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Nuclear–Physical Analysis Methods in Medical Geology: Assessment of the Impact of Environmental Factors on Human Health

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Abstract—The procedure for geomedical studies is outlined, and the niche occupied by the nuclear–physical analysis methods in these studies is pointed out. The necessity of construction of an efficient complex of the most modern analytical methods is demonstrated. The metrological parameters of methods applied in the analysis of natural environments and biological materials are evaluated. The current state of pollution of natural environments with heavy and toxic metals is characterized in two specific industrial hubs: the towns of Gus-Khrustalny and Podolsk. The levels of pollution of diagnostic biological materials (hair and blood) from children living in various urban districts are studied in the light of specific features of the manufacturing industry in these towns and the life environment of child population. The results of studies focused on evaluating the effect of environment on the health of child population are detailed. The actual damage to child health, their neuropsychic development and behavior, and the effect of socioeconomic factors are determined. Preventive problems among the child population exposed to lead and other toxic metals are evaluated, and ways to solve them are proposed. A system of early diagnosis and preventive measures for the mitigation of adverse effect of toxic metals (Pb, Cu, Mn, Zn, Cr, Ni, As, etc.) on the neuropsychic development of children is developed based on an actual ecogeochemical estimation of the state of the region under study.

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INTRODUCTION

Several different interpretations of the term "geological medicine" are known. In the most narrow and conservative interpretation, it is the study of the effect of geographic factors on the development and the course of human diseases. The progress in these studies led at the time to the discovery of specific diseases with certain areas of distribution (Keshan, Kashin–Beck, Itai-itai, Blackfoot, and Minamata diseases and endemic goitre). It was found that these diseases were associated with specific patterns of the microelemental composition of soils or bottom sediments in the studied areas. These patterns produced an excess or deficiency of certain microelements in human organisms [1–4]. The soil in this case acted as a deposit medium subjected to geological, geochemical, and anthropogenic influences. It inherited those chemical elements that are present in the soil-forming material produced as a result of geological evolution of a given region. In the geochemical context, the formation of soil is a complex and time-evolving process of exchange of matter between the lithosphere, the atmosphere, and terrestrial organisms. In recent decades, anthropogenic human activities have become actively involved in the processes of migration of elements in natural environments. In certain cases, the amount of chemical elements entering the ambient environment as a result of technogenesis is significantly larger than the level of their natural supply. The integration of anthropogenic fluxes into natural migration cycles results in a rapid dispersal of pollutants throughout the natural landscape components, when it becomes impossible to avoid the interaction of these pollutants with humans. The amount of pollutants containing heavy and toxic metals increases every year. They cause damage to the natural environment, disrupt the established ecological balance, and have a negative impact on public health. All this has led to gradual broadening of the term "geological medicine." In modern understanding, it is a branch of science that studies the problems of interaction between humans and objects of the geosphere and works out a closed interdependent cycle. Therefore, the synthesis of knowledge, experience, and methodology of geological, geochemical, ecological, and biomedical disciplines becomes necessary.

STUDY PURPOSES AND OBJECTIVES

The present research was aimed at studying the effect of environment on the health of child population with the application of techniques used in medical geology. A system of early diagnosis and preventive measures for the mitigation of the adverse effects of toxic metals (Pb, Cu, Mn, Zn, Cr, Ni, As, etc.) on the neuropsychic development of children was also developed. To this end, we performed the following steps:

(i) studied the intensity and spatial pollution patterns of natural environments in specific industrial hubs;

(ii) chose the objects for biomedical studies based on the obtained data;

(iii) evaluated the effect of ecogeochemical factors on the state of the life environment of a child population;

(iv) studied the level of toxic-metal pollution of diagnostic biological materials (hair and blood) from children;

(v) determined the actual damage to child health based on the evaluation of the results of tests of their neuropsychic and physical development and behavior and on the evaluation of the effect of socioeconomic factors; and

(vi) evaluated the prophylactic problems for child population subjected to toxic metals and probable remedies.

RESEARCH METHODS

The very definition of the term "geological medicine" indicates that the research is conducted at the intersection of several disciplines, including geology, geochemistry, atmospheric chemistry, hydrochemistry, ecology, biochemistry, and medicine. The research methodology incorporates several stages, and each of these relies on the methodology of the corresponding discipline. The landscape pattern and the geochemical specifics of the region under study are examined using the techniques applied in geology and geochemistry; aerosol fallout and the characteristics of potable and surface waters are studied with the methods of atmospheric chemistry and hydrochemistry; soils, vegetation, and the composition of biological materials are analyzed using the methods of ecology and biochemistry; and medicine studies the condition of human organisms and human health. It should be noted that each of these disciplines utilizes its specific research techniques, and the link between them is provided by the analytical methods (in the present case, nuclear–physical methods of analysis of matter) used. The algorithm of geomedical studies (in a sense, the roadmap for the whole process) incorporates several stages:

(1) All the available literature sources containing the data on the ecogeochemical environment of the object of the planned study are examined. The primary sources of technogenic pollution of the environment and the range of principal pollutant elements are determined based on the literature data. The primary water passages and sources of potable water (open or closed) are marked, and the wind pattern is determined. The complex of analytical methods needed to complete the studies is evaluated tentatively.

(2) Ground reconnaissance is performed. A work plan with sites for the collection of samples of natural media is devised, the expected amount of field work is evaluated, and the overall number of samples of natural media is determined. The volume and the list of required analytical works are specified.

(3) In the process of talks with local administration and sanitary and epidemiological inspectorate, the plan of future work is validated. The obtained feedback and suggestions are taken into account.

(4) Field works are carried out. Samples of natural media (soils, atmospheric aerosols, surface waters, bottom sediments, and agricultural vegetation) are collected in accordance with the plan devised earlier.

(5) The obtained samples are prepared for analysis (dried, crushed, mineralized, and packed). The samples are analyzed with the use of the chosen set of methods.

(6) The obtained analytical data are processed, maps of technogenic pollution are plotted, and the ecogeochemical situation in the region (city) at the time of the study is evaluated. The presence of sources of technogenic pollution that were already known is verified, new sources are revealed, and the set of principal pollutant elements is specified. Public places (nursery schools and schools) located in the areas with the highest and the lowest technogenic impact levels are identified.

(7) Samples from the life environment (aerosols of the indoor air, wall paint, dust sweepings, potable water, and food rations) are taken at the chosen objects. The children's parents are asked to fill out a (voluntary) questionnaire in order to evaluate their socioeconomic status, assess the family environment, and determine the exact place and conditions of employment of both parents.

(8) Diagnostic biomaterials (hair and blood) are collected from children at the chosen objects. The physical and psychophysical condition of each child is assessed via medical testing.

(9) The diagnostic biomaterials are analyzed. The risk group is identified based on the data on the concentration of xenobiotics in the biomaterials and the results of medical testing. The effect of socioeconomic and ecological factors on child health is evaluated.

(10) A complex of preventive measures for mitigating the negative effect is devised and proposed.

As is evident from the foregoing, the complex of analytical methods is of key importance in the study methodology. This complex is either applied directly

Table 1. Objects under study

Town	Object	Urban area	Nursery school territory	Nursery school facilities
Gus-Khrustalny (five nursery schools)	Air	–	5 sampling sites	8 sampling sites
	Soil	45 samples	12 samples	–
	Water	1 sample	–	10 samples
	Dust sweepings	–	–	10 samples
	Paint	–	–	6 samples
	Daily food rations	–	–	5 samples
	Blood	–	–	132 samples
	Hair	–	–	119 samples
Podolsk (four nursery schools)	Air	9 sampling sites	7 sampling sites	5 sampling sites
	Soil	80 samples	10 samples	–
	Water	10 samples, Pakhra River	–	4 samples
	Bottom sediments		–	–
	Daily food rations	–	–	4 samples
	Blood	–	–	143 samples
	Hair	–	–	139 samples

at the stages mentioned above, or the results of its application define the direction and volume of further research work. The need to analyze samples that differ greatly in their macro- and microcompositions, aggregative states, and concentrations of the identified elements often arises within the framework of a single study. It is also possible that an addition to the complex of analytical methods or a change in the extent of analysis performed with the use of the already applied methods would be required.

OBJECTS UNDER STUDY

The studies were conducted in Gus-Khrustalny (Vladimir oblast) and Podolsk (Moscow oblast). They are considered to be typical small towns of central Russia with a well-developed infrastructure and technologically varied industry.

Table 1 lists the objects under study and the numbers of samples taken.

Gus-Khrustalny. The primary sources of environmental pollution in the town of Gus-Khrustalny are the crystal factory (established in 1750) and the fiberglass factory. These factories are located in the historic center of the town to the south of the town water reservoir (Fig. 1). A total of 13–38.7 t of lead and 0.8–13.6 t of arsenic were vented into the atmospheric air in Gus-Khrustalny in a year [5].

Podolsk. The primary sources of environmental pollution in the town of Podolsk are the machine building, battery, cable, chemical and metallurgical, and cement factories; the refractories plant; etc. These factories vent a considerable amount of pollutants (including lead, copper, zinc, nickel, tungsten, other metals, dust, etc.) into the atmosphere. The annual volume of lead emissions from the electrical engineering industry is as high as 3.38 t [6]. It should be noted that all these factories are now operating fairly efficiently; therefore, the environmental impact is of a multiplex nature and is produced primarily via air emissions. The town is divided into the residential (western) and the industrial (eastern) districts by a railway line (Fig. 2). The wind pattern is such that the atmospheric aerosols are transported primarily in the southeastern direction; therefore, the pollution of residential areas should be minimal.

SAMPLING

The samples of atmospheric aerosols, soils, potable water and water from surface streams, vegetation, food rations, and biological materials were taken in the present study. The methodology for sampling of natural media is fairly well understood, standardized, and described in a number of State Standards and methodological instructive regulations [7–11]; therefore, there is no need to present a detailed account of them. On the contrary, the methodology for sampling of biological materials (hair, blood) warrants a detailed description.

Blood. Blood contains a liquid fraction (plasma, 55–65%) and cells suspended in it (formed elements, 35–45%). Plasma contains water (about 94%), pro-

Fig. 1. Sampling sites in Gus-Khrustalny.

teins and salts (6%), carbohydrates, fats, vitamins, hormones, enzymes, etc. Erythrocytes, leukocytes, thrombocytes, and other cells are the formed elements of blood. Toxic elements that enter the bloodstream reflect the impact on the organism at the moment of sampling. More than 95% of lead, 90% of zinc, and almost all manganese and cadmium in blood are contained in erythrocytes. In order to make the blood sample representative, one has to ensure its homogeneity during storage. This is achieved with the use of special containers with a blood thinner (heparin or EDTA [12]). Small-volume (up to 0.5 mL) containers (microtainers) are used for the collection of capillary blood. Evacuated containers with a volume of up to 10 mL (vacutainers) are used for the collection of venous blood. In the process of sampling, blood is quickly pumped into a vacutainer under the influence of vacuum, and the risk of external sample contamination is thus minimized. This is especially important for the identification of microelements and in the screening of children. The volume of sampled blood amounts to several milliliters at best. Even the smallest (of the order of 1 μg) amounts of external microelements may introduce a significant error into the analysis results. The containers used for the collection of blood are also a source of external pollution; therefore, their cleanliness with respect to the identified component should be monitored in the process of analysis, and the corresponding correction to the analysis result should be introduced when needed. Generally speaking, the procedure for blood sampling involves the following operations:

(1) A new pair of gloves is used for each patient.

(2) The registration card of a new patient is filled out.

(3) All the materials and instruments needed for sampling are laid out on a disposable tissue.

(4) The package of all disposable materials and instruments is removed.

(5) The sampling site on the patient's body is sterilized as necessary, and venous blood is collected with a disposable syringe.

(6) The collected blood is transferred into a container with a blood thinner and stirred by shaking.

Fig. 2. Soil sampling sites in Podolsk.

(7) A label with the sample designation is glued to the container with blood.

(8) The sample designation is noted in the patient's registration card.

(9) The marked container is placed into a refrigerator or a freezer with deep freeze for storage.

