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Trace element biomonitoring in hair of school children from a polluted area by sector field inductively coupled plasma mass spectrometry

Evgenii J. Drobyshev [a], Nikolay D. Solovyev [b,*], Natalya B. Ivanenko [a,b], Maria Yu. Kombarova [c], Alexander A. Ganeev [b]

[a] Institute of Toxicology of Federal Medico-Biological Agency, 192019 St. Petersburg, ul. Bekhtereva, 1, Russia
[b] St. Petersburg State University, 199034 St. Petersburg, Universitetskaya nab., 7/9, Russia
[c] Research Institute of Hygiene, Occupational Pathology and Human Ecology, Federal Medico-Biological Agency, 188663, Leningradskaya Oblast', Vsevolozhskiy District, Kuz'molovskiy, Kapitolovo, 93, Russia

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ABSTRACT

In the current study, a biomonitoring of 18 hair trace elements (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Se, V, Zn, Ca, Na and P) in school children from Leningradskaya Oblast' is reported. A case group, residing in a proximity to the toxic waste disposal grounds (Krasniy Bor), has been assessed vs. controls from a non-urban settlement Seltso. In total, 166 hair samples were analysed using double focusing sector field inductively coupled plasma mass spectrometry after microwave-assisted sample digestion with nitric acid. For the determination of Ca, Na and P inductively coupled plasma optical emission spectrometry was employed. For the validation, a reference material and spiked hair samples were analysed. The data obtained was processed using parametric statistics and factor analysis. Determined concentrations of trace elements were in agreement with the previously published results on chemically polluted areas. In the case group, linear correlations between Al, Cr, Cu, Fe, Ni and V were observed. Also, these metals correlated to selenium hair content in the case group. Additionally, a correlation between hair Se and P was observed in the case subjects. Several gender differences in trace content were observed within each group. However, no age- or body index-related difference was found. The obtained results show that closely located waste disposal grounds intensifies trace element exposure in school children of Krasniy Bor. However, judging from rather high values for the controls, total environmental status of the region seems to be unstable, so additional monitoring and chemical safety measures are required.
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1. Introduction

Trace element biomonitoring is a well-accepted tool for the study of occupational exposure and environmental safety assessment [1]. First of all, biomonitoring studies continue to draw special interest in the highly industrialised regions with a high level of anthropogenic pollution [2]. In such areas, significant alterations in natural biogeochemical cycles of the trace elements are present, amongst other environmental issues. Consequently, trace element pollution and human exposure assessment is an important task for the occupational medicine [3]. Our previous studies in adults have shown that for the population of the Russian Federation, the most common trace metal toxic exposure may be related to cadmium, chromium, mercury, manganese, nickel and lead [4,5]. Nevertheless, the children aged below 11 years have higher rates of metabolism, so for them the health risks of metal exposure may be higher [6].

Since there are different routes of exposure for different pollutants, the most important task is to choose an appropriate media for the biomonitoring [3]. For the biomonitoring purposes, possible biomarkers are determined in different biological media such as blood [4,7], blood plasma or serum [8], urine [4,9,10], saliva [11], hair [12] and nails [10]. All these media have certain drawbacks. Low concentrations of most metals are rapidly eliminated from the blood after sub-chronic and chronic intakes, so in some cases blood and urine would not indicate the exposure [13]. On the other hand, hair and nails are accumulating the contaminants long term, allowing for integral assessment of occupational and environmental exposure. At the same time, hair and nails are inhomogeneous media for the trace element analysis, also having quite high probability of external contamination during sampling and

* Corresponding author at: 199034 St. Petersburg, Universitetskaya nab., 7/9, Russia.
E-mail address: n.solovyev@spbu.ru (N.D. Solovyev).

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Table 1
Population under study.

Parameter	Control group (Seltso)	Case group (Krasniy Bor)
Number of subjects	84	82
Male/Female	37/63	38/62
Age	8.1 ± 1.1	7.6 ± 1.3
Height, cm	126.2 ± 8.4	122.7 ± 9.5
Body weight, kg	26.4 ± 6.1	25.7 ± 6.8

sample preparation [14]. So, the methodological requirements are rather strict. Currently, inductively coupled plasma mass spectrometry (ICP-MS) could be regarded as an optimal trace element biomonitoring method [15,16]. In this study, the results of 18 trace elements biomonitoring in hair of school children from Leningradskaya Oblast', residing in the proximity of toxic waste disposal grounds (Krasniy Bor) are presented. The case group was assessed against gender- and age-matched controls from the non-urban settlement Seltso, located 50 km from the hazardous object. The samples were analysed using double focusing sector field ICP-MS after microwave-assisted digestion under elevated pressure.

2. Materials and methods

2.1. Instrumentation

For the determination of the majority of the elements a double focusing sector field mass spectrometer Thermo Element 2 (Thermo Scientific, Bremen, Germany) with nickel cones, a Peltier-cooled Scott spray chamber and a glass Meinhard-type concentric nebuliser was used. Working parameters were as follows: cooling argon flow 16 L min $^{-1}$; auxiliary flow 0.72 L min^{-1}; nebulising flow 0.933 L min^{-1}; radiofrequency power 1170 W; spray chamber temperature + 2 °C [4]. For the determination of calcium, sodium and phosphorus ICP optical emission spectrometer Optima 2100DV (PerkinElmer, Shelton, CT, USA) was used (wavelengths 317.933, 589.592, 213.617 nm, respectively). For the sample preparation, microwave digestion system UltraClave (Milestone, Sorisole, Italy) was employed.

