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### **ON APPLICABILITY OF HUMAN HAIR AS A BIOINDICATOR FOR ENVIRONMENTAL MERCURY POLLUTION**

*SUMMARY. This article deals with the issue of applying hair analysis for trace elements which has become widespread in recent years to assess health status and environmental influence. It has proved to be very convenient and useful for assessment of health status and environmental influence. Content of heavy metals (including mercury) in human hair is an indicator of possible intoxication and environmental pollution degree. The advantages and disadvantages of mercury determination in hair in comparison with other bioindicators (blood and urine) are considered. The ways of input of different mercury species into the human body and peculiarities of their accumulation in hair are shown. Endogenous and exogenous mercury is reviewed, as well as the possibility of receiving inaccurate results in case of strong environmental pollution (exogenous mercury) at the assessment of human body intoxication degree. Admissible levels of mercury content proposed by various international organizations are described. The U.S. EPA reference dose (RfD) of mercury content in hair is critically evaluated. Range of mercury concentrations in hair is given.*

*KEY WORDS. Mercury, hair, reference dose.*

Environmental pollution has been a major factor affecting the health of a certain individual and of the population as a whole. Air, surface water and soil analyses give an idea of the ecological state of the environment, but does not help to evaluate the impact of pollution on human body. Content of trace elements in human body and their modification may serve as an indicator of excess or deficiency of specific nutrients in the diet, as well as the indicator of toxicants impact in unfavorable environmental conditions. Therefore, biomonitoring begins to acquire more and more significance being the means of assessing the resulting impact of pollution on humans. It is based on measuring the concentrations of chemicals and their metabolites in human biological media – blood, urine, saliva, hair or tissue. In recent years, hair analysis for trace elements has become widespread. It has proved to be very convenient and useful to assess the state of health and environmental impact.

Nowadays, almost any element in hair can be detected and quantified. However, these measurements are not always possible to interpret because of the large number of variables affecting the concentration of elements in hair.

Analysis of the traditional bioindicators – urine and blood – is well-known, widely used and usually giving reliable results. However, a simple urine test helps to determine the acute effect only during the period from 36 to 72 hours. Concentrations in the blood fall similarly. These bioindicators are most useful for assessing the recent or chronic exposure. In contrast, the hair provides a permanent registering of trace elements related to metabolism and absorption from the environment, and retains this information for quite a long time.

In the order of metabolic activity hair is the second tissue after bone marrow. Blood is the nutritious source of growing hair; it contains traces of everything that enters the body. Any xenobiotics and its metabolites can be enclosed to the matrix of the growing hair, forming a temporary profile. In addition, the hair is exposed to contamination from the external sources because it can accumulate surface exogenous products. Growing in average by 0.2-0.5 mm per day, the hair collects and stores the information about the state of a person and the environment in which he lives. If biological fluids give information for a short period of time – up to 24 hours, then the hair, depending upon its length, may disclose the period from several days to several months or even several years. Finally, a human hair is a good example of the tissue, which is easy to select, easy to store and prepare for the analysis because it does not require special techniques. That is why in recent years chemical analysis of hair has so widely spread [1].

Mercury is not an essential element and its role in physiology is still unclear. Until now, the impact of mercury on vital processes has been regarded solely in terms of toxicology. However, one should not deny its biological role if one lacks the knowledge on the biochemical mechanisms of mercury impact. Mercury is widely spread in the environment and it has still been a global pollutant, despite the significant reduction of its use. Its peculiar physical and chemical properties make its biogeochemical cycle complex and not yet fully comprehensible. It includes such processes as evaporation-condensation, adsorption-desorption, methylation- demethylation and formation of multiple forms.

Mercury gets into human body in several ways: with the delivery of water and food, as well as through the inhalation of polluted air (including smoking). Elemental mercury ( $Hg^0$ ) is the predominant form in the atmosphere, inorganic salts are the basic chemical forms in drinking water, and fish and seafood are the main source of organic mercury (methylmercury).

Mobility, toxicity and accumulation of Hg in the body depend on its shape. Metallic elemental mercury is very poorly absorbed in the digestive tract, and up to 80% of  $Hg^0$  vapors are adsorbed in lungs [2], as for methylmercury, it is almost completely absorbed in the digestive tract. When in blood, it takes Hg for about four days to disperse in all tissues, accumulating mainly in brain and kidneys.

