

ORIGINAL ARTICLE

Soil Contamination by Heavy Metals in Playgrounds of Kindergartens in Vilnius

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Abstract

The soil contamination by heavy metals in playgrounds of kindergartens in Vilnius city is analysed in this article. The aim of this research is to investigate and evaluate soil contamination by heavy metals in playgrounds of kindergartens in different territories of Vilnius city. Concentrations of heavy metals were measured using Thermo Fisher Scientific Niton® XL2 X-ray fluorescence spectrometer. Maximum allowable and background concentrations that are given in Lithuanian hygiene standard and Lithuania geochemical atlas are used to compare and evaluate concentrations of heavy metals. Concentrations of heavy metals and their spatial distribution were analysed in order to exclude the most contaminated areas relating with different functional areas of the city. Geo-statistical analysis and maps of spatial distribution were developed using IDW interpolator in ArcMap software. Detail soil surveys helps to assess the extent of anthropogenic impact in different parts of the city which can be harmful to the soil ecosystem and human health. Such researches can help to change or select different function for city areas in territorial planning process.

Key words : Heavy metals, Soil contamination, Kindergartens, Spatial distribution, X-ray fluorescence spectrometer

1. Introduction

High concentration of human activities which is typical to cities leads to the formation of anthropogenic urban landscape (Baubinas et al., 2003). Eventually cities fill with densely urbanized areas where components of the environment get high load of pollution. One of the most important components of the living environment is the soil. It is a physical basis for settlements and is a result of a dynamic human activity (Davidson et al., 2006; Miguel et al., 1999).

Common changes and different use of urban areas leads to the inclusion of different physical and chemical substances from a variety of sources

(Davidson H. et al., 2006). High amounts of chemical elements exceeding background levels are constantly released from transport and industrial objects which are dispersed into the environment through air and various types of waste (Taraskevicius, 2011). Soil in urbanized territories is technogenically affected due to the constant pollution therefore it loses characteristics of a natural soil and eventually becomes a depositing medium, which accumulates a variety of pollutants (Taraskevicius, 2003). Due to all of these processes in general, each city occurs as a characteristic and specific geochemical sub-region (Taraskevicius and Zinkute, 2011).

Most of the pollution sources concentrate in cities and also these areas are densely populated. For this

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reason human health is closely linked to the urban environment soil quality (Davidson et al., 2006; Morais et al., 2012). Results of researches of foreign and Lithuanian scientists show that surface layer of soil in urban and suburban areas are often enriched with heavy metals (Taraskevicius, 2011; Siu et al., 2006). The group of heavy metals have a negative impact on environment and is particularly dangerous to human especially children (Jarup, 2003; Dulskiene, 2003).

Results of studies of heavy metals (Pb, Cu, Zn, Ca) in contaminated areas of Lithuania showed that morbidity of adults and adolescent is 1.4-1.5 times higher and morbidity of children younger than 14 years 1.5-3.9 times higher than average morbidity of children with the same disease in uncontaminated regions of Lithuania (Juozulynas et al., 2008).

In order to prevent possible health problems concentrations of hazardous substances are restricted by hygiene standards. Soil contamination by chemicals (including heavy metals) is regulated by HN:60 (hygiene norm) in Lithuania and synergistic effects of elements is expressed as a total contamination index Z_d (Lithuanian hygiene standard HN 60:2004).

In cities where the architecture is dominated by apartment buildings children most of their free time spend playing in outdoor playgrounds. It is clear that most urban soils tend to accumulate a variety of contaminants including heavy metals and is recognized that ingestion of contaminated soil has an important impact on health of children recently safety of playgrounds has taken an interest (Bordajandi et al., 2004; Hemond, 2004; Zagury, 2005).

Contamination studies of playgrounds of children often reveals that more than one third (Bergen, Norway - 45%, Zagreb, Croatia - 30%) of playgrounds do not meet the hygienic and other environmental requirements therefore pose a threat to health of children (Ottesen et al., 2008; Miko et al., 2009).

In order to select territories for cleaning and to

provide a framework for future permanent condition monitoring the investigation of soil and ground was started in Vilnius 2006-2007. Kindergartens as one of the least affected by contamination incidents were included in mentioned investigation for the first time in 2008 (Taraskevicius R., 2008).

