. Particularly, women, living in Moscow Region are characterized by high level of hair Mg, Ca, Pb, Ni, Cd, Sn, Fe, Mn and low level of As, that is, probably, determined by complex of natural geochemical and technogenic factors.

#### Influence of distance from the city to the place of residence

Analysis of the data about hair elemental content of adult inhabitants of Moscow Region has allowed to conclude that values, obtained from men and women living at different distances from Moscow city, considerably differ, and the difference is the most distinct in men. Thus, in men concentrations of 12 chemical elements differ significantly, while in women concentrations of only 2 elements — Si and Sn — do so.

In the investigated women significant ( $p<0.05$ ) differences in Si (deficiency) and Sn (excess) concentration between inhabitants of fare zone of Moscow Region and those of nearest and middle zone were found.

Unlike women, men have no significant differences in hair concentration of Si and Sn. At the same time, concentration of most observed elements in men’s hair (Ca, Mg, Na, Pb, Fe, Cu, Mn) increases with the distance from Moscow city while the levels of As and Se decrease. I.e., degree of hair mineralization in men from middle and far zones of Moscow Region is considerably higher than that in men from the nearest zone, that may be due to both increased intake of chemical elements with water or food (intake of non-refined locally cultured products, often grown near roads (Pb)) and (this is obvious to be the main factor), higher abundance of men, exposed to physical strain or occupational pollutants in the middle and far zones unlike the nearest zone of Moscow Region and Moscow city, where people, as a rule, are employed in tertiary industries or mental work.

#### Influence of geographical location of the place of residence

An estimation of elemental status of adult population was also carried out using comparison of the average and relative values, obtained from different geographical directions.

The most peculiar data was obtained in the southern direction, where male population is characterized by considerably higher hair concentration of P (232.94±17.87 mg/kg, vs. 162.15±9.32 to 182.64±13.82 mg/kg in the other directions); two-fold excess of Na concentration over other directions — 680.45±116.17 mg/kg (except northern and northeastern directions, where Na concentration was similar — 693.55±142.77 and 620.68±115.37 mg/kg, respectively); and considerably higher Fe level — 46.37±7.49 mg/kg (the minimum concentration was 21.33±2.99 mg/kg in south-west). At the same time, the maximum level of Pb and Cd (3.77±1.45 and 0.3±0.06 mg/kg, respectively) in hair is found here. We have not found any special features of men’s hair elemental content in the other directions.

Analysis of women’s hair elemental content in Moscow Region has not show any clear dependences of the “elemental portrait” from the geographical direction. The only significant difference was lower concentration of Sn in hair of women, living in southwestern direction (0.93±0.23 mg/kg).

TABLE 2. PECULIARITIES OF ELEMENTAL BALANCE OF MOSCOW REGION INHABITANTS (20–40 y.o.).

Direction	Women	Men
North	$\frac{Sn}{Mn, Cr, Si, Se, K, Fe, Na}$	$\frac{K, Na, Sn}{Zn, Mn, Cr, Si, Se, Fe}$
North-East	$\frac{Sn, Mg}{Mn, Cr, Si, Se, K}$	$Si, K \frac{Na, Cu, Ca}{Mn, Cr, Se, Fe}$
East	$\frac{Mg, Ca, Sn}{Mn, Cr, Si, Se, K, Fe}$	$Cr \frac{Na}{Zn, Mn, Si, Se, K, Fe, Mg}$
South-East	$\frac{Ca, Sn}{Mn, Cr, Si, K}$	$Se \frac{Na, Sn}{Mn, Cr, Si, K}$
South	$\frac{Mg}{Mn, Cr, Si, Se, K, Fe}$	$Cr \frac{Na, Cu}{Zn, Mn, Si, Se, Fe}$
South-West	$Si \frac{Mg, Ca, Cu}{Zn, Mn, Cr, Se, K, Na}$	$Mn, Cr \frac{Si, Cu}{Zn, Se, Fe}$
West	$\frac{Mg, Sn}{Mn, Cr, Se, K, Fe}$	$\frac{K, Na, Sn}{Zn, Mn, Cr, Si, Se, Fe}$
North-West	$Cr, Si \frac{Mg, Sn}{Mn, Se, K, Fe}$	$Cr \frac{Sn, Al}{Zn, Si, Se, K}$

Risk of elementosis  $\frac{\text{risk of hyperementosis}}{\text{risk of hypoelementosis}}$