Methylmercury penetrates easily into the hair during their formation and its concentration in hair is proportional to the concentration in the blood. Levels in hair

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exceed blood levels by 200-300 times with considerable individual variations. It should be borne in mind that there is a time interval of 2-4 weeks between mercury is found in the blood and the corresponding segment of the hair appears above the skin surface. Peak appearance of MeHg in the blood occurs through 4-14 hours after exposure to the organism. The half-life period of mercury is 35-100 days (65 days on the average) [3].

Unlike MeHg, the inorganic forms of Hg are less inclusive in the period of the hair growth. This is confirmed by the cases of severe intoxication with metallic mercury and its inorganic salts, when at high levels of mercury content in the blood, there was relatively small content of it in the hair (see example [4]). It is therefore considered that human hair is the best indicator to assess the impact of namely methylmercury.

Organic forms of mercury are the most toxic. It is known that MeHg is capable to disrupt neural cell division and their migration during the brain development. The ability of this compound to cross the placental barrier makes MeHg especially dangerous to the developing fetus. Its prenatal influence is connected with growth retardation and neurovegetative system alteration of the fetus. However, chronic exposure to Hg and MeHg can have destructive effects on neurological activity of an adult, too. Major part of mercury in hair is in the form of methylmercury, the proportion of which may reach 90-100% in some regions.

Children and adults chronic exposure to mercury can damage the nervous system, cause coning of vision, hearing and speech pathology, ataxia (motor disfunction), and peripheral neuropathy. Methylmercury accumulates in many tissues of the body, including the central nervous system, heart, muscles, liver and kidneys.

Elemental Hg may accumulate in the hair due to usual sorption from the atmosphere in case there are volatile inorganic forms of Hg in the environment, e.g., in chlor-alkaline production or small scale artisanal production of mercury or gold.

Determination of the mechanism of exogenous mercury binding [5] showed a high affinity of mercury to the hair surface, and thiol groups (SH) are most likely the places of its binding. As a result, exogenous mercury can form an inconvertible binding with the hair surface, which is difficult to destroy using traditional techniques of cleaning hair from external pollution. The usage of more stringent methods of hair cleaning does not exclude the possibility of partial removal of the endogenous mercury received from the blood during the growth process. Therefore, if hair is used as a biomarker to evaluate mercury intoxication, the results may be inaccurate. Nevertheless, even in this case, the high content of total (endogenous and exogenous) mercury in the hair helps to evaluate the degree of pollution. This is especially useful when examining large groups of population, as in the case of particular patients Hg content may depend on individual characteristics. It should be noted that the average content may vary from one geographic region to another, depending on the natural background, including soil constitution, concentrations in water and food, and feeding habits. For this reason, results of the surveyed region have to be compared with the values of the control group, a priori unexposed to mercury.

For the hair to become an acceptable indicator of mercury impact, the range of its normal content should be set. Unfortunately, at the present time, scientists and legislators from international and national organizations have not obtained consensus on the recommendations for methylmercury intake with food, and, consequently, on the specifications of its content in biological media (blood, urine, hair). This is due to the fact that such organizations as Food and Agriculture Organization of the United Nations (FAO), the World Health Organization (WHO) [6], the U.S. Department of the Food and Drug Administration (FDA), the Agency for Toxic Substances and Disease Registry (ATSDR) [7], the United States Environmental Protection Agency (USEPA) [8] and Joint FAO/WHO Expert Committee on Food Additives (JECFA) use different epidemiological studies for making recommendations. FDA bases its recommendations on MeHg intake from the collection of data obtained from the study of mass poisoning in Minamata and Niigata (Japan) and in Iraq; ATSDR and USEPA – from the study groups in the Seychelles and the Faroe Islands, respectively, and the WHO considers the groups of both Seychelles and Faroe Islands. The difference in the recommended values is quite significant (Fig. 1).