Fifty samples for heavy metals and petroleum products analysis were taken from kindergartens, 8 different Vilnius city territories. The results of geo-hygienic evaluation revealed that soils from 36% (18) of kindergartens do not meet hygiene standards and were attributed to moderate hazard level. In terms of the total contamination index Z_d 42% (21) of investigated soils of kindergartens were not attributed to the category of permissible contamination (exceeded the allowable limit for total contamination index $Z_d > 16$) (Taraskevicius R., 2008).

Commonly Zn, Pb, Ag, Cu and Sn concentrations are exceeding maximum allowable concentrations in soil of Vilnius kindergartens. The most polluted areas are mainly located on the former industrial territory as well as near major highways and railways (Taraskevicius R., 2008, 2010).

Despite the investigation of soil pollution that was started in Vilnius kindergartens this area of research is insufficiently examined. A small part of kindergartens soil has been investigated for this time which are mainly in the central part of city and such research is carried out only once in a few years. There is a lack of reliable information on soil quality and safety of kindergartens in different sub-districts of Vilnius.

The aim of this work was to analyse and evaluate soil contamination by heavy metals in playgrounds of kindergartens in different territories of Vilnius city.

2. Materials and methods

Research was carried out in forty kindergartens in Vilnius city (from 2014-10-17 to 2014-11-07). Forty



Fig. 1. Sampling points in Vilnius city 2014.

soil samples were taken from playgrounds of kindergartens that are located in 13 districts of Vilnius (Fig. 1).

Previously conducted studies formed the basis of this study and selection of sampling points. 18 kindergartens were selected from studies that were carried out in 2009 and 22 kindergartens from 6 districts that were not investigated previously. Coordinates of sampling points and geometric centres of plots of kindergartens were calculated using the ArcMap software. The distribution of kindergartens in districts of Vilnius city is given in Fig. 1.

2.1. Sampling

Soil samples were taken from the whole territory of playgrounds of kindergartens. Every 10-15 meters

(depending on the area of playgrounds of kindergartens) pre-samples from the surface soil layer using stainless unpainted steel trowel were taken using principle of “envelope” and placed in the clear plastic bucket (for food use). 6-7 pre-samples taken from playground of kindergarten were then homogenized mixing the overall content of samples for 10-15 minutes.

300 grams of homogenized sample was taken from different places of bucket and was placed in plastic bag. The sample is recorded indicating sampling location sample number and other relevant information. All sampling equipment is thoroughly cleaned in order to avoid cross-contamination.

Potential pollution sources in the playground of

kindergartens were taken into account during the collection of samples. The most common potential pollution sources were streets, roads and parking lots also painted components in playgrounds of kindergartens like swings, benches, arbours and other equipment.

Soil samples were taken in accordance with the Lithuanian hygiene standard HN 60:2004 "Maximum allowable concentrations of dangerous substances in soil" and Requirements for eco-geological research (Regulation for eco-geological research, 2008).

2.2. Preparation of samples

Samples were transported to the laboratory, placed in "petri" dishes and dried in a drying oven for 9 hours at 110°C to the constant weight. Dry samples were grinded in porcelain mortar until homogenous mass. Obtained mass was filtered through three-chamber sieves - 2.00 mm, 250 µm and 125 µm. Filtrate was placed in special caps which were put into the X-ray fluorescence spectrometer. Samples were analysed using Thermo Scientific Niton XL2 Series X-ray fluorescence spectrometer. 28 elements can be detected using this type of fluorescence spectrometer (As, Hg, Cd, Ba, Sb, Sn, Ag, Pd, Zr, Sr, Rb, Pb, Se, Au, Zn, W, Cu, Ni, Co, Fe, Mn, Cr, V, Ti, Sc, Ca, K, S). The further analysis of the results was performed for those metals that are potentially anthropogenic and indicating certain human activity impact on the soil ecosystem. The total relative analytical error was 5%.

2.3. Calculation of contamination coefficient (K_0) and total contamination index (Z_d)

Contamination coefficient (K_0) is calculated using the concentration of chemical element in soil with the maximum allowable concentration:

$$K_0 = C/DLK \quad (1)$$

C - Concentration of chemical element detected in the sample (mg/kg);

MAC - Maximum allowable concentration in soil (mg/kg).