2.2. Studied groups

Overall, 166 schoolchildren from two settlements of Leningradskaya Oblast', Tosnenskiy district, were studied. Namely, 82 subjects from Krasniy Bor (ca. 5500 inhabitants, case group), and 84 subjects from Seltso (ca. 2000 inhabitants, control group) were investigated. The distance between case and control territories of this study is about 50 km. Whilst Seltso is a rural area there are toxic waste disposal grounds in Krasniy Bor, located in the direct proximity to the living settlement (3.5 km from the centre). The Krasniy Bor grounds are the largest disposal plant for medical, chemical and metallurgic wastes in the regions of Leningradskaya Oblast' and St. Petersburg. It is a well-known regional source of possible environmental hazards. Additionally, conflagrations in the disposal grounds cause pollutants volatilisation and their spreading with aerosols and precipitations. The locations of the settlements under study relatively to each other and to the closest megalopolis St. Petersburg (ca. 5 million inhabitants) are shown in Fig. 1. The description of the groups is presented in Table 1. The human-based cohort research was conducted in concordance with the ethical guidelines, according to the Declaration of Helsinki, 1964. Parents or legal representative of all the participants have given a written consent prior to inclusion into the study, according to the decree of the Ministry of Health of the Russian Federation No 1177н, dated 20.12.2012. The study was approved by the local Bioethics committee.

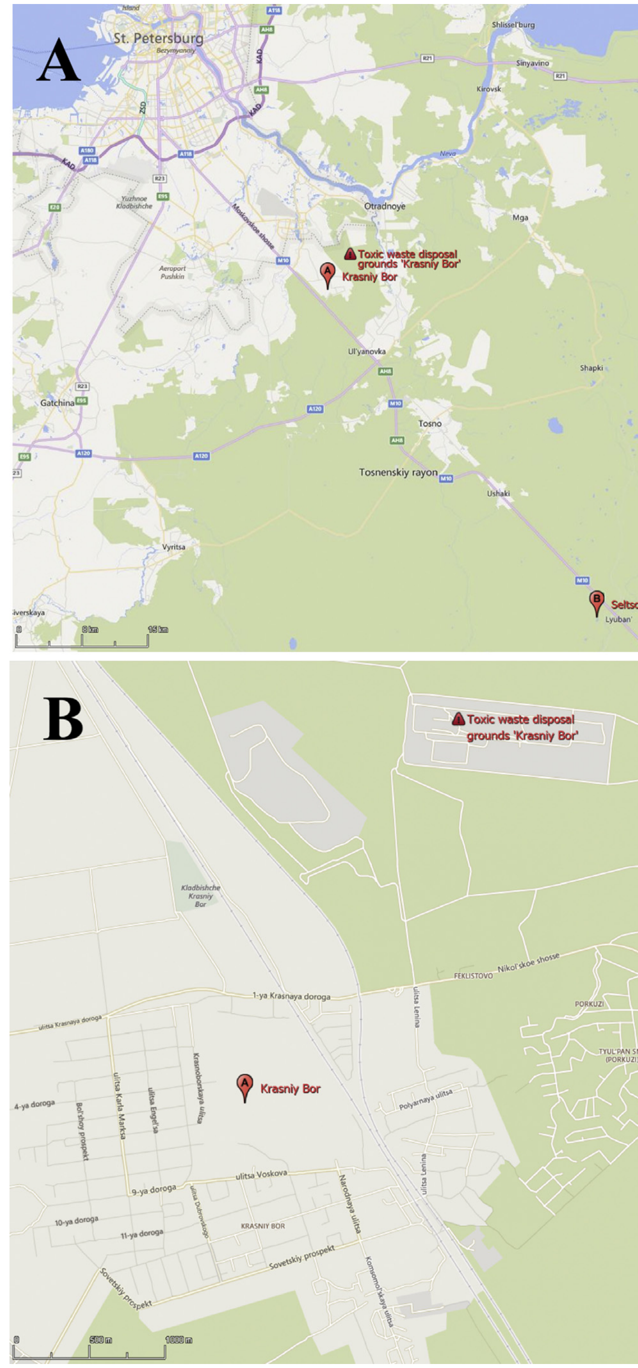

Fig. 1. Relative locations of the territories under study to each other and St. Petersburg (A); the location of the waste disposal grounds relatively to Krasniy Bor settlement (B) – map source bing.com.

2.3. Samples

Hair sampling was performed from the occipital part of the head with stainless steel scissors, previously rinsed in Milli-Q water. The hair was cut as close to the skin as possible. Average length of sampled hair in girls was about 8–11 cm, whereas in boys only 3–5 cm. The samples were hermetically packed into the polyethelene bags (pre-washed with 5% nitric acid and rinsed with Milli-Q water), tagged with identifying numbers and shipped to the laboratory for the trace element analysis. The care was taken to avoid contamination at all stages of sample handling.

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