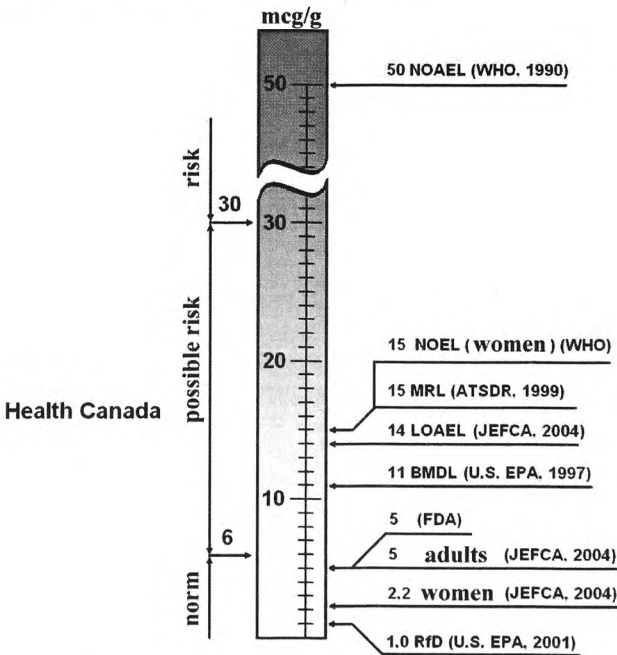


Fig. 1. Recommendations of different organizations on the critical level of mercury in the hair. BMDL – Below Minimum Detectable Limits; LOAEL – Lowest Observed Adverse Effect Level; MRL – Minimal Risk Level; NOAEL – No Observed Adverse Effect Level; NOEL – No Observed Effect Level; RfD – Reference Dose

In the Russian Federation the following background levels of mercury are accepted: 2 mcg/100 ml in blood, 2-5 mcg/l in urine, 0.5-1 mcg/g in hair. The following content of mercury is considered biologically acceptable: 5 mcg/100 ml in blood, 10 mcg/l in urine, 5.0 mcg/g in hair [9].

However, the issue remains open, whether it is correct or not to compare extreme situations of technogenic pollution and poisoning with natural biochemical cycle of mercury accumulation in living organisms. We will try to evaluate this on the example of the most mentioned Reference Dose of the United States Environmental Protection Agency [5].

The USEPA Reference Dose (RfD) for human hair is 1.0 mcg of Hg/g and is an estimation (“rather uncertain, covering perhaps the order of values”) of methylmercury amount, which can be consumed for 70 years every day without observable risk of adverse affect. It is based on the worst case of chronic mild impact, which nevertheless leads to the hair benchmark dose value, the lower confidence limit of which (BMDL) is 11 mcg/g. It is then divided by the extremely conservative rate of “uncertainty” equal to 10, being a sort of “airbag”. In other words, some excess RfD does not mean an increased risk because the level of 11 ppm causes no observable adverse effect (NOAEL). However, RfD is the value, which most scientists are guided by.

The range of mercury content in hair is very large. Normally, the level of mercury in hair of a human, who lives in ecologically clean region and does not eat fish, is less than 1 mcg/g, and can reach 30 mcg/g in hair of those who eat fish often. The highest content mentioned in literature was 2436 mg / g [10].

Fish is the main source of methylmercury, as of all the food products only fish and seafood contain MeHg. However, definition of various forms of mercury (differentiation in the endogenous and exogenous components) can provide additional important information about the nature of entry either from human blood into the hair, or from the contaminated atmosphere being adsorbed by the surface of the hair.

Determining the content of mercury in the hair, it should be considered, firstly, that it often does not correlate with symptoms of toxicity (cases of high content – more than 300 mg/kg – are known in the total absence of symptoms) and secondly, that it often does not correlate with the concentration of mercury in blood, as blood may contain large amounts of inorganic mercury which is poorly transferred into the hair.

Thus, human hair can be a good indicator of environmental pollution. Hair analysis allows to quickly and inexpensively examine large social groups for qualitative assessment of both health and environmental influences. Despite the difficulties with the differentiation of endogenous and exogenous mercury in the hair and determination of reference range, high concentrations may indicate the influence of the environment. Finally, the development and improvement of methods for the mercury determination in the hair, primarily, determination of the forms of mercury, can solve many controversial problems related to the behavior of mercury in the human body.

Despite the limitations, the hair remains an excellent means of control, because the method of its selection is simple and noninvasive, and their analysis allows to make a preliminary screening of mercury impact on the human in the conditions of anthropogenic impacts.

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