Hair and Wool as Indicators of Environmental Pollution by Man-Made and Geochemical Sources

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Abstract: The concentration of trace elements in the human body is regulated very finely. This control is carried out by certain proteins, hormones and depositing systems (bone tissue, hair, cornea, etc.). On the other hand, the relationship between metal ions and their binding substances is so close that changes in the state of the body can be the result of both increased and decreased content of metal ions compared to the norm. The study of tissues and body fluids for the content of elements is therefore a very important diagnostic test.

A human body weighing 70 kg contains 1050 g Ca, 245 g K, 105 g Na, 35 g Mg, 700 g P, 100 g Cl, 3 g Fe, 20 mg Mn. Some of the elements such as Cs, Rb, Sr, Ni are relatively non-toxic. Others are highly toxic - Sb, As, Ba, Rb, Hg, Ag, etc. The toxicity is strongly influenced by the form in which the metal ion is located. The formation of fat-soluble complexes with organic ligands increases toxicity. A classic example is Minimat’s disease, the cause is the transformation of inorganic mercury from wastewater into methylmercury under the action of vitamin B12 contained in microorganisms, which then enters the body with water or food.

Key words: Trace element, toxicity, indicator, hair, wool, technogenic, geochemical, heavy metals, background concentration, technogenic province, metallothioneins, ligand systems.

Before judging changes in the chemical composition of the organism under the influence of external influences, it is necessary to carefully study the background contents of chemical elements under the specific natural and economic conditions of the region. Of great importance for biological monitoring is the choice of the analyzed indicator or so-called “critical” organ. It must meet certain general requirements, that is, be easily accessible, objectively reflect the level of exposure and provision of the body with microelements. These requirements, according to a number of authors, are met by hair and wool. In connection with the foregoing, we studied the possibility of using this test in the natural and economic conditions of the region. At the same time, we, first of all, faced two tasks: to find out the background concentrations of microelements in the absence of pollution and to establish how objectively hair and wool reflect the microelement status of a person under the studied conditions.

The purpose of the study: The study of tissues and body fluids for the content of trace elements and the study of hair and wool as an indicator of environmental pollution by technogenic and geochemical sources.

Research materials and methods: Successful biogeochemical research requires the development of non-destructive methods for obtaining objective information about the mineral metabolism of animals and humans, reflecting their physiological state, the influence of environmental factors and nutritional levels. In this aspect, the most promising and practically significant are hair and wool, which are easily accessible for analysis and contain high concentrations of all chemical elements present in the body. To resolve the issue of the suitability of epidermal structures as bioindicators, it was necessary, first of all, to find out the
dependence of the behavior of more than 40 chemical elements found in the hair on its main organic components of pigments and proteins, to develop new and modify existing chemical-analytical methods for determining the levels of elements in hair. these materials and use the obtained data for the purposes of biogeochemical zoning and assessment of the technogenic load of the environment. In studies, to determine the background concentrations of trace elements, we selected black hair samples from 16 girls and 16 boys aged 7-12 years old, studying in a rural school. The hair of children better than the hair of an adult reflects the microelement status of the body, since it is less exposed to various cosmetic products.

To identify the impact of emissions from the chemical plant on the microelement status of yellow ground squirrels, 14 animals were caught in the territory of the technogenic province and 11 in the control zone.

The extraction concentration method is most often combined with atomic absorption. For extraction concentration in atomic absorption, extraction of intracomplex compounds is used. The selectivity of atomic absorption makes it possible to widely use group reagents, such as diethyl- and pyrrolidinedithiocarbamites, dithizone, oxyquinoline, etc.

More widely, ammonium pyrrolidine dithiocarbamate (APCA) is used for extraction concentration in atomic absorption. This reagent also interacts with many metals, and in solutions it is more stable than sodium DDC (sodium diethyldithiocarbamate).

Atomic absorption determinations were carried out on Saturn and Spektr instruments. The device "Spectrum" was modified. Modification and improvements concerned the introduction of a pulsed "furnace-flame" atomizer and related components.

To analyze the solution, an atomizer was used, which is a graphite rod with a longitudinal groove with strictly specified dimensions. The absorption signal was recorded using a KSP-4 potentiometer or an IO-2 integrator connected by a compensation circuit to the potentiometer. The temperature of the graphite rods was measured with an optical device.

**Results and their discussion:** The results of the analysis of the hair of children from the control zone indicate that the content of copper in the hair of girls from the zone not affected by industrial emissions, aged 6-10 years, is 21, and boys -24 mg/kg. It is interesting to note that in a woman's hair, the copper content at the age of 11-12 is 15, and in a man's hair it is more than two times higher - 37 mg / kg. In our studies, the background level of copper in the hair of boys was also higher than that of girls, but the difference was not so significant. We also observed higher levels of lead and manganese in the hair of girls than boys. We did not find differences in the level of arsenic in the hair of children of different sexes. According to the level of manganese 1.0 mg/kg for girls, 1.1 mg/kg for boys. Data on the concentration of lead in the hair of children living in an industrial area covers a wide range of fluctuations - from 10.7 to 112.3 mg/kg.

Our results correspond to the average values given for a human hair for the above elements, which are copper - 19, zinc - 220, manganese - 0.25-5.7, lead - 3-70, arsenic - 0.60-3.7 mg/kg.