The storage and transportation of blood samples requires special care. The samples in plastic containers may be stored in a refrigerator for a limited amount of time or in a freezer at a temperature of –20°C for more than 1 month. They also may be transported within the space of 1–3 days (it is undesirable to increase the transportation time further) in specialized portable refrigerators filled with gel packs or dry ice. Depending on the analysis technique applied later, blood is diluted or mineralized (partially or fully) to determine the concentration of elements. When atomic absorption spectrometry (AAS) with flameless atomization is applied, blood is diluted by a factor of 3–20 in order to reduce its viscosity, facilitate its dosing into a graphite atomizer, and suppress foaming at the drying stage. Aqueous solutions of Triton X-100 with various modifiers needed for the subsequent identification via flameless AAS are used as dilution agents. When a blood sample is mineralized partially, it is treated with a suitable reagent in order to disrupt erythrocytes and transfer the metal ions contained in them into the solution. Nitric acid with a concentration of 0.8–1.0 M is most often used as a reagent. The reagent may at times contain various additives and modifiers needed for the analysis of the obtained solution with the application of a certain technique. Complete mineralization is most often performed with the use of

nitric and perchloric acids and hydrogen peroxide in open or closed (autoclave and microwave) systems. The main challenge in blood mineralization consists in minimizing the value of the blank experiment. When small lead amounts in blood are identified, minimizing the possibility of accidental contamination of the analyzed sample with lead at various sample preparation stages is of paramount importance. A significant contribution to the sample contamination is produced by chemical reagents and acids that are used to decompose the blood samples. If deionized water and additionally refined nitric acid are used, the value of the blank experiment is reduced considerably. When lead is identified in blood at the lower boundary of the range of detectable concentrations (1 μg/dL), the lead content in the blank experiment should not exceed 3 μg/L at a dilution factor of 5. The sample is then analyzed with the use of any appropriate method (atomic absorption or mass spectrometry with inductively coupled plasma).

Hair. Hair is a complex tissue of epidermal origin that consists of cells of several varieties and a multitude of chemical components. The visible hair part that resides above the skin surface is called a stem, and the hair root with a bulb and the surrounding tissues are located in a follicle. The hair papilla (a connective-tissue structure that contains nerve fibers and blood vessels) is located at the base of the bulb and provides it with compounds needed for the multiplication of cells and hair growth. The bulk (85–93%) of a hair is composed of protein amino acids. Hair contains 2.3% of lipids, 4–13% (depending on the air humidity) of water, 4.1% of sulfur, and 0.2–0.8% of ash. The net microelement content of a hair is a combination of microelements of internal (endogenic) and external (exogenic) origin. Endogenic microelements enter a hair at the stage of its formation from the blood stream of the organism and from lipids and sweat that are produced by oil and perspiratory glands connected to the hair follicle. Elements are "fixed" in the process of keratinization and move along the stem as the hair grows. In three weeks, the hair reaches the skin surface. Further variation of its microelementary composition is governed by the processes of sorption of elements by hair from the external environment (exogenic elements). These sorption processes are influenced by a multitude of factors: environmental conditions, the state of health, the use of certain detergents, the periodicity of hair washing, smoking, etc. Microelements of endogenic origin are an indication of the microelement status of the organism at the time of formation of the corresponding hair segment. A hair segment with a length of 1 cm is an integral characteristic of a period of about two months (the hair growth rate is about 1 cm per month, and about three weeks pass before the hair appears at the skin surface). Each additional centimeter increases the length of the characterized period by a month (i.e., a 3-cm-long segment characterizes the past four months). The IAEA protocol [13] still remains the only available set of instructions pertaining to hair collection and preparation for the analysis. According to this protocol, one should collect a strand of hair from the back of the head in immediate proximity to the skin (not further than 1–2 mm from the skin surface). The proximate segment with a length of no less than 3 cm should be cut off from the strand for analysis. The weight of a 5-cm-long sample should be no less than 10 mg (the typical weight is 100 mg).

Hair samples are collected in accordance with the following procedure:

(1) A new pair of rubber gloves (not treated with talc) is put on after the collection of each sample.

(2) The registration card is filled out for each patient. This card contains the data on the shampoos and hair conditioners used.

(3) A comb, scissors, and beak clips are taken out of an isopropyl alcohol solution and transferred onto a disposable tissue for drying.

(4) A region of the scalp with its boundaries going between the tips of the ears and the back of the neck is marked with aluminum or plastic clips.

(5) A total of 10–20 near-root strands of hair with a length of 3–5 cm are cut with stainless-steel surgical scissors at 5–10 various regions at the back of the head (without shaving them completely; see Fig. 3). The haircut of the patient should not appear ragged.

(6) The obtained hair strands are placed into a clean hermetic plastic sachet with a clasp, and a label with sample designation is glued to it.

(7) The sample designation is noted in the patient's registration card.

The samples are stored in clean plastic sachets with a clasp. The storage and transportation of hair samples requires no special care (except when the package becomes physically damaged). The preparation of hair samples for the analysis consists in removing the surface contaminants and degreasing. All the analysis procedures include the stages of cleaning the hair samples with a detergent, repeated rinsing with distilled water and degreasing with an alcohol–ether mixture or acetone, and drying in the open air at moderate temperatures. If the instrumental neutron activation analysis (INAA) is to be performed later, the sample is packed and sent off for irradiation and analysis without any additional treatment. Other analysis methods require mineralizing the hair samples. The mineralization of hair presents the same problems as that of blood. The primary problem consists in minimizing the value of the blank experiment. Dry mineralization is performed in a muffle furnace at 480°C, and the residue is dissolved in a diluted acid. When acid mineralization of hair is performed, various combinations of chemical agents (HNO_3 and H_2O_2, HNO_3 and $HClO_4$, H_2SO_4 and H_2O_2, etc.), heating at an atmo-

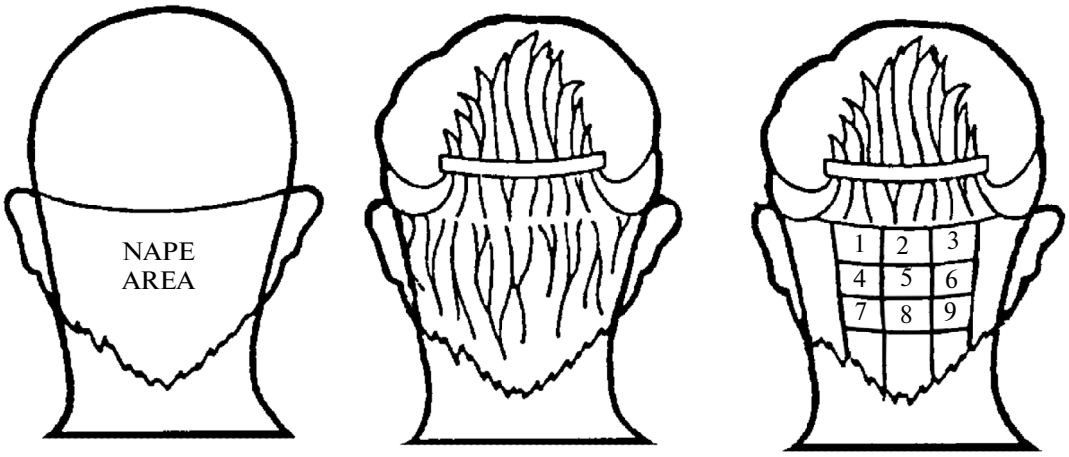


Fig. 3. Hair collection diagram.

spheric or elevated pressure, and microwave or ultrasonic treatment of the sample are applied. The typical weight of the analyzed sample is 100–500 mg, and the acid volume is 2–12 mL.

SAMPLE ANALYSIS

The analytical characteristics, implementation, and methodological support of the methods to be used, the complexity of the sample preparation procedure, and economic and time factors should be taken into account when choosing the analytical support for ecological studies. The methods used should solve the problems at hand within the framework of the entire study, and their total number should also be minimized. Therefore, the development of appropriate analytical methods that would provide reliable analytical data is a required stage of preparation for our studies. In view of the study specifics, matrix effects in the identification of various elements, the potential to identify simultaneously a wide variety of elements with the needed sensitivity, the ease of sample preparation, and the cost of analysis seem to be the most important characteristics of methods. Therefore, instrumental analysis methods (X-ray fluorescence analysis (XRF) and instrumental neutron activation analysis (INAA)) are the optimum ones. These methods almost completely satisfy the demand of the majority of ecological studies for microelement analysis of various objects of the environment (outside and indoor air, food, soils, bottom sediments, and components of the human environment and human biological materials) in a wide range of concentrations. The simultaneous use of XRF and INAA allows one to identify the following elements in solid samples: Ag, As, Au, Ba, Br, Ca, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, Hg, Ir, K, La, Lu, Mg, Mn, Na, Pb, Rb, Re, Sb, Se, Sc, Sm, Sr, Ta, Tb, Th, Ti, U, W, Yb, and Zn. The exception is provided by several elements, the most ecologically, biochemically, and medically important of which are nickel, cadmium, mercury, and lead (in biological samples and in water). If these elements are to be identified, it is advisable to introduce AAS into the utilized analytical complex based on XRF and INAA. The AAS method is advantageous in that it offers a very high selectivity, high detection sensitivity, and the ease of analysis. This method is also characterized by a weak effect of the analyzed object matrix on the analysis results. This relaxes the requirements for the preparation of solid samples for analysis and allows one to use almost all acids for exposing them. The chosen analytical complex based on XRF, INAA, and AAS is also advantageous in that it comes with certified analysis procedures that are approved as regulatory documents [14–25]. When small concentrations of a wide variety of elements in biomaterials and water are to be identified, mass spectrometry with inductively coupled plasma (ICP MS) should be used [23, 26].

The instrumental neutron activation analysis was performed at the IBR-2 (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research) and IRT (National Research Nuclear University MEPhI) research reactors. Induced activity was measured with the use of spectrometers based on large-volume high-purity germanium detectors produced by Canberra with an energy resolution of 1.3 keV at the 1332 keV line of Co^{60} and the GEM 25185 detectors produced by Ortec with an energy resolution of 1.85 keV at the 1332 keV line of Co^{60}.

The atomic absorption analysis was performed with the use of the Kvant-2A (KORTEK, Moscow) atomic absorption spectrometer complemented with a deuterium corrector of nonselective absorption and the appropriate hollow-cathode lamps. The identification of Zn, Pb, Cu, and Cd was performed in a propane–air flame; Fe, Mn, and Ni were identified in an acetylene–air flame. The concentration of mercury was

determined with the use of the Yuliya-5K atomic absorption analyzer with "cold vapor."

The X-ray spectroscopic analysis was performed with the use of the S4 Pioneer sequential wave XRF spectrometer produced by Bruker AXS. The obtained results were processed with the help of the S4 Spectra Plus software package.

Mass spectrometry was performed with the use of the Perkin Elmer high-resolution mass spectrometer with inductively coupled plasma.

Element detection limits, the accuracy and reliability of analysis, and the cost are the most important characteristics of the complex of analytical methods. Detection limits for certain macro- and microelements obtained as a result of the analysis of grounds, soils, biological materials, and water with the chosen complex of analytical methods are listed in Table 2.

The problem of reliability of the analytical data is now a pressing one. Comparative tests have showed that the results of identification of one and the same element in one and the same specially prepared hair sample obtained in different laboratories may differ by a factor of several tens [23, 26]. The results of mass-spectrometric analysis of hair obtained in an interlaboratory study (with the participation of 20 laboratories located all over the world) in 1999 revealed a satisfactory reproducibility of results only in the case of Zr. The minimum and the maximum content of Bi and U differed by a factor of 3, the same for Mo and Sb differed by a factor of 5, Cu and Zn showed a sevenfold difference, the content of Cd differed by a factor of 8, and the minimum and the maximum content of the other 17 elements (including As and Pb) differed by a factor of 10 or more (for example, the content of Al differed by four orders of magnitude) [26]. In general, the quality and reliability of analysis are improved via intralaboratory and external monitoring. Intralaboratory monitoring is performed by following the standard procedures that form the basis for laboratory accreditation [27]. External monitoring is performed by conducting professional analytical tests in which the composition of the reference sample is not known to the laboratory being tested and as a part of programmes of certification of reference standards. Table 3 lists the international programmes for testing the analytical laboratories and certifying reference standards; the complex of analytical methods mentioned above took part in all these programmes. Table 4 lists the results of certification of one of the IAEA reference standards (IAEA-452 scallop meat, 2009).