According to the results degree of hazard is determined: <1 - permissible, 1-3 - moderate hazard, 3-10 - hazardous, >10 - particularly hazardous.

Z_d index is used when soil is contaminated with several substances or chemical elements (Lithuanian hygiene standard 60:2004). Total contamination index (Z_d) is calculated according to the formula:

$$Z_d = \sum K_K - (n-1) \quad (2)$$

n - The number of chemical elements;

K_K - The concentration coefficient of chemical element:

$$K_K = C/C_f \quad (3)$$

C - Concentration of chemical element detected in the sample (mg/kg);

C_f - Background concentration of the chemical element (mg/kg);

*C - The average concentration of the chemical element detected in samples (used for the calculation of Z_d by average values).

K_K values are taken into account only if the concentration coefficient is >1. The results are classified into contamination categories: <16 - permissible degree of contamination; 16-32 moderate danger degree; dangerous 32-128, >128 particularly dangerous.

3. Results and discussion

XRF method was used to make analysis of 40 soil samples and detect heavy metal concentrations in soil of playgrounds of kindergartens. A total of 17 metal concentrations were identified (out of 28 tested) which were higher than detection level.

Comparison of the results and the assessment of soil quality were carried out using maximum allowable

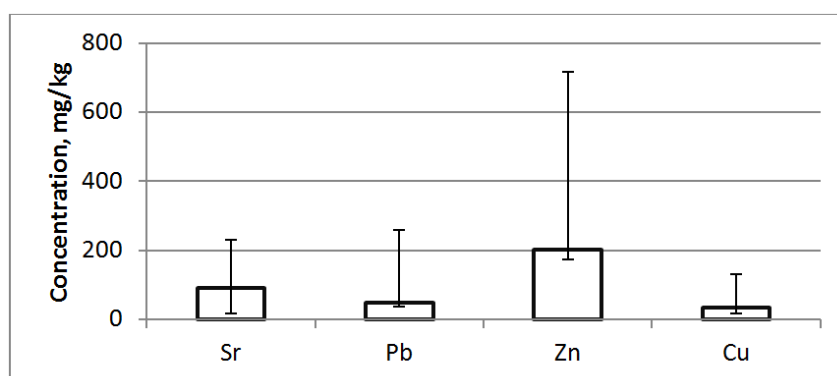


Fig. 2. Maximum, minimum and overall mean concentrations of heavy metals that are potentially of anthropogenic origin.

concentrations given in Lithuanian hygiene standard HN 60:2004, background concentrations of heavy metals (Lithuanian geological survey, 1999) as well as calculated Zd values and interpolation results.

The high degree of variability (Fig. 2) is typical for the soil pollutants which reflect the variety of sources of the contamination within urban area and the complex of the contaminated materials from various urban sources (Krein and Schorer, 2000). Zn, Pb and Sr have the highest variability as these elements clearly reflect the point sources of pollution in the whole territory that was analysed. Zn, Cu and Pb are used to a considerable extent in the technosphere because of their special features. Their applications range from the electrical industry, transport or mechanical engineering through to construction and civil engineering. As far as the building sector is concerned, they are traditionally used materials for roof constructions, gutters, drainpipes, chimneys, roof flashings and coverings (Environmental research, 2005). There is also a long tradition of covering entire roofs with these materials.

3.1. Comparison of the results with the maximum allowable concentrations and contamination coefficient (K_0)

Zn, As, Se, Pb, Co exceeds ($K_0 > 1$) maximum

allowable concentrations (MAC) in Vilnius city playgrounds of kindergartens, 4 of them are heavy metals (Zn, As, Pb, Co). MAC was mostly exceeded by Zn - 8 playgrounds of kindergartens, As, Se - 3 playgrounds, Pb - 2 playgrounds, Co - 1 playground of kindergarten.

The results of geo-chemical assessment by maximum contamination index (K_0): 65% (26 out of 40) of soil samples in playgrounds of kindergartens are attributed to permissible contamination category ($K_0 > 1$), 30 (12 out of 40) - moderate hazard category ($1 < K_0 < 3$) (Fig. 3.). Two playgrounds of moderate hazard category are in Antakalnis, three playgrounds in Karoliniskes and Naujamiestis, one playground in Naujininkai, Senamiestis, Snipiskes and Vilkipede sub-districts of Vilnius. In these particular playgrounds of kindergartens MAC is exceeded by: As, Pb - 2 playgrounds ($K_0 = 3.09$; $K_0 = 2.11$), Se - 2 playgrounds ($K_0 = 1.61$) and Zn - 8 playgrounds ($K_0 = 1.71$).

