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Heavy metals as criteria of health and ecological well-being of the urban environment

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ABSTRACT

The study of the content of Pb, Cd, Ni, Zn, Mn, Cr, and Cu in biological media (the hair) of children living in the zones of the city of Kazan with different pollution levels was carried out. The identification of the zones in the city of Kazan was performed on the basis of the snow cover and soils pollution with heavy metals, which are natural accumulators of chemical substances and heavy metals (HM). Statistically significant differences ($p < 0.01$) in the content of certain metals in the hair, lead and cadmium in particular, were revealed in children living in the technologically polluted zone (Teplocontrol). Microelement composition of the hair in children with respiratory diseases (RD) varied widely in the content of lead ($p < 0.05$), and a statistically significantly lower level of zinc ($p < 0.01$) and copper ($p < 0.05$) compared with all the rest groups of children was determined in genitourinary diseases (GUD). However, relatively high values of toxic elements in the control zone show that the ecological status of the city and region is instable, and implies additional measures of the environmental monitoring and activities on chemical safety in certain city zones.

1. Introduction

Human biological monitoring (HBM) is an important tool to support environment and health policy [1]. Biomonitoring was regarded as "a Gold Standard" for the ecological effect assessment of chemicals [2–4], because it demonstrated and measured the markers for a biologically absorbed chemical in the human body. Appreciating the value of the biomonitoring data resulted in a widespread incorporation of biomonitoring in research development dedicated to the study of potential associations between the population health indicators and the exposure to chemicals in the environment [5,6].

However, the identification of regional (local) levels with the account of a complex of ecologo-hygienic factors in the territory under study, such as, morbidity of the population, the environmental status and assessment of the health risk on exposure to hazardous environmental factors, remains an important aspect [7,8]. For the biomonitoring purposes, possible biomarkers are determined in different biological media such as blood [7,9], urine [10], saliva [11], hair [12] and nails [13]. On the other hand, hair and nails are accumulating the contaminants long term, allowing for integral assessment of occupational and environmental exposure.

The aim of this study is to make sure that heavy metals can be certain criteria of health and reflect the ecological state and well-being of the urban environment.

Research in the territories (zones) in the city of Kazan with different levels of pollution with heavy metals included the analysis of Pb, Cd, Ni, Zn, Mn, Cr, Cu in the hair of children aged 8–12 years old. At the first stage of work, we identified the research zones in the territory of the city of Kazan. Identification of zones in the city of Kazan was carried out on the basis of the snow cover and soils pollution with heavy metal. Taking into consideration that snow and soils are natural accumulators of chemicals contained in the atmospheric air, then in a large industrial city, they can characterize a long-term pollution [14]. Atmospheric processes such as dry and wet deposition of trace elements play a crucial role in cleansing mechanism. Several studies have highlighted that atmospheric cycling of HMs (dispersion, transport, deposition) depends on a broad spectrum of environmental factors and local/regional anthropogenic sources [15].

According to research data, the major influence on the fine particle volume (mass) in the snow melt was concluded to be due to the elements from anthropogenic sources [16]. The advantage of the environment quality control as far as the extent of snow pollution lies in the fact that snow sampling is extremely simple, and it does not require complex equipment. The measurement of the pollutant parameters is carried out once a year during the period of maximal snow accumulation till the beginning of spring snowmelt. According to observation results, concentration of pollutants found in snow appears to be 2–3 orders of magnitude greater than in atmospheric air [17].

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2. Materials and methods

An outpatient examination of 180 children aged from 8 to12 years old living in different areas (zones) of the city of Kazan was carried out. The examination included an interview with filling out the questionnaire, medical examination and analysis of the hair samples for the content of basic biologically significant chemical elements (Pb, Cd, Ni, Cr, Mn, Zn and Cu). The surveyed children included a group of practically healthy children and children with different diseases, who were divided into several groups: the 1st – practically healthy children, the 2nd - frequently ill children, and those with chronic diseases of the upper respiratory tract, the 3rd – with genitourinary diseases. The urban pollution with HM was studied by means of snow chemical survey. Investigations in the city of Kazan were carried out according to the results of expeditionary data of the Institute for the Ecological Problems and Subsurface Resources Management under the Academy of Sciences of the Republic of Tatarstan in accordance with Guidelines on assessment of the degree of settlements' atmospheric air pollution with metals according to their content in the snow cover and soil (No 5174-90). The snow cover sampling was carried out at the sites without traces of natural occurrence disturbance at 100–400 sites (depending on the year) on the territory of 200 km^2 at the end of March – the beginning of April over the period from 2009 to 2013. A snow sampler, made of polyethylene tube, 100 cm long and 9.5 cm in diameter, which was squeezed vertically into the snow mass as far as the soil, was used for sampling and determination of the height of the snow cover. The lower part of the snow core (0.5–1.5 cm), which was polluted with soil particles, was discarded. From 2 to 5 cores were taken for one sample. The snow density was determined by means of standard snow sampler.