RESULTS AND DISCUSSION

Soil

The pollution of soil in areas intended for building presents the most danger to population. Considering that children are prone to geophagy, this danger is particularly great for them, since they come in direct contact with soil while outside. A total of 57 soil samples were analyzed in the process of studies in Gus-Khrustalny. The gross content of lead ranged from 4.6 to 15000 mg/kg, while the background content in sandy soils and sandy loam typical for the region under study is 6 mg/kg. The approximate permissible concentration (APC) of lead for sandy soils and sandy loam typical for that region (32 mg/kg) was exceeded in 30% of the analyzed samples. The mobile lead content in soils (ammonium–acetate buffer, pH = 4.8) fell within a range of 1.7–1600 mg/kg and amounted to 11–47% of its gross content. No correlation between the mobile and gross lead content was observed. The maximum gross lead content in soil (4400–15000 mg/kg) was determined at sampling sites located in the floodplain of the Gus River below the industrial zone. This may be attributed to the stormwater runoff from the crystal factory into the river and the transfer of the resultant accumulation of lead compounds in bottom sediments into the floodplain upon spring floods. This conclusion is reinforced by the observation that the gross lead content in the floodplain is reduced downstream and a low mobile (ammonium–acetate buffer, pH = 4.8) lead content in these samples (11–26%). The map of lead distribution in the town soils was plotted based on the obtained analysis results (Fig. 4).

The region of maximum pollution encompasses the crystal factory site and the areas located as far as 2 km to the south of it. The APC of arsenic for sandy soils and sandy loam (2 mg/kg) was exceeded in more than 50% of the samples (37 samples). The maximum determined content was 63–230 mg/kg.

The distribution of arsenic in soils is similar to the distribution of lead, only the area of the maximum pollution region is somewhat smaller (Fig. 5). The nursery schools in which the screening of children was performed were chosen based on the results of these soil studies. Nursery schools located in districts with various lead pollution levels at a distance of up to 1, 1–3, and more than 3 km from the crystal factory (the primary source of lead pollution) were chosen. The average lead content in soil on the premises of nursery schools nos. 2, 20, and 8 in Gus-Khrustalny significantly exceeded the APC for sandy soils and sandy loam and fell within the range of 60–100 mg/kg. The lead content in soil at the site of nursery school no. 38 and in the sand of sandpits in all the studied nursery schools was 7–10 mg/kg. The arsenic content in soil on the premises of nursery schools nos. 20 and 8 was high (9–12 mg/kg) and the arsenic content in the sandpit of nursery school no. 8 was elevated (4.8 mg/kg). The degree of pollution and the total index of pollution with lead and arsenic (hazard class I elements) of certain soil regions in Gus-Khrustalny was evaluated (Tables 5 and 6) [28, 29].

Table 2. Element detection limits for different methods

Element	Ground, soil, mg/kg				Biomaterials, mg/kg			Water, mg/L	
	XRF	INAA	AA	ICP MS	INAA	AA	ICP MS	AA	ICP MS
Na	50	5	–	5	5	–	4	0.1	0.01
Mg	20	100	–	5	50	–	1	0.1	0.01
Cl	–	50	–	–	20	–	–	–	–
K	10	150	–	5	100	–	5	0.1	0.02
Ca	4	300	–	5	100	–	5	0.1	0.01
Sc	3	0.005	–	0.1	0.001	–	0.1	–	0.0001
Ti	3	100	–	5	100	–	2	–	0.0001
V	2	50	–	0.5	30	–	0.1	–	0.0001
Cr	5	0.5	–	0.1	0.1	–	0.1	1.5	0.0001
Mn	2	1	0.1	0.1	0.5	0.1	0.1	0.005	0.0001
Fe	5	50	2	5	30	2	2	0.02	0.001
Co	0.7	0.1	0.5	0.1	0.05	0.5	0.1	3	0.0001
Ni	3	–	0.5	0.1	–	0.5	0.1	3	0.001
Cu	7	10	0.1	0.1	5	0.1	0.1	0.4	0.0001
Zn	2	5	2	5	1	2	0.4	0.001	0.0005
As	3	0.05	0.1*	0.1	0.01	0.1*	0.1	50	0.00005
Se	–	0.5	0.1*	0.1	0.1	0.1*	0.1	70	0.0005
Br	–	0.5	–	0.1	0.1	–	0.1	–	0.01
Rb	1.5	5	–	0.1	1	–	0.1	–	0.003
Sr	1	50	–	0.1	10	–	0.1	–	0.0005
Mo	1.5	0.5	–	0.1	0.1	–	0.1	10	0.0001
Ag	–	0.5	–	0.1	0.2	–	0.1	0.3	0.0001
Cd	–	2	0.05	0.05	1	0.05	0.05	0.2	0.00001
Sb	–	0.05	–	0.1	0.01	–	0.1	10	0.000005
Cs	–	0.1	–	0.1	0.05	–	0.1	–	0.000005
La	6	0.5	–	0.05	0.1	–	0.05	–	0.000005
Ce	10	1	–	0.05	0.5	–	0.05	–	0.000005
Hf	–	0.05	–	–	0.05	–	0.02	–	0.0001
Ta	–	0.2	–	–	0.1	–	0.01	–	0.0001
W	–	0.5	–	0.1	0.2	–	0.1	–	0.00005
Au	–	0.005	–	–	0.001	–	0.03	–	0.00005
Hg	–	0.05	0.001**	0.08	0.01	0.001**	0.08	0.0001**	0.00001
Pb	3	–	0.5	0.1	–	0.5	0.1	2	0.00001
Th	2	0.1	–	0.05	0.1	–	0.03		0.000005
U	2	0.5	–	0.05	0.5	–	0.03	–	0.000005

* Atomic absorption analysis with hydride generation.

** Atomic absorption analysis with "cold vapor."

A total of 90 soil samples were analyzed in the process of studies in Podolsk. Considering the polyelement anthropogenic impact on the soils in Podolsk, Cr, Cu, Mn, Ni, V, and Zn were determined here alongside As and Pb. The summarized results for the total and mobile element forms are listed in Table 7.

The APC clay soils (65 mg/kg) that are typical for natural undisturbed soils of the Podolsk region was exceeded in 30% of the samples. The total lead content in 15% of the samples (all of them were collected in the industrial area) exceeded the APC for neutral sandy soils and sandy loam that constitute the major

Table 3. Participation of the laboratory in the international programmes for testing the analytical laboratories and certifying reference standards

Object	Identified elements	Reference	Organizer	Year
Fish	As, Br, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Na, Ni, Rb, Se, Zn	IAEA-407	IAEA	2003
Food diet	Cd, Co, Cr, Cu, Fe, K, Mn, Na, Zn	IAEA-CRP	NFA, Sweden	2003
Lichen	Cd, Cu, Fe, Mn, Pb, Zn	Lichen IAEA-338	IAEA	2003
Scallop meat	Cd, Cr, Fe, Ni, Pb	Round T-8	NFA, Sweden	2003
Flour	Cd, Cu, Mn, Pb, Zn	Round T-9	NFA, Sweden	2004
Bottom sediments	As, Co, Cr, Cu, Fe, Hg, K, Mn, Na, Ni, Pb, Sb, Sr, Zn	IAEA-433	IAEA	2004
Food diet	Cd, Fe, Ni, Pb	Round T-10	NFA, Sweden	2005
Fish (tuna)	As, Br, Cd, Cu, Fe, Hg, Mn, Rb, Zn	IAEA-436	IAEA	2006
Bottom sediments	As, Ba, Br, Ce, Cd, Co, Cr, Cs, Cu, Fe, Hg, La, Mn, Ni, Pb, Rb, Sb, Sc, Sr, Th, V, Zn	IAEA-158	IAEA	2007
Food diet	Cd, Cu, Ni, Pb, Se	Round T-15	NFA, Sweden	2007
Milk	Cd, Pb, Zn	Round T-17	NFA, Sweden	2008
Tobacco leaves	Ba, Br, Cd, Co, Cr, Cs, Cu, Fe, Hf, La, Mn, Na, Ni, Pb, Rb, Sc, Sm, Th, Zn	INCT-OBTL-5; INCT-PVTL-6	Institute of Nuclear Chemistry and Technology	2008
Scallop meat	Ag, As, Br, Cd, Co, Cr, Cs, Cu, Fe, La, Mn, Na, Ni, Pb, Rb, Sc, Se, Th, Zn	IAEA-452	IAEA	2009
Andesite	Ba, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Tm, U, V, Y, Yb, Zn, Zr	GeoPT27/MGL-AND	International Association of Geoanalysts (IAG)	2010
Bottom sediments	Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	IAEA-456	IAEA	2010
Shale	As, B, Ba, Be, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Ge, Hf, Ho, La, Lu, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr	GeoPT28/SBC-1	(IAG)	2010
Sewage sludge	Cd, Co, Cu, Pb, Zn	IAEA-CU-2010-02	IAEA	2011
Nephelinite	Ba, Be, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Li, Lu, Nb, Nd, Ni, Pr, Rb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Tm, U, V, W, Y, Yb, Zn, Zr	GeoPT29/NKT-1	(IAG)	2011

Fig. 4. Distribution of lead in the soil in Gus-Khrustalny.

part of the urban area. The regions with an elevated lead content are located in the industrial area, at a distance of up to 2 km to the west from the battery factory, and along the major traffic routes of the town (Fig. 6). The level of pollution of territories lying outside the area of direct influence of industrial production facilities was considerably lower and did not exceed the standard for neutral soils.

An excess over the maximum permissible concentration (MPC) and APC for total and mobile forms of As, Cu, Pb, and Zn was found in the soils in Podolsk (Table 6). The total Pb, As, and Zn content was elevated within the boundaries of the industrial area (Figs. 6–8). In addition to this, zinc anomalies were located along the traffic routes (Fig. 8). The obtained data do not contradict the literature data, which suggest that the maximum lead and zinc concentrations were found in road dust in the district with the heaviest traffic [30].

The behavior of the mobile lead form differed from one studied town to the other. No correlation between the mobile and gross forms was observed in Gus-Khrustalny, whereas the mobile lead, copper, and zinc (ammonium–acetate buffer, pH 4.8) concentration depended logarithmically on their total content in Podolsk (Fig. 9, $p < 0.01$). The fraction of mobile lead in contaminated samples with the gross lead content in excess of 300 mg/kg was as high as 40–45%. The mobile lead content in the samples with the maximum gross lead content was 11–26% in Gus-Khrustalny. The difference in the behavior of mobile lead may be caused largely by the difference in technogenic lead