**Table 1.7. The content of trace elements in the hair of children from the technogenic province**

<table>
<thead>
<tr>
<th>Elements sampling location, gender</th>
<th>Copper</th>
<th>Zinc</th>
<th>Lead</th>
<th>Manganese</th>
<th>Arsenic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Technogenic province (n=32)</strong></td>
<td>23</td>
<td>190</td>
<td>8.8</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Girls (n=16)</td>
<td>22.5±1.2</td>
<td>182±11</td>
<td>9.2±0.4</td>
<td>1.3±0.1</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td>Boys (n=16)</td>
<td>23.5±1.5</td>
<td>198±8</td>
<td>8.4±0.2</td>
<td>1.3±0.1</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td><strong>Background (n=32)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Girls (n=16)</td>
<td>25.0±0.7</td>
<td>232±6</td>
<td>2.3±0.1</td>
<td>1.3±0.1</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>Boys (n=16)</td>
<td>29.0±1.0</td>
<td>208±10</td>
<td>2.1±0.1</td>
<td>1.1±0.2</td>
<td>0.3±0.1</td>
</tr>
</tbody>
</table>
As can be seen from Table 1, the level of copper and zinc in the hair of 7–12 year old children in the area affected by emissions from the chemical plant is lower than in children from the control area. According to the content of these elements in the hair, the same picture is observed as in the wool of farm animals and yellow ground squirrels, as well as the smoothing of sex differences in the concentration of these elements. There were no significant differences in the content of manganese in the hair. The hair of children from the technogenic province is enriched with lead by more than 3 times and arsenic by 4 times compared with the control.

To identify the impact of emissions from the chemical plant on the microelement status of yellow ground squirrels, 14 animals were caught in the territory of the technogenic province and 11 in the control zone. The results of the determination of trace elements in the organs and tissues of ground squirrels are presented in Table 2. As follows from the table, the copper content in the organs and tissues of animals in the technogenic province is significantly lower than the background values. The greatest difference (2 times or more) was noted for the brain, wool and liver. In other organs and tissues, these differences range from 10-38% and are not always statistically significant.

<table>
<thead>
<tr>
<th>Table 1.5</th>
<th>The content of trace elements in the organs and tissues of yellow ground squirrels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Background (household) (n=11)</td>
</tr>
<tr>
<td>Bone</td>
<td>0.9±0.3</td>
</tr>
<tr>
<td>Brain</td>
<td>9.4±2.72</td>
</tr>
<tr>
<td>Wool</td>
<td>5.3±1.1</td>
</tr>
<tr>
<td>muscles</td>
<td>1.8±0.4</td>
</tr>
<tr>
<td>Lungs</td>
<td>14.8±4.16</td>
</tr>
<tr>
<td>Kidneys</td>
<td>1.6±0.4</td>
</tr>
</tbody>
</table>

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Thus, the depletion of the body with copper under the influence of emissions of phosphate production is observed in full in rodents and is not associated with the structural features of the digestive tract.

It is interesting that in gophers, unlike ruminants and humans, the kidneys are richer in copper content than the liver. Such a picture is observed both in the conditions of the physiological norm and in the technogenic province. A similar situation is observed in rats, in which the copper content in the kidneys reaches 22 mg/kg, with 7.6 mg/kg of fresh liver tissue. This phenomenon is associated with an increased ability of the rat organism to synthesize metallothioneins. Metallothioneins are low molecular weight proteins that do not have enzymatic activity. Containing a significant amount of sulphhydryl groups and a very high resistance to some metal ions (zinc, cadmium, copper, lead, mercury, gold and bismuth). As in ruminants, ground squirrels from the technogenic biogeochemical province have a significantly reduced content of zinc in organs and tissues. The greatest differences are observed in the content of this element for bone and wool, and less significant, but statistically significant differences - for the liver and kidneys. The level of zinc in other studies of organs and tissues also shows a downward trend, which, however, does not reach the first statistical threshold of significance.

Wool of ground squirrels, as well as other animal species, objectively reflects the level of copper and zinc in their body, as evidenced by the high correlation coefficient between the content of these elements in wool and indicator organs.

No noticeable differences between the animals from the technogenic province and the control were found in the content of manganese, while in the level of lead these differences are very significant. They are especially noticeable for wool, in which the level of this element exceeds the control almost 5 times, and for bone, liver and kidneys (2 times). A similar increase in the content of lead was noted in the body of rats that received 20 mg of lead per kilogram of live weight for 14 days. The concentration of this element in the liver increased 3.3 times, in the kidneys 2.5 times, in the brain - 2 times, with a simultaneous decrease in the level of copper and zinc in these organs. Thus, the level of copper and zinc in the organisms of animals from the technogenic province is affected, apparently, not only by sulfur compounds, but also by lead.

Thus, the hairline of various animals and humans can be considered an indicator of the content of a number of important elements in the body. The levels of the content of elements depend on the condition and age of the person and animal, as well as on the chemical impact of various environmental factors.

**Conclusion:** Based on the concept of the interaction between hard and soft ligands and complexing metals, new data on the coordination of metal ions by the main ligand centers of hair and wool have been obtained, which make it possible to distinguish three main groups of metal complexes in them: eumelanin, pheomelanin, and caratin groups. The content of copper,
manganese, zinc and lead in the hair and wool of animals objectively characterizes the microelement status of animals. According to the content of copper, the closest correlation was established with the liver and brain, for zinc - with muscles and the skeleton, for manganese - with the kidneys and liver, and for lead - with the skeleton. In this regard, the analysis of animal hair and wool makes it possible to assess the conditions of their mineral nutrition and use it in combination with other indicators in biogeochemical studies and the assessment of environmental pollution with heavy metals. For the accuracy of the assessment, it is necessary to compare the results of the analysis of hair and wool of the same color, taken from a certain part of the body from healthy organisms.

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