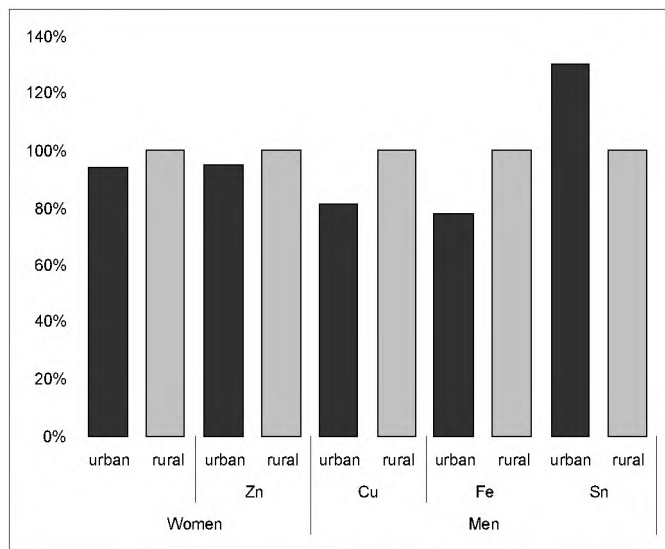


Fig.1. SIGNIFICANT DIFFERENCES BETWEEN HAIR ELEMENTAL CONTENT OF URBAN AND RURAL INHABITANTS (100% — concentration of elements in hair of rural population).

Table 2 shows deviations in elemental balance, characteristic for inhabitants of Moscow Region in different directions.

As Table 2 shows, high frequency of Cr, Se, Fe, Mn and Si deficiencies is characteristic for both men and women in all locations. Also some imbalances in elemental content, characteristic for just either men or women are found in Moscow Region. Thus, a special feature of men is high abundance of low Zn level in hair, which is very rare in women (except the southwestern direction), and high concentration of Na. At the same time, low concentration of K, detected in hair of women in all directions of Moscow Region, is less abundant in men (east, south-east and north-west of Moscow Region), and excess level of Mg in hair, characteristic for women (all directions except northern and southeastern ones), is absent in men.

Analysis of abundance of the risk of toxic elements excesses shows high frequency of Sn (except southern and southwestern directions) excess in women and, more rarely, in men (usual for northern, southeastern and northwestern directions). It is notable that, unlike children, adults virtually do not demonstrate high concentration of Pb and Cd in hair.

Comparison of hair elemental content of urban and rural residents shows moderate differences (Fig. 1). Thus, significant difference ( $p < 0.05$ ) is found in hair Zn and P level in women of 20–40 y. o.: the concentration is lower in urban inhabitants than in rural ones. According to literature data (Passwater, Cranton, 1983; Skalny,

2000 etc.), this fact may indicate lower provision of urban women with protein-rich (meat, fish, beans). Also, lower level of Zn and P in hair may reflect relative decrease of immune status, because Zn and P play an important role in regulation of immune response (Skalny, Koudrine, 2000).

As the present study shows, men, living in rural areas of Moscow Region, are featured by significantly higher hair content of Fe, Cu, and relatively lower — Sn. Such situation may be due to different factors: difference in nutrition (Passwater, Cranton, 1983), alcohol intake (Skalny, 1990), occupational peculiarities, peculiar features of water supply.

## Conclusions

1. Trace element status of men and women from Moscow region depends on ecological and geographical factors;

2. Middle and far zones of Moscow region are characterized by highest concentration of most chemical elements (both toxic and essential ones);

3. For all parts of Moscow region the risk of Cr, Se, Fe, Mn and Si deficiencies is typical for men and women, low hair Zn and high Na — only for men and low K and high Mg — for women;

4. Differences between elemental hair content of urban and rural populations are moderate.

## References

- Caroli S., Senofonte O., Violante N. 1992. Assessment of reference values for elements in hair of urban normal subjects // *Microchem. J.* Vol.46. No.2. P.174–183.
- Passwater R.A., Cranton E.M. 1983. Trace elements, hair analysis and nutrition. New Canaan: Keats Publ. 420 p.
- Skalny A.V. 1990. Investigation of influence of chronic alcohol intoxication on Zn, Cu and Li in organism: dissertation for the degree of Medicine candidate. Moscow. 137 p.
- Skalny A.V. 2000. Ecological-physiological reasoning of effectiveness of major and trace elements use for correction of homeostatic disturbances in patients from different climatogeographical regions: dissertation for the degree of Medicine Doctor. Moscow. 361 p.
- Skalny A.V., Koudrine A.V. 2000. Radiation, trace elements, antioxidants and immunity. Moscow: Lir Maket. 421 p.
- Veldanova M.V., Skalny A.V. 2001. Multielement analysis of human hair in children, suffering from goiter // Abstract of 1-st International Congress “Trace Elements and Minerals in Medicine and Biology”, May 16–19, 2001. Venice, Italy. P.121.

Аннотация: анализ 1206 образцов волос человека 20–40 лет, собранных в Московской области (за исключением города Москвы) методом ICP-AES, показал, что по сравнению со средними данными, полученными в нашей лаборатории для европейской части России и города Москвы, наблюдались более низкие концентрации As в волосах и более высокие концентрации Mg, Mn, Ca и Fe в Московской области у мужчин и женщин. Сравнение с Москвой показывает повышенный уровень Cd в волосах у мужчин и женщин и уровень Pb, Sn — только у мужчин. Достоверные различия между концентрациями волос в сельской и городской местности (более высокий уровень Zn, P у женщин, проживающих в сельской местности; установлено более низкое содержание Sn и более высокое содержание Cu, Fe у мужчин, проживающих в сельской местности Московской области). Существует