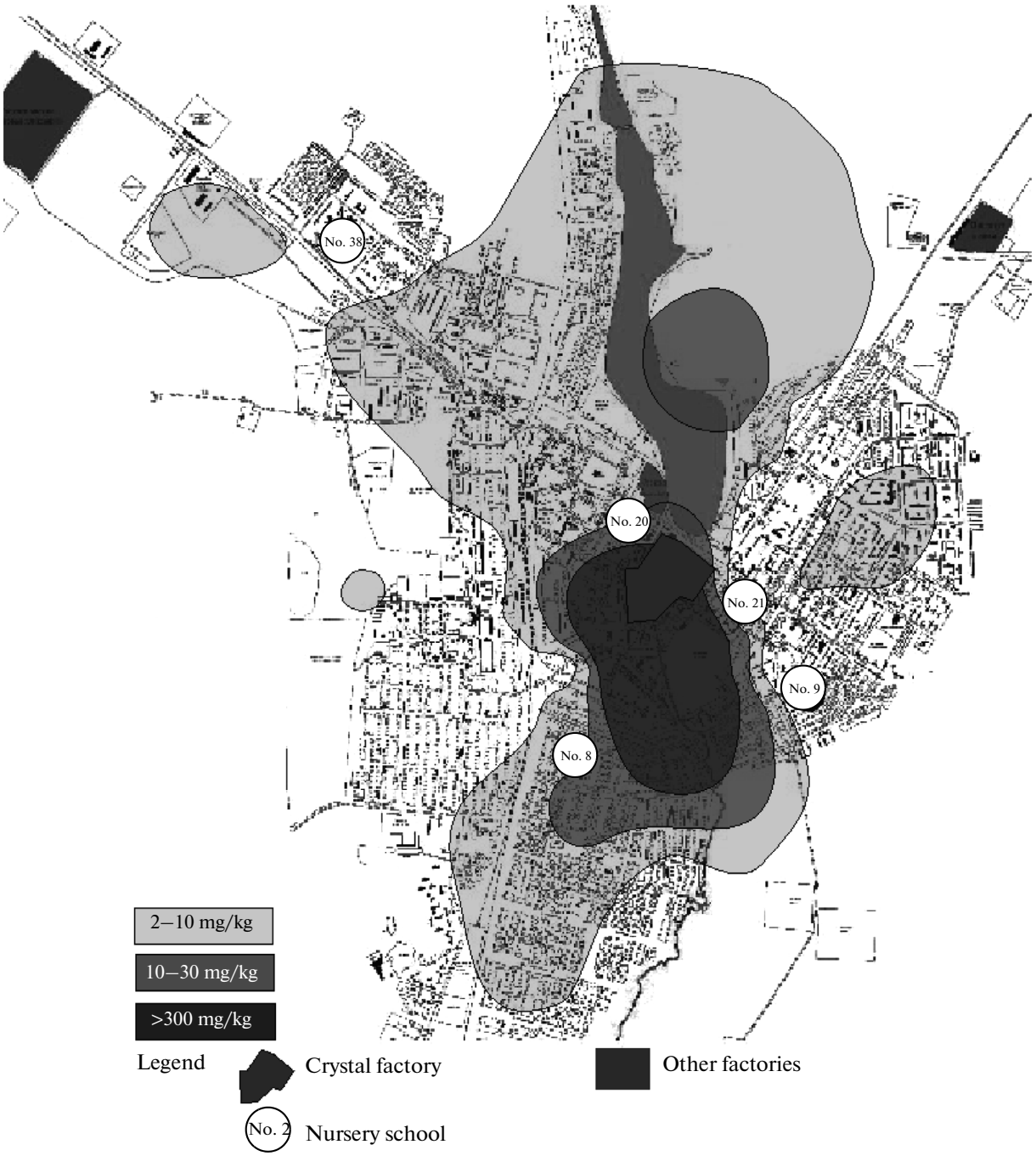


Fig. 5. Distribution of arsenic in the soil in Gus-Khrustalny.

forms entering the environment. The soil in Gus-Khrustalny is contaminated with practically insoluble lead oxides, while salts associated with some specific manufacturing procedures may act as contaminants in Podolsk.

The mobile chromium content was tens of times lower than the MPC and exhibited almost no dependence on its total content. This suggests that the source of Cu, Pb, and Zn that enter the soil differs in its nature from the source of Cr. Emissions from industrial enterprises produce the main contribution to the Cu, Pb, and Zn content in soil. It appears that chromium is primarily of natural origin. Just as in Gus-Khrustalny, the nursery schools in which the screening of children was performed were chosen in Podolsk based on the results of the soil studies. Nursery schools located in districts with various lead pollution levels at a distance of up to 1, 1–3, and more than 3 km from

Table 4. Results of certification of the IAEA-452 reference standard (scallop meat), mg/kg. Laboratory code 31

Element	Measured		Certified	Z-Score
	mean	std. dev.		
Na, %	5.6	0.25	4.39	2.19
Sc	0.27	0.001	0.3	–0.8
Cr	6.4	0.15	4.85	2.56
Mn	263	5	273	–0.29
Fe	1026	34	1021	0.04
Co	2.1	0.17	1.62	2.37
Ni	3.2	0.27	2.99	0.56
Cu	9.1	0.17	10.8	–1.27
Zn	156	4	166	–0.48
As	18.8	1.5	17.5	0.58
Se	7.7	0.36	6.55	1.4
Br	500	35	500	0
Rb	8.2	0.43	7.85	0.36
Ag	13.1	0.74	11.8	0.88
Cd	28	0.84	29.6	–0.43
Cs	0.3	0.023	0.3	0
La	0.81	0.043	–	–
Pb	2.3	0.16	2.31	–0.03
Th	0.41	0.011	–	–

Z-Score is an indicator characterizing the deviation of the studied value from the discriminant line.

Table 5. Concentration of As and Pb in the soil in Gus-Khrustalny and Podolsk, mg/kg

Characteristic	As		Pb	
	Gus-Khrustalny	Podolsk	Gus-Khrustalny	Podolsk
Mean	12.9	6.65	398	97.5
Median	3.6	6.4	17	46
Std. dev.	38.1	2.17	2059	166
Min	2	2.3	4.6	12
Max	230	13	15000	1200
MPC, APC	2–10		32–130	

Table 6. Evaluation of the total index of pollution with lead and arsenic of certain soil regions in Gus-Khrustalny

Region	C_{1As}, mg/kg	C_{1Pb}, mg/kg	K_c* (As)	K_c (Pb)	Z_c**	Soil pollution hazard class
1	11	520	7.3	87	93.3	Hazardous
2	17	1300	11.3	217	227.3	Exceptionally hazardous
3	63	4400	42	733	774	Exceptionally hazardous
4	230	15000	153	2500	2652	Exceptionally hazardous

* The coefficient of element concentration in the soil $K_c = C_i/C_{ib}$, where C_i is the concentration of the ith element and C_{ib} is the regional background of this element ($C_{b\mathrm{As}} = 1.5$ and $C_{b\mathrm{Pb}} = 6$ mg/kg).

** The total pollution index $Z_c = \Sigma(K_c) - 1$ (for two elements). At $Z_c > 128$, the soil pollution is exceptionally hazardous. At $128 > Z_c > 32$, the soil pollution is hazardous..

Table 7. Concentration of microelements in the soils in Podolsk, mg/kg

Value	As	Cr		Cu		Mn	Ni	Pb		V	Zn	
	Total	Total	Mobile	Total	Mobile	Total	Total	Total	Mobile	Total	Total	Mobile
Min	2.3	33	<0.1	9	0.16	180	4	12	1.1	16	36	3
Max	13	520	0.2	430	19	1100	54	1200	450	110	1200	400
Mean	6.7	151		42	2.6	540	24	98	53	66	175	56
Background [85]	2.2	20	–	15	–	150	30	15	–	–	45	–
MPC, APC	2–10	–	6	66–132	3	1500	40–80	32–130	–	150	110–220	23

Table 8. Concentration of microelements in the soils at playgrounds in nursery schools in Podolsk, mg/kg

N/s	C	As	Cr	Cu	Mn	Ni	Pb	V	Zn
n/s no. 16 (less than 1 km)	Min	4.6	160	30	330	12	49	39	110
	Max	9.9	220	110	530	22	69	59	290
	Mean	7.3	190	72	430	17	59	49	200
n/s nos. 9 and 26 (1–3 km)	Min	6.7	170	28	490	19	61	57	133
	Max	7.3	180	36	640	31	73	110	139
	Mean	7	175	32	515	20	67	84	136
n/s no. 53 (more than 3 km)	Min	6.1	57	18	560	21	19	69	66
	Max	6.3	91	19	650	21	22	72	68
	Mean	6.2	74	19	610	21	21	71	67
MPC, APC		2–10	–	65–132	1500	40–80	32–130	150	110–220

the battery factory (the primary source of lead pollution) were chosen.

In Podolsk, the minimum Cr, Cu, Pb, and Zn content in the soil at playgrounds was found in nursery school no. 53, while the maximum one was determined in the soil in nursery school no. 16 (Table 8).

Outside Air and Indoor Air

The aerosol component of the outside air at sampling sites in urban areas (including the playgrounds in nursery schools) and of the indoor air in nursery schools was analyzed in Podolsk. Elevated lead concentrations in the outside air at the level of 0.1–0.14 μg/m^3 (MPC daily average (MPC_{da}) is 0.3 μg/m^3) were detected in the industrial area near the battery and cable factories (and not far from nursery schools nos. 16, 9, and 26). The lead content in the populated part of town and in the indoor air in the examined nursery schools ranged from 0.02 to 0.09 μg/m^3. The obtained lead concentrations did not exceed the MPC_{da} value, but were tens of times higher than its background content in the outside air in the forest reserves in central regions of Russia (0.003–0.01 μg/m^3) [31–33]. The MPC_{da} value for copper was exceeded in the industrial area at the sampling site near the cable factory (4.1 μg/m^3, while MPC_{da} is 1.0 μg/m^3) and in the populated part of town (including the playgrounds in the examined nursery schools; 1.5–1.7 μg/m^3). The copper content in the indoor air ranged from less than 0.01 to 0.03 μg/m^3. The aerosol component of the outside air at the playgrounds in nursery schools and of the indoor air in nursery schools was analyzed in Gus-Khrustalny. The lead content in air in Gus-Khrustalny ranged from 0.03 to 0.09 μg/m^3. No statistically significant differences in the lead content in air in Gus-Khrustalny and in Podolsk were found. The distribution of elements between the outside air and the indoor air in both cities is shown in Fig. 10.

In Podolsk, higher element concentrations were observed in the outside air; in Gus-Khrustalny, the concentrations were higher in the indoor air in nursery schools. This is most likely attributable to the state of rooms and windows and the quality of cleaning [34].

The content of the majority of elements (except lead and copper) in the air in both towns was 1.5–4 orders of magnitude lower than MPC_{da}. However, a statistically significant difference in the average concentrations of those elements that characterize the industrial specifics of a given town was found in Gus-

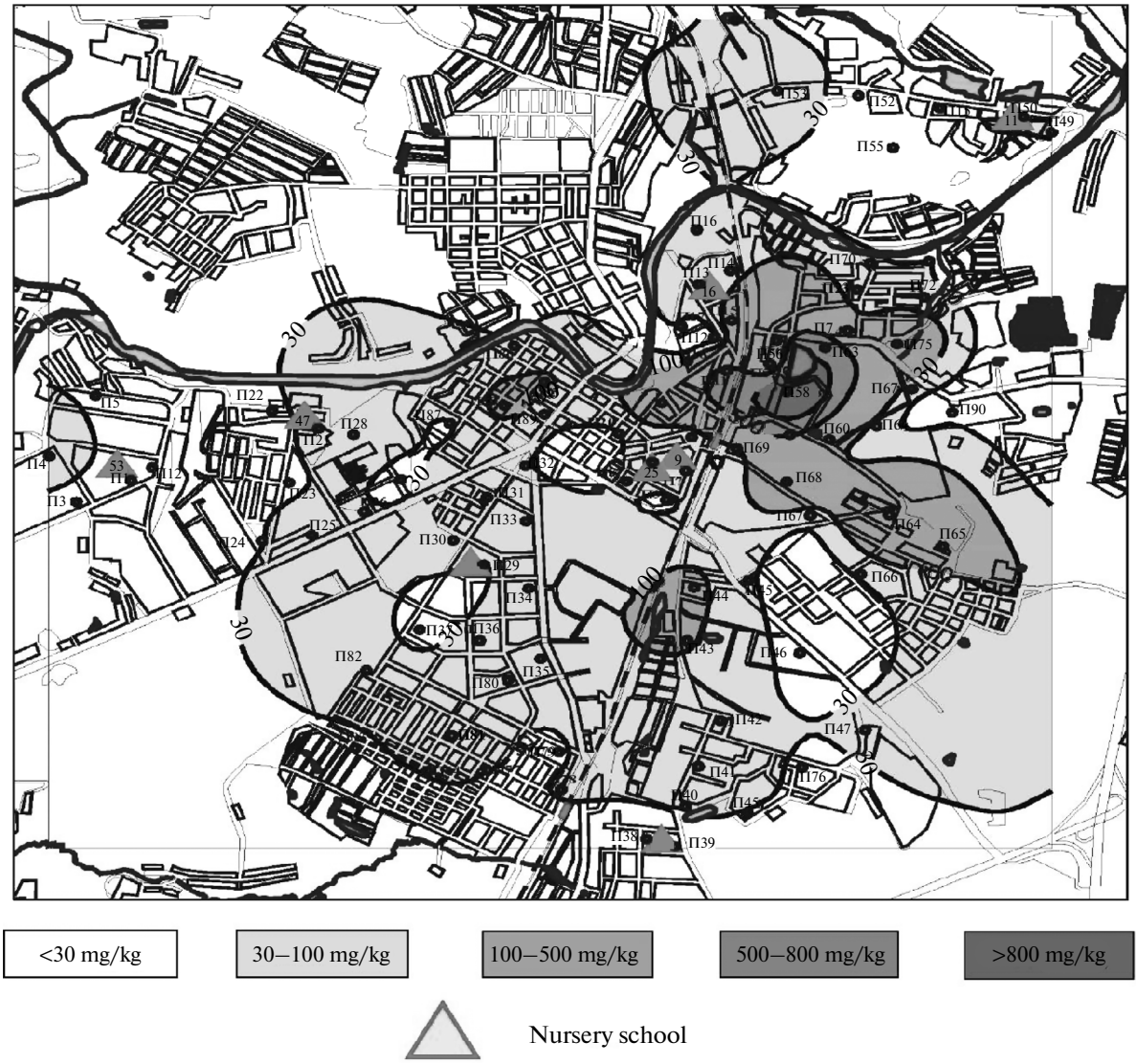


Fig. 6. Distribution of lead in the soil in Podolsk.