The snow sample with the mass of 2.0–3.5 kg was placed into polyethylene bags, delivered to the laboratory, where it was poured into polyethylene buckets and melted at the room temperature. To accelerate the process, a vacuum filtration of snow water was carried out. The snow water was filtrated in vacuum on the 120 ml porcelain Buchner funnel with inserted 70 mm diameter paper filter (white band). The capacity of the Bunzen receiving flask is 1liter. Vacuum was created by means of a water injection pump, powered by "Kama"– type electropump. The water circulated according to the following scheme: the electropump – the water injection pump – the 50 L tank – the electropump.

The sediment, which settled down on the bucket walls in the process of filtration, was rubbed away with a glass rod with rubber tip (a policeman). One liter of the snow water filtrate was evaporated to dryness on a water bath, the second liter – was kept as a safeguard and used for determination of electrical conductivity; the rest amount of water was poured out.

The filters with solid precipitate were carried onto the Petri dishes and dried in a drying cabinet at the temperature of 105 °C for 24 h; thereafter they were weighed on the analytical balance. The sediment, which remained after filtration in the dish, was dissolved in 10 ml mixture of concentrated sulphur and nitric acids on heating on a water bath. Then the solution was run through a filter (blue band) into a 50 ml measuring flask. The dish and the filter were rinsed with 0.5 H nitric acid before filling of a measuring flask. Analysis of snow samples for of heavy metals content was carried out by means of flame and electrothermal atomization atomic absorption spectrometry (AAC) at the Central Certified laboratory for Analytical Control under the Ministry of Ecology and Natural Resources of the RT. The snow cover pollution of the urban territory was determined from pollution coefficients calculated with the use of regulations for household and drinking water and water for amenity needs. Summation of pollution factors can give the total pollution coefficient (K_{total}) characterizing the overall pollution rate of the territory at the sampling site, and it allows identifying districts with different levels of pollution with HMs in the city territory [14].

Assessment of the soil pollution was carried out in keeping with SanPiN "Sanitary and Epidemiological Soil-Quality Requirements" (2003), Hygienic Standard in Russian 2.1.7.2041-06 "Maximum Allowable Concentration (MAC) of Chemicals in Soil" according to concentration factors of certain metals (K_c) and total pollution coefficients (Z_c). The basic stages, methodological approaches and methods of assessing the total coefficients of the snow cover and soil pollution with heavy metals (HM) in certain districts of the city of Kazan are given in our article «Approaches to urban area ranking accordingly to the level of heavy metal pollution» [14].

The soil samples were taken in accordance with GOST 17.4.3.01, "Methodological Recommendations for carrying out field and laboratory studies of soils and plants when controlling the environmental pollution with metals" and "Temporary Methodological Recommendations for control of soil pollution" by "sealed code envelope method", 5 soil samples being taken with plastic spades at the depth of 10 cm from the points of "elementary" site. The choice of sampling points was determined by location of the traffic movement area of the residential quarters, enterprises and concordance with the snow sampling points. About 1 kg (0.5 L in volume) was taken from each point. The soil samples were packed into polyethylene bags.

Roots were thoroughly removed from the air-dried combined soil, and a soil sample with the mass of 0.2 kg was taken by quartering method.

The selected soil sample was grinded in a large porcelain mortar and sifted through a caprone sieve with 1 mm mesh diameter. Unsifted lumps of soil were grinded and resifted. Weighed quantities for analysis were taken from obtained soil sample.

The content of HM in the soil was determined by the method of atomic absorption analysis based on Guiding Document 52.18.191-89 in accordance with Methodological Instructions "Methods of measurements of the weight ratio of acid-soluble metal forms (copper, lead, zinc, nickel, cadmium) in soil samples by means of atomic absorption analysis" (1989).

The content of certain elements in the soil was determined according to formula:

$$A = k \cdot C,$$

where A – the value characterizing the light absorption (optical density, absorption), or %;

k – absorption coefficient;

C – analyte concentration, μg/ml.

The absorption value of light is proportional to the content of analytes, whereupon their quantification is based.

To recalculate an air-dried soil sample for an absolutely dry one, the determination of hydroscopic water in soil samples was performed.

The mass of absolutely dry soil sample was calculated according to the following formula:

$$\Delta P_{dry} = \Delta P_{air\text{-}dried} \cdot K,$$

where $\Delta P_{dry.}$ – the mass of absolutely dry soil sample, g;

$\Delta P_{air\text{-}dried}$ – the mass of air-dried soil sample, g;

K – recalculation coefficient.

To determine the mass of an air-dried soil sample, the weighed quantities of an air-dried sample with about 1.00 g of soil were taken in dry glasses with ground-in lids (sample bottles) on the analytical balance with accuracy up to 0.01, not less than three weighed quantities.

At first, one should weigh an empty sample bottle and write down its mass (P_0), then weigh the same sample bottle with a soil sample and write down its mass ($P_{air\text{-}dried}$). The mass of an air-dried soil sample ($\Delta P_{air\text{-}dried}$) should be determined from the following relationship:

$$\Delta P_{air\text{-}dried} = P_{air\text{-}dried} - P_0.$$

Coefficient (K) should be determined according to the formula:

$$K = \frac{100 - q}{100}$$