Khrustalny and Podolsk. Higher concentrations of arsenic, chromium, lanthanum, and cerium in indoor air and arsenic and chromium in outside air were found in Gus-Khrustalny. This serves as an indication of the components and admixtures of raw materials used in the production of specialized and color glasses [35, 36]. The concentration of antimony in outside and indoor air was definitely higher in Podolsk. This is most likely associated with the production and recycling of batteries containing antimony–lead alloys. These differences were detected at low concentrations of elements in air: the average concentration of chromium was lower than MPC_{da} by a factor of 15–70, and that of antimony was lower than MPC_{da} by a factor of more than 1000. The arsenic concentration was close to the background levels in the outside air of weakly urbanized districts (0.05–4 ng/m^3) and the outside air in the forest reserves (1.2–1.8 ng/m^3). The obtained lanthanum and cerium content was close to the published data on their background content in the atmosphere [37, 38].

Paint, Dust, Food, Water, Bottom Sediments

In order to characterize the sources of influence on child health more thoroughly, we performed an additional analysis of dust sweepings and paints in nursery schools, potable water, food and daily rations in nursery schools, surface water, and bottom sediments. A whole set of toxic elements (lead, arsenic, chromium, antimony, zinc, and cobalt) was found in the samples of paints applied to interior walls in nursery schools in

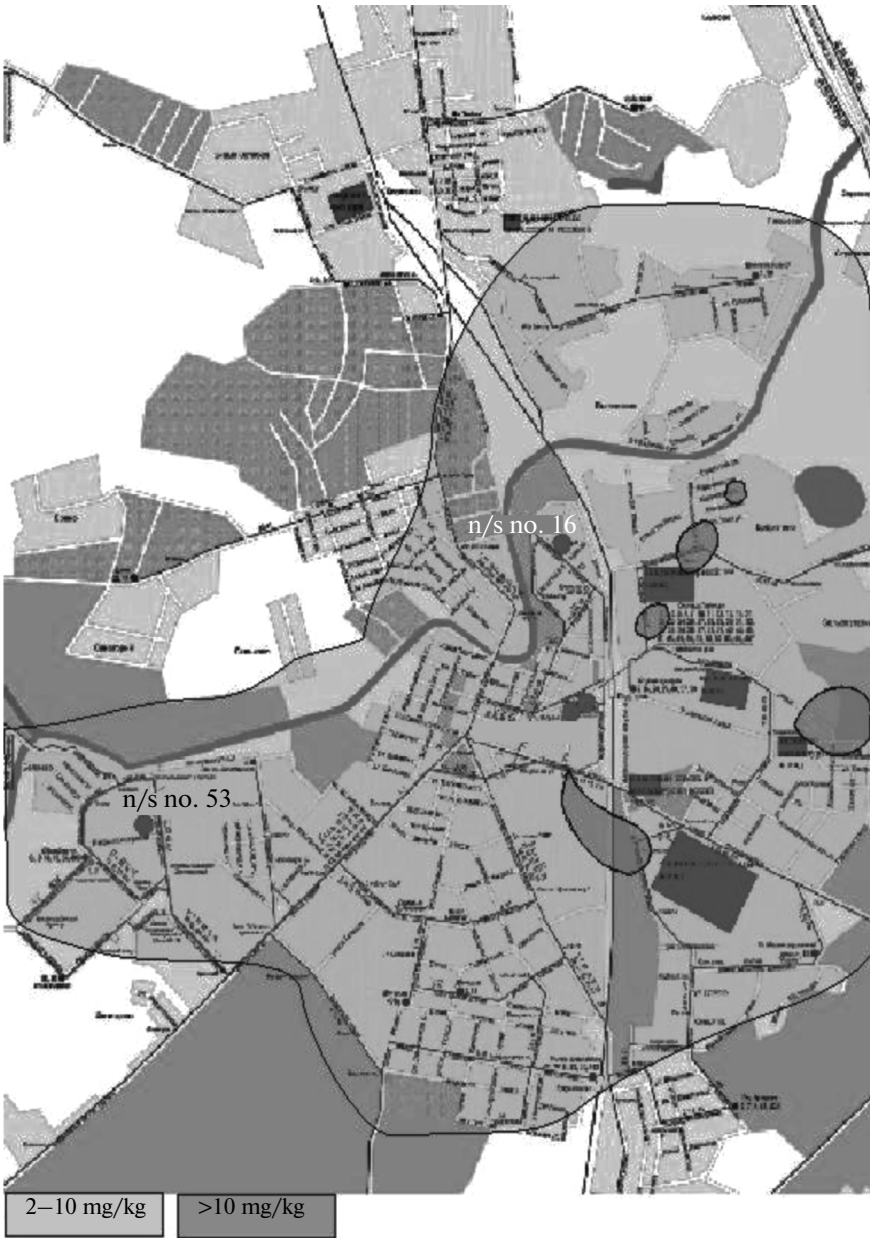


Fig. 7. Distribution of arsenic in the soil in Podolsk.

Gus-Khrustalny (Table 9). In Russia, the rated lead content (0.01%) is specified only for zinc white paint [39]. The MPC of lead in paint is set at the level of 0.5% in the US [40].

Toxic elements were also found in dust in nursery schools (Table 10). The microelementary composition of dust is not rated in Russia. The lead content in dust does not exceed the US standard limit of 110 μg/m^2.

The concentration of microelements in potable water in both towns was low (Table 11). An exception here is provided by iron and manganese: the detected concentrations of these elements exceeded the MPC value in both towns and were as high as 780 mg/dm^3 (Fe) and 130 mg/dm^3 (Mn). This suggests that water-supply pipes are worn and the municipal water supply system experiences certain problems. This conclusion is reinforced by a large spread of iron concentrations in the samples of potable water collected in different nursery schools.

The results of determination of microelements in surface water (Pakhra River) in Podolsk revealed an excess over the MPC value for iron and manganese (Table 12). Elevated concentrations of lead, cadmium, and zinc were determined at the water sampling sites near the points of entry of stormwater runoff from the urban area (the suspension bridge over the Pakhra

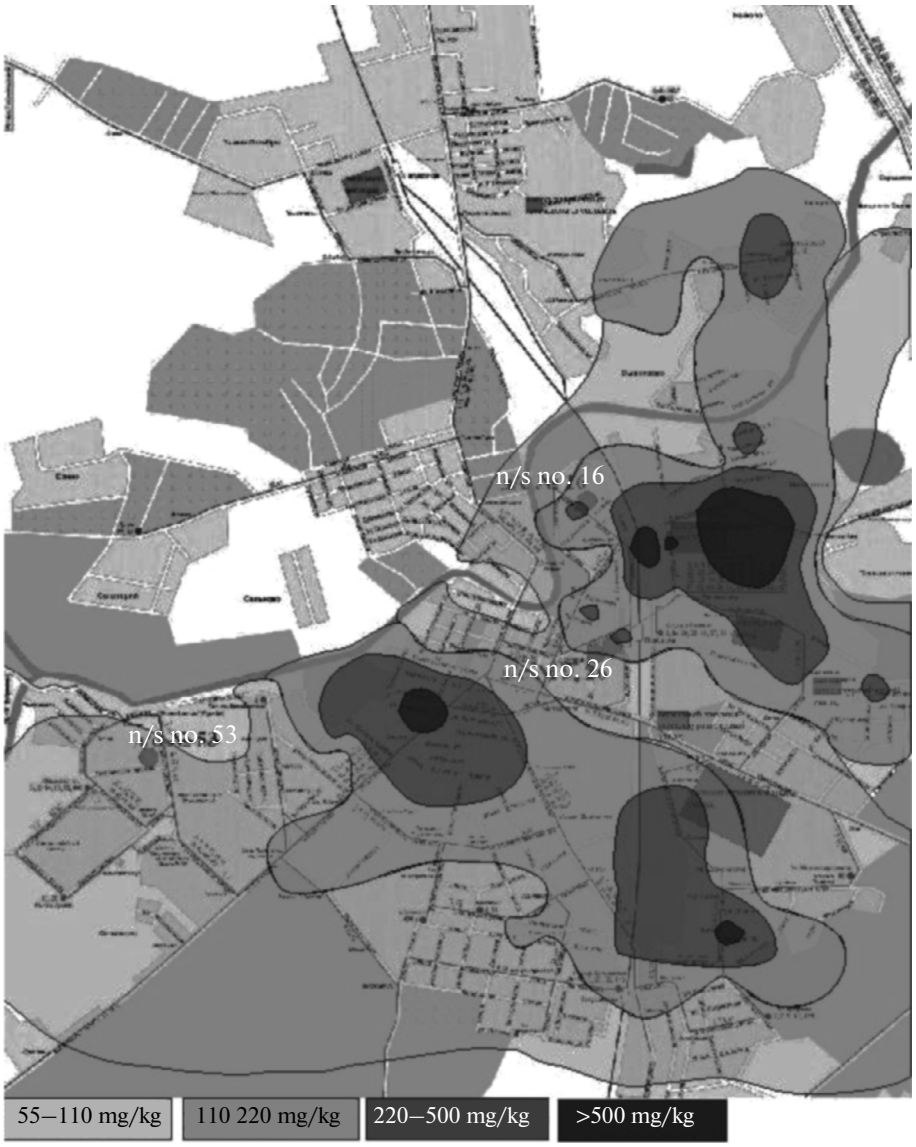


Fig. 8. Distribution of zinc in the soil in Podolsk.

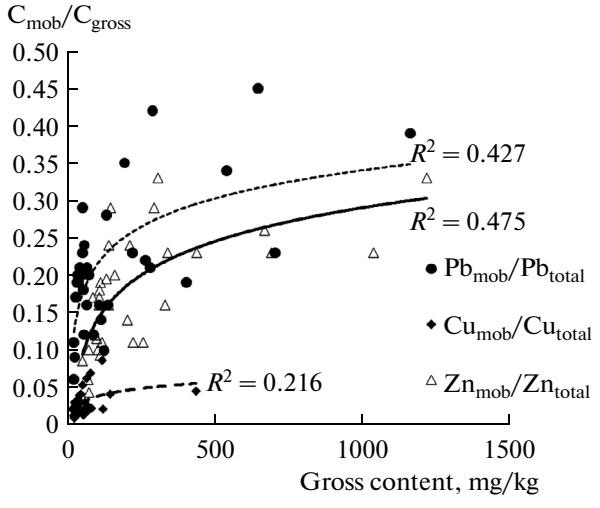


Fig. 9. Dependence of the concentration of mobile forms of Pb, Cu, and Zn on their gross content in the soil in Podolsk.

River and the northern end of the Mramornaya Street). No significant accumulation of microelements in bottom sediments in the Pakhra River within the urban area was found (Table 13).

Table 14 lists the data on the concentration of microelements in food rations in nursery schools in Gus-Khrustalny and Podolsk. Each sample included breakfast, dinner, snack, and supper (with liquids). Each sample was homogenized, dried, and ground. No excesses over the MPC values for all the rated toxic elements were found.

Thus, the results of studies of the state of environment, life environment, potable water, and food in Gus-Khrustalny (Vladimir oblast) and Podolsk (Moscow oblast) allow us to conclude the following:

(1) High levels of soil pollution with lead (300 mg/kg and higher) and other elements were

found in Gus-Khrustalny at the crystal factory site and at a distance of up to 2 km to the south from it, and in Podolsk at a distance of up to 2 km to the west of the battery factory. In accordance with the sanitary–hygienic standards, the pollution of certain soil regions with As and Pb in Gus-Khrustalny and with Cu, Pb, and Zn in Podolsk is classified as hazardous or exceptionally hazardous.

(2) Elevated lead concentrations were detected in outside air in the industrial area of Podolsk, and an excess over the MPC_{da} value for copper in the urban area (including the playgrounds in the examined nursery schools) was found. The content of all other elements in the air in both towns was 1.5–4 orders of magnitude lower than MPC_{da}. In Podolsk, higher element concentrations were observed in the outside air; in Gus-Khrustalny, the concentrations were higher in the indoor air in nursery schools.

(3) A statistically significant difference in the average concentrations of those elements that characterize the industrial specifics of a given town was found in Gus-Khrustalny and Podolsk. Higher concentrations of arsenic, chromium, lanthanum, and cerium in indoor air and arsenic and chromium in outside air were found in Gus-Khrustalny. The concentration of antimony in outside and indoor air was definitely higher in Podolsk.

(4) A whole set of toxic elements (lead, arsenic, chromium, antimony, zinc, and cobalt) was found in the samples of paints and dust. The lead content in all the samples of paints and dust was at a safe level.

(5) The concentrations of lead and other microelements (except for iron and manganese) were not elevated in potable water, food products, and food rations in nursery schools. The lead content in vegetables increased as its content in soil became higher and the distance from the crystal factory was reduced.

(6) The main sources of elevated element concentrations entering the human organism from the environment are the outside air (indoor air) and soils (dust).

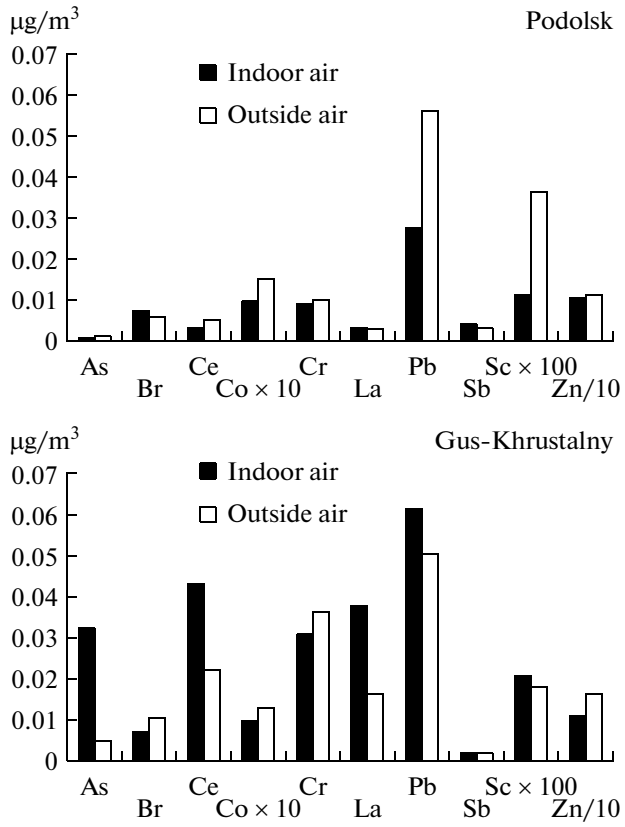


Fig. 10. Distribution of microelements in the outside air and the indoor air in nursery schools in Podolsk and Gus-Khrustalny.

Biological Materials (Biosubstrates)

The chosen nursery schools where the screening of children was performed were located in districts with various lead pollution levels at different distances from the primary industrial sources of lead pollution:

(i) at a distance of up to 1 km (nursery schools nos. 2 and 20 in Gus-Khrustalny and nursery school no. 16 in Podolsk);

(ii) at a distance of 1–3 km (nursery schools nos. 8 and 9 in Gus-Khrustalny and nursery schools nos. 9 and 26 in Podolsk); and

Table 9. Concentration of microelements in paints in nursery schools in Gus-Khrustalny, mg/kg

N/s no.	Sample (color)	As	Co	Cr	Hg	Pb	Sb	Th	Zn, %
8	Cyan	6.4	25	1400	<1	3000	69	<1	24
9	White	<0.5	24	22	<1	2400	62	<1	12
9	Blue	0.5	38	27	<1	1400	32	<1	1.9
38	Lilac	21	16	10	<1	1400	37	<1	7.3
38	Light-lilac	31	21	10	<1	3800	29	1.1	7.4
38	Bluish-green	29	27	51	<1	1100	60	<1	3.9

Table 10. Concentration of elements in dust sweepings in nursery schools in Gus-Khrustalny, μg/m^2

N/s no.	As	Ce	Co	Cr	Fe	Hg	La	Pb	Sb	Th	Zn
2	0.34	0.49	0.015	3.4	220	0.034	0.43	19	0.20	0.031	49
20	0.88	1.0	0.044	10.2	560	0.081	0.73	3	0.34	0.08	66
8	0.36	0.59	0.023	2.8	210	0.016	0.43	90	0.16	0.049	34
9	0.05	0.38	0.002	0.64	25	<0.002	0.35	10	0.03	0.005	16
38	0.30	0.48	0.023	2.9	200	0.021	0.44	11	0.22	0.016	51

Table 11. Concentration of microelements in potable water in nursery schools in Podolsk and Gus-Khrustalny, μg/L

Element	Podolsk				Gus-Khrustalny				MPC
	Mean	Std. dev.	Min	Max	Mean	Std. dev.	Min	Max	
As	1.25	0.26	0.9	1.5	ND	–	–	–	50
Cd	0.08	0.017	0.05	0.09	<0.05	–	–	–	1
Co	<1	–	–	–	<1	–	–	–	100
Cr	<0.7	–	–	–	<0.7	–	–	–	50
Cu	8.25	3.97	4.2	13	4.2	6.7	1	22	1000
Fe	355	306	100	770	423	298	25	780	300
Mn	39	26	18	77	45	30	16	130	100
Ni	2.9	0.48	2.6	3.6	ND	–	–	–	100
Pb	<1	–	–	–	<0.2	–	–	–	30
Zn	20	10.4	9.3	30	3.6	6.25	1	21	1000

(iii) at a distance of 3 km and longer distances (nursery school no. 38 in Gus-Khrustalny and nursery school no. 53 in Podolsk).

The following preliminary work was done in order to form a stratified random sample of children:

(1) The total number of children in the age of 4–7 years attending these nursery schools was determined.

(2) The volume of a random sample was calculated based on the total number of children in each district (a total of 120–150 children in the age of 4–7 years).

(3) Lists of names of children in the age of 4–7 years to be examined were compiled. The children permanently residing in the chosen town district and having no clinically apparent nervous or mental diseases (phenylketonuria, Down syndrome, fetal alcohol syndrome, etc.) were included into the study. The

Table 12. Concentration of microelements in surface water of the Pakhra River, μg/L

Element	Mean	Std. dev.	Min	Max	MPC [64–66]
As	2	0.15	1.8	2.2	50
Cd	0.09	0.08	0.07	0.31	1
Co	0.56	0.36	0.44	1.1	100
Cr	1.2	0.7	0.67	2.3	50
Cu	2.9	1.8	2	5.4	1000
Fe	317	302	150	850	300
Mn	37	46	18	110	100
Ni	4	2.2	3.2	5.7	100
Pb	1.1	1.2	0.8	4.3	30
Zn	8.6	8.3	3.2	20	1000

Table 13. Concentration of microelements in bottom sediments of the Pakhra River, mg/kg

Element	Mean	Std. dev.	Min	Max
As	3.8	2.1	1.9	6.6
Co	5.3	3.6	<2	9
Cr	53	51	15	220
Cu	20	12	<3	40
Mn	290	211	90	980
Ni	9.9	9.5	2	28
Pb	28	33	8.8	100
V	45	23	23	85
Zn	66	62	17	150

fraction of girls in the examined group of children was 46% in Gus-Khrustalny and 54% in Podolsk.

Hair and blood were analyzed in the present study. Hair strands were collected from the back of the head at a distance of no more than 1–2 mm from the scalp in order to study the microelementary composition of children's hair. The length of the collected samples was recorded. Proximal sample segments with a mass of no less than 100 mg were analyzed. The lengths of all the collected samples were taken into account when the length of the analyzed segment was chosen. The actual length range of the analyzed samples was 2–4 cm.

Concurrently with the collection of biosubstrate samples, medical professionals examined children in order to reveal probable disorders in their neuropsychic development that would serve as a specific sign of chronic subtoxic lead effect on child health. The examination was performed with the use of standard psychometric tests covering various areas of neuropsychic activity and adapted for Russian children [41]. Tables 15 and 16 list the concentrations of lead in blood and hair of children in Gus-Khrustalny and Podolsk. In accordance with the classification developed by the U.S. Centers for Disease Control and Prevention (CDC), the lead content in blood determined in both towns is interpreted as normal and alarming. The concentration of lead in blood of the majority of children in both towns ranged from less than 1 to 10 μg/dL. An excess over the "alarming" level of 10 μg/dL was found in blood of 2.3% of children in Gus-Khrustalny and 7.0% of children in Podolsk. The lead content in blood of 25% of children in Gus-Khrustalny and 28% of children in Podolsk exceeded the safe concentration boundary of 5 μg/dL [42, 43].

The lead content in hair is not rated. According to [44], a 90% cutoff point for nonprofessional population corresponds to a value of 10.8 μg/g. Certain authors consider a level of 8–9 μg/g to be a permissible lead content [44–46].

The lead content in hair obtained in the present study corresponds to the literature data on "background" levels. An elevated (greater than 8 μg/g) concentration was found in the hair of 7.6% of children in Gus-Khrustalny and 10.8% of children in Podolsk. The lead content in blood of children from Gus-Khrustalny (Podolsk) fell within a range of less than

Table 14. Concentration of microelements in daily food rations in nursery schools in Podolsk and Gus-Khrustalny, mg/kg (on dry weight basis, 105°C)

Element	Gus-Khrustalny				Podolsk				MPC
	Mean	Std. dev.	Min	Max	Mean	Std. dev.	Min	Max	
As	0.17	0.14	0.05	0.31	0.08	0.07	0.04	0.15	1
Br	7.83	1.97	5	9.6	5.3	1.25	3.3	7.8	–
Cd	0.03	0.01	0.02	0.04	0.04	0.02	0.02	0.06	0.1
Co	0.08	0.01	0.06	0.09	0.05	0.03	0.03	0.08	–
Cr	0.33	0.25	0.13	0.7	0.19	0.15	0.1	0.23	0.3
Cu	2.25	0.58	1.6	3	2.8	1.3	1.5	3.6	10
Fe	29	8.4	16	34	33	10	21	45	–
Hg	<0.01	–	–	–	<0.002	–	–	–	0.15
Mn	8.8	2.8	6.9	13	18	8.6	9.3	25	–
Pb	0.043	0.026	0.02	0.07	0.031	0.022	0.02	0.05	0.5
Sb	0.017	0.012	0.01	0.03	0.03	0.021	0.011	0.038	0.5
Se	0.015	0.006	0.01	0.02	0.013	0.005	0.01	0.02	1
Th	<0.01	–	–	–	<0.01	–	–	–	–
U	<0.1	–	–	–	<0.1	–	–	–	–
Zn	27	7.9	18	37	15	6.3	9.2	26	40

Table 15. Average lead content in blood and hair of children in Gus-Khrustalny

Blood, μg/dL						
Distance from the pollution source	N/s, sample	Min	Max	Av. geom. ± std. dev.	Av. ± std. dev.	Median
300 m	No. 20, n = 8	<1	5.9	3.7 ± 1.8	4.1 ± 1.6	4.4
500 m	No. 2, n = 31	2	13	4.1 ± 1.7	4.7 ± 2.6	3.9
1–2 km	No. 9, n = 27	<1	10	3.5 ± 1.7	3.9 ± 1.9	3.6
1.5–3 km	No. 8, n = 11	<1	8	4.6 ± 1.7	5.1 ± 1.9	5.2
More than 3 km	No. 38, n = 53	<1	7.3	3.3 ± 1.4	3.5 ± 1.2	3.4
Total	n = 132	<1	13	3.7 ± 1.6	4.1 ± 1.9	3.7
Hair, μg/g						
Distance from the pollution source	N/s, sample	Min	Max	Av. geom. ± std. dev.	Av. ± std. dev.	Median
300 m	No. 20, n = 8	2.1	27	4.4 ± 2.3	6.6 ± 8.3	3.5
500 m	No. 2, n = 31	0.9	21	3.9 ± 2.0	5.0 ± 4.1	3.7
1–2 km	No. 9, n = 21	<0.5	6.9	2.3 ± 2.1	2.9 ± 1.6	2.4
1.5–3 km	No. 8, n = 12	0.9	8.8	2.7 ± 2.0	3.4 ± 2.4	2.6
More than 3 km	No. 38, n = 46	0.5	16.4	2.3 ± 2.2	3.1 ± 2.8	2.2
Total	n = 118	<0.5	27	2.8 ± 2.2	3.8 ± 3.7	2.9

1–13 (less than 1–20) μg/dL. This allows one to assume that the absolute endogenic lead content in children's hair is generally lower in Gus-Khrustalny. In general, the use of identical procedures for cleaning the hair samples from external contaminants guarantees that the absolute amounts of residual exogenic lead are also equal. Thus, it appears that the fraction of endogenic lead in children's hair is lower in Gus-Khrustalny. The obtained differences in the significance of correlations may be indicative of the fact that the lead exposure level in Podolsk is higher than that in Gus-Khrustalny. This conclusion is reinforced by higher maximum values of lead content in children's blood in Podolsk (Tables 15 and 16) and an increased fraction (7.0%) of children with an elevated (more than 10 μg/dL) lead content in blood in Podolsk (the same fraction in Gus-Khrustalny is 2.3%).

Microelements in Hair

The results of microelementary analysis of children's hair are listed in Table 17.

Differences in the concentrations of elements characterizing the industrial specifics of each town were found. Higher concentrations of arsenic, lanthanum, and cerium in children's hair are typical for Gus-Khrustalny. The concentrations of these elements significantly exceeded the ones given in literature. Higher concentrations of As, Ce, and La in the indoor air in nursery schools and of As and Cr in outside air were also found in Gus-Khrustalny (Fig. 10). These elements are associated with the specifics of crystal and glass production: arsenic trioxide is used as a refining agent, and rare-earth elements and chromium are added to the raw material when specialized glasses are produced [35]. Higher concentrations of antimony in children's hair were found in Podolsk. Antimony is present in antimony–lead alloys used in the battery production; consequently, higher concentrations of antimony in the outside and indoor air were measured in Podolsk. In addition to the above-listed elements, the multielement technogenic impact on the population of Podolsk is reflected in the concentration of silver and tungsten in children's hair. Silver and tungsten were found in the samples collected from 90% of the examined children in Podolsk, while the content of these elements in similar samples from Gus-Khrustalny was below the detection limit. These elements are typical for the atmospheric emissions of machine and metalworking factories, plants specializing in nonferrous metals processing, and chemical and metallurgical factories located in Podolsk. Thus, the results of studies of the microelementary composition of children's biosubstrates in Gus-Khrustalny (Vladimir oblast) and Podolsk (Moscow oblast) allow us to conclude the following:

(1) Elevated lead concentrations in children's biosubstrates are a specific indication of lead exposure in both towns.

Table 16. Average lead content in blood and hair of children in Podolsk

Blood, μg/dL						
Distance from the pollution source	N/s, sample	Min	Max	Av. geom. ± std. dev.	Av. ± std. dev.	Median
600 m	No. 16, n = 50	1.6	20	4.4 ± 1.9	5.4 ± 3.8	4.8
1 km	No. 9, n = 35	<1	7.7	2.6 ± 1.7	3.0 ± 1.8	2.5
1 km	No. 26, n = 29	1.6	13.6	4.0 ± 1.7	4.6 ± 2.8	3.6
More than 3 km	No. 53, n = 29	1	20	2.3 ± 1.9	3.0 ± 3.5	2.1
Total	n = 143	<1	20	3.3 ± 1.9	4.2 ± 3.3	3
Hair, μg/g						
Distance from the pollution source	N/s, sample	Min	Max	Av. geom. ± std. dev.	Av. ± std. dev.	Median
600 m	No. 16, n = 49	0.8	15	3.4 ± 2.0	4.4 ± 3.4	3.2
1 km	No. 9, n = 34	0.8	12.2	2.7 ± 2.1	3.5 ± 2.5	2.9
1 km	No. 26, n = 28	1	17	4.4 ± 1.9	5.3 ± 3.5	4.7
More than 3 km	No. 53, n = 28	0.6	20	4.2 ± 2.0	5.1 ± 3.7	4.5
Total	n = 139	0.6	20	3.5 ± 2.0	4.5 ± 3.3	3.5

Table 17. Concentration of microelements in children's hair in Podolsk and Gus-Khrustalny, μg/g

Element	Gus-Khrustalny					Podolsk				
	Mean	Std. dev.	Median	Min	Max	Mean	Std. dev.	Median	Min	Max
Na	48.9	14.7	45	12.7	90	55	21	51	21	120
Ca	1422	536	1330	534	2830	1155	553	1100	310	2510
Sc	0.007	0.002	0.007	0.002	0.013	0.004	0.002	0	0.001	0.008
Cr	0.53	0.33	0.4	0.1	2.1	0.5	0.29	0.5	0.2	1.7
Fe	35	12	35	10	69	43	15	37	15	77
Co	0.084	0.023	0.08	0.02	0.14	0.04	0.03	0.04	0.01	0.17
Zn	96.7	35.2	94	23	180	99	45	89	32	220
As	0.12	0.07	0.11	0.013	0.43	0.09	0.05	0.07	0.01	0.23
Se	0.37	0.16	0.3	0.1	0.9	0.34	0.16	0.3	0.1	0.7
Br	5.3	8.6	3.3	0.4	62	5.3	4.6	3.8	0.8	19
Ag	<0.1	–	–	–	–	0.4	0.48	0.3	0.1	2.4
Sb	0.04	0.05	0.03	0.01	0.41	0.1	0.05	0.09	0.04	0.32
La	0.45	0.42	0.3	0.1	2.1	0.05	0.02	0.05	0.02	0.09
Ce	0.65	0.52	0.5	0.2	2.8	0.09	0.05	0.08	0.03	0.21
W	<0.05	–	–	–	–	0.07	0.03	0.05	0.01	0.17
Au	0.021	0.032	0.013	0.002	0.221	0.06	0.13	0.03	0.005	0.774
Hg	0.23	0.12	0.2	0.1	0.6	0.23	0.1	0.19	0.08	0.57
Th	0.015	0.005	0.015	0.005	0.02	0.015	0.008	0.01	0.007	0.03
U	0.2	0.12	0.16	0.1	0.5	<0.1	–	–	–	–

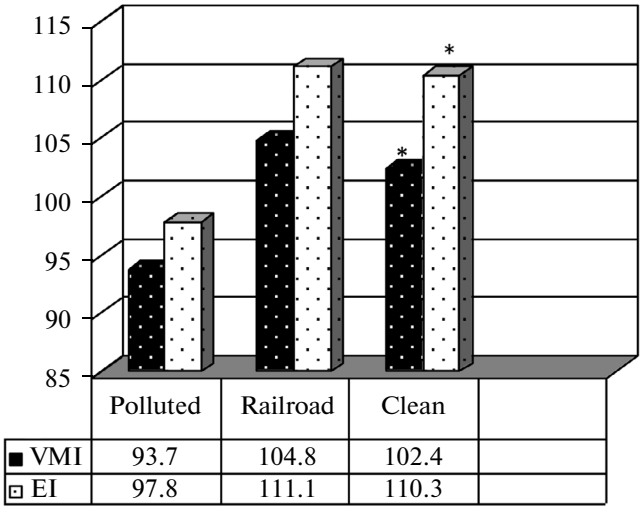


Fig. 11. Average levels of the verbal memory index (VMI) and the educability index (EI) of children in various districts of Podolsk.

(2) The average content of almost all elements (except for lanthanum and cerium in children's hair in Gus-Khrustalny) does not exceed the background levels cited in literature.

(3) The towns differed in the concentration of elements characterizing the industrial specifics of each town. The difference was found in concentrations in the outside and indoor air and in children's hair (including the difference at the background content level of As, Ce, La, and Sb).

Evaluation of the Degree of Impact of Environmental Pollution on Child Health

The results of a sample epidemiological survey of children in Podolsk showed that, in terms of the primary neuropsychic development indicators, the majority of children were characterized by a normal development pattern corresponding to their age and gender. For example, the average verbal memory index in the entire examined group of children was 100.7, and the average educability index was 106.5. Significant differences between children of different ages were found in the process of ranking the obtained survey results over town districts. Therefore, all the results of psychometric testing presented below in tables and figures are standardized as a function of age.

Figure 11 shows the average levels of verbal memory and educability indices for various levels of the anthropogenic lead load. A statistically significant reduction in the values of these indicators in a polluted town district located in the area affected by the battery factory was found. The indices here were 9–12 points lower than the ones determined in a clean district.

Similar statistically significant trends regarding other neuropsychic development indicators were also traced. As the anthropogenic lead load was increased, the values of indicators of fine motor skills, speech expressiveness, and general neuropsychic development of children definitely went down (Fig. 12). The degree of neurological abnormalities was also increased (Fig. 13). The children living in a polluted town district showed an almost twofold reduction in the speed of small movements. Superfluous orofacial

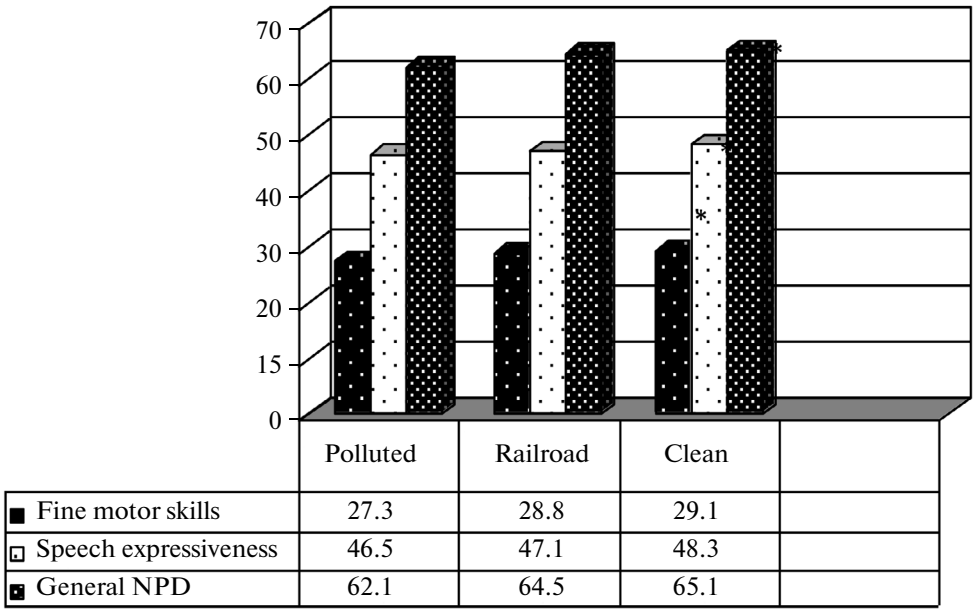
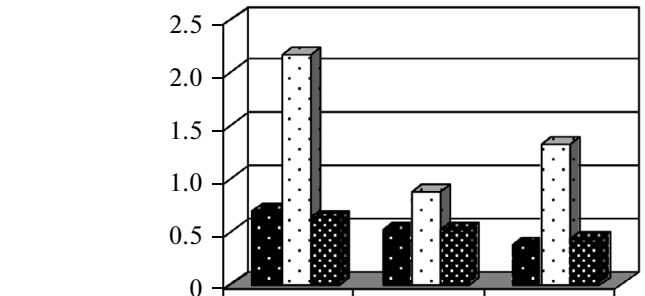


Fig. 12. Average values of motor activity, speech development, and general neuropsychic development (NPD) indicators of children in various districts of Podolsk.



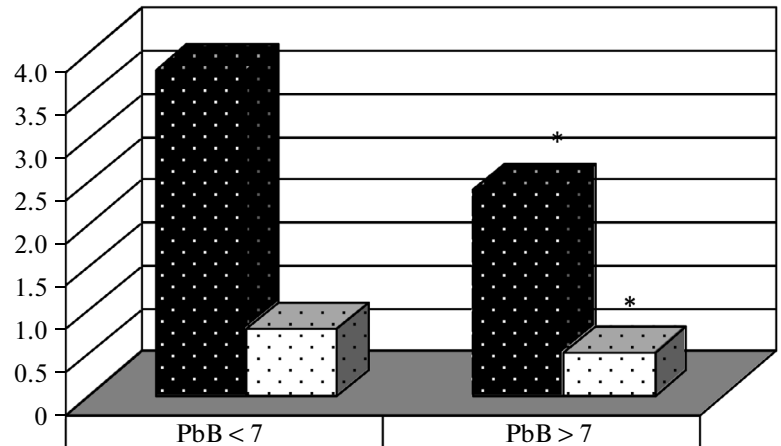
	Polluted	Railroad	Clean
Small movements speed	0.69	0.51	0.37
Superfluous consecutive proximal movements	2.16	0.88	1.33
Superfluous consecutive orofacial movements	0.63	0.52	0.43

Fig. 13. Minimum neurological abnormalities of children in various districts of Podolsk.

and proximal consecutive movements were also observed more frequently in the polluted district.

Close results were obtained in the analysis of the results of psychometric testing of children with different concentrations of lead in blood. Figure 14 shows that a statistically significant reduction in the quality of rapid movements and an increase in the speed of small movements were found at lead levels in blood in excess of 7 μg/dL. It was determined in the course of the study that the neuropsychic development of children is affected not only by the level of anthropogenic pollution with lead and other toxic metals, but also by the interaction with other risk factors (specifically, smoking in the family). Figure 15 shows that elevated concentrations of lead in children's blood coupled with smoking in the family led to an additional threefold reduction in the verbal memory index. Similar statistically significant trends were traced for long-term memory and educability.

It should be noted that smoking in the family is quite widespread. A poll among the parents of the examined children found that 53.6% of fathers and 25% of their mothers smoked. In most cases (57.5%), a single member of the family smoked; the families where two members smoked were encountered less frequently (40%). However, the most troublesome fact is that 36.4% of smokers in the families smoked indoors and 23% of them smoked in the presence of the child. The multifactorial regression analysis data showed that the largest negative contribution to the indicators of neuropsychic development (NPD) of children was produced by high concentrations of lead in blood (about 30% of the children's NPD variability may be attributed to them). In addition to the PbB concentration, significant influences are exerted by the following factors: alcohol consumption during pregnancy and smoking in the family (about 40% of the children's NPD variability may be attributed to them; see Table 18). Thus, preventive activities aimed at improving the children's NPD indicators should be planned in such a way as to cover a complex of ecological (lead and other neurotoxic heavy metals), behavioral, and psychological risk factors. A comparison between the prevalence of indicators characterizing the NPD of children with various levels of anthropo-



	PbB < 7	PbB > 7
Quality index of rapid movements	3.79	2.41
Small movements speed	0.79	0.5

Fig. 14. Minimum neurological abnormalities of children with different lead content in blood (μg/dL).

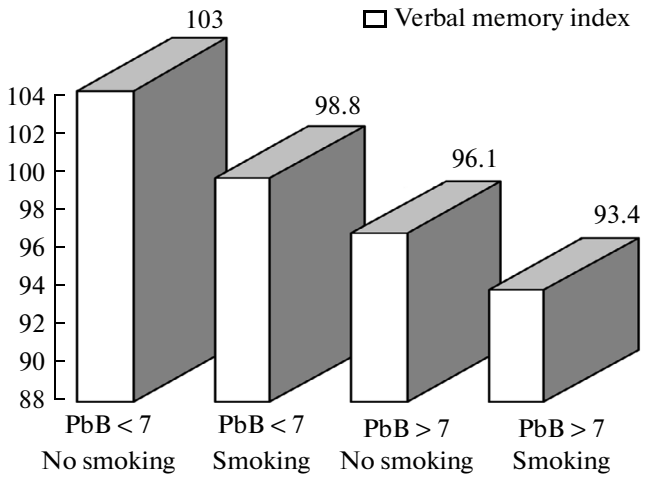


Fig. 15. Dependence of the verbal memory index on the lead level in blood and smoking in the family.

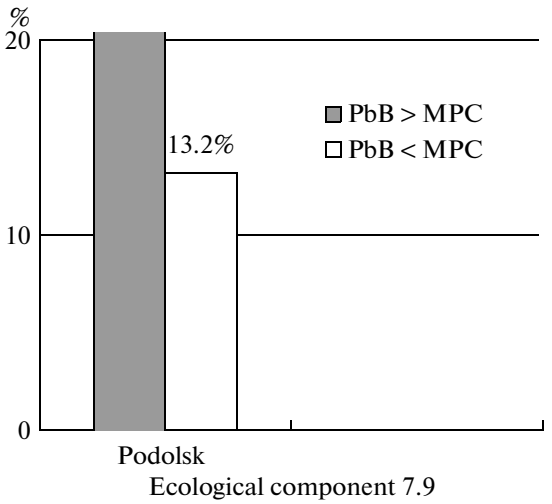


Fig. 17. Prevalence of a reduced EI in children with different lead levels in blood.

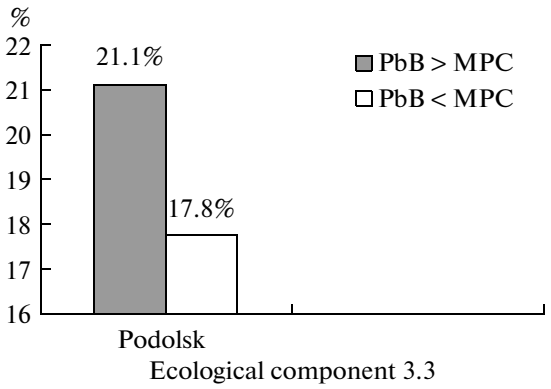


Fig. 16. Prevalence of a reduced VMI in children with different lead levels in blood.

genic toxic-metal load showed that the ecological component for different NPD indicators ranged from 3 to 8%. Figure 16 shows the prevalence of a reduced verbal memory index (less than 1.5 SD) in two groups of children with lead concentrations in blood higher and lower than the permissible concentration.

The prevalence of children's NPD abnormalities at lead concentrations in blood lower than the permissible level was assumed to be a background one. Ecology-related variations in the children's NPD were not that widespread: they accounted for a total of 3.3% of children with abnormalities in verbal memory indicators. At the same time, the high background prevalence is alarming. This suggests that the problem should be viewed not only as an ecological one, but also as a sociomedical one, and the search for other causes for abnormalities in the neuropsychic development of children should be continued. Figure 17 presents the results of a similar analysis for the educability index. It can be seen that the share of ecology-related abnormalities is 7.9%, while the share of background abnormalities that are not associated with ecological factors is almost two times larger (13.2%). The analysis of general awareness of parents of the examined children and medical and pedagogical staff at nursery schools and child health centers regarding the effect of toxicant metals on child health revealed that the awareness level was extremely low (almost nonexistent). The literacy of girls and young women in the issues regarding the effect of alcohol, smoking, and

Table 18. Relevance of concentrations of heavy metals in children's blood and sociomedical factors to the development of memory and educability of children (multifactorial regression analysis data)

Children memory and educability indicators	Significant factors related to heavy metals (total contribution = R^2)	Significant sociomedical factors (total contribution = R^2)
Verbal memory index and educability index	PbB ($R^2 = -0.26$–0.27)	Number of cigarettes smoked in the family ($R^2 = -0.24$) Alcohol consumption during pregnancy ($R^2 = -0.48$)

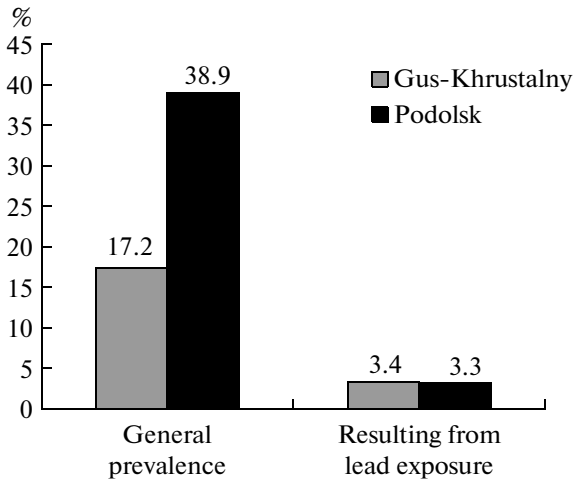


Fig. 18. General and lead-related prevalence of NPD delays in children, % (based on the verbal memory index).

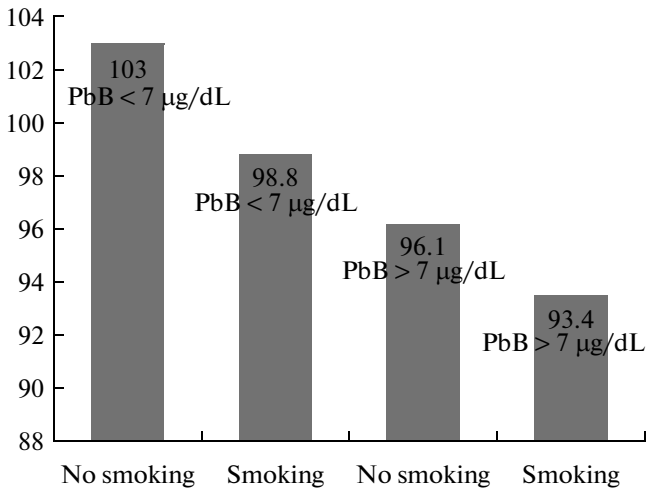


Fig. 19. Dependence of the average values of the verbal memory index on the lead concentration in blood and smoking in the family (in Podolsk).

salts of heavy metal on the gestation course and child health was also studied and found to be poor.

The detected elevated lead concentration in children's biosubstrates is a specific indicator of lead exposure in both towns. This is confirmed by the results of a medical examination of the children which was performed concurrently with the microelement studies. The medical examination was aimed at detecting abnormalities in the children's NPD that serve as a specific indicator of chronic subtoxic lead exposure. The examination was performed with the use of standard psychometric tests covering various areas of neuropsychic activity and adapted for Russian children [42, 43, 45].

The examination results showed that, in terms of the primary NPD indicators, the majority of children in Gus-Khrustalny and Podolsk were characterized by a normal development pattern corresponding to their age and gender. The average values of memory and educability indices of children from Podolsk were definitely lower than that of children of the same age from Gus-Khrustalny. Neuropsychic development abnormalities were already detected at a lead content of 7 μg/dL in children's blood. The results of lead determination in blood and the medical examination of children revealed that, for certain NPD indicators, the lead exposure alone caused 3–8% of children's health-related conditions in both towns (Fig. 18). Combinations of adverse factors (specifically, smoking in the family) that intensified the negative effect of lead were of importance. Figure 19 shows the reduction in the verbal memory index with smoking in the family and increasing lead content in blood.

Following the examination, all parents were provided (via the nursery school administrators) with reports on the NPD status of their children and therapeutic recommendations. The needed preventive measures were determined based on the study results. Since the intensity of exposure to lead (and other toxic metals) is very low (the fraction of children with lead concentrations in blood in excess of 10 μg/dL was about 5% or 12% in the area affected by the battery factory), the focus should be on strengthening child health and neuropsychic health and the primary prevention of ecology-related health changes. The examined child population is in practically no need for complex therapy.

CONCLUSIONS

(1) The procedure for early diagnosis and risk assessment of the effect of heavy and toxic metals on the health of preschool children was developed as a result of the present study. This procedure incorporates three basic units (ecological, analytical, and medical) and involves performing a ecogeochemical examination of the living environment of children, studying the chemical composition of diagnostic children's biosubstrates, performing medical testing and evaluation of the neuropsychic development of children, and providing recommendations on mitigating the effect in each specific case.

(2) When planning the activities on strengthening child health and preventing ecology-dependent changes, one should systematically monitor the state of environment with respect to the primary pollutants (Pb, Cd, Hg, Zn, Cu, etc.) in industrial emissions from the main factories located in a given town and try to raise the community awareness of the ecological, behavioral, and social risk factors. It is also advisable to advance and expand counseling for specialists on this subject and encourage physicians and hygienists to

participate in prophylactic and educational community outreach programs.

(3) Educational modules for target groups should become the dominant technology in the implementation of this program. Healthcare professionals, educators, sanitation and epidemic control officers, and the general population (primarily parents) should be designated as target groups. Active cooperation with local mass media for the purpose of motivating and raising the population awareness should be a formula for success of a program of this type.

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