5% (2 out of 40) of soil in playgrounds of kindergartens are attributed to the hazardous ($3 < K_0 < 10$) category (Fig. 3.). As ($K_0 = 3.9$) and Se ($K_0 = 1.25$) exceeded MAC in playground of kindergarten "Naminukas" in Antakalnis sub-district and Co ($K_0 = 5.26$) in playground of "Riesutelis" kindergarten in Lazdynai sub-district (Fig. 1.).

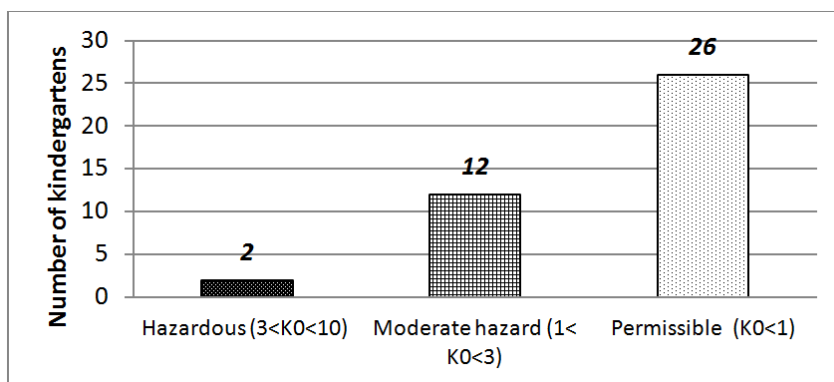


Fig. 3. The distribution of kindergartens by contamination coefficient (K_0).

3.2. Comparison of the results with the background values

In most cases 8 chemical elements exceeded background concentrations in playgrounds of kindergartens in Vilnius. The exceedance of Zr, Sr, and Zn background values were detected in all 40 (100%) playgrounds of kindergartens. Zr 3.48 times and Sr 1.9 times exceeded background concentrations in soil of playgrounds of kindergartens.

Zn concentrations up to 16.58 times exceeded background value. The highest concentrations of Zn were detected in the old part of city i.e. former industrial district (Vivulskis street, Naujamiestis). The average concentration of Zn in soil was 202.81 mg/kg, background concentration (30.9 mg/kg) was exceeded 6.5 times in average. Zn concentrations that dozens of times exceeded background concentrations were detected in Antakalnis, Snipiskes, Naujininkai and Karoliniskes sub-districts. Also high concentrations of Zn were detected in kindergartens that are located near railway and heavy-traffic streets. Background concentration of Ti was up to 1.55 times exceeded in 37 (92.5%) playgrounds of kindergartens.

The exceedance of background concentrations of Rb and Pb were determined in 31 (77.5%) playgrounds. Rb - 1.8 times and Pb up to 13.5 times exceeded

background concentrations in the same sub-district (Naujamiestis). The average concentration of Pb was 39.3 mg/kg, background concentration in city soil was exceeded 2.6 times in average.

In most cases Cu concentrations were higher than background value (8.8 mg/kg) in Vilnius city territory. The exceedance of background concentrations of Cu were in 29 (72.5%) playgrounds of kindergartens. Cu concentrations up to 10.86 times exceeded background value in Vivulskis street. The average concentration of Cu was 35.5 mg/kg, background concentration was exceeded 3.3 times in average.

The exceedance of background concentration (up to 3.19 times) of V was determined in 10 (33.3%) playgrounds. Cr up to 2.54 times exceeded background concentration in 8 (20%) playgrounds of kindergartens. Se up to 40.5 times exceeded background concentration in 7 (17.5%) playgrounds. Also Mn, Co, Sc exceeded background concentrations in some samples (respectively: up to 1.56, 32.89, 31.3 times).

3.3. Results of the total contamination index (Z_d)

Chemical elements for the calculation of the total contamination index (Z_d) were only those with detection of at least 50% of all samples (Zr, Sr, Rb, Pb, Zn, Cu, Mn, Ti). Values of Z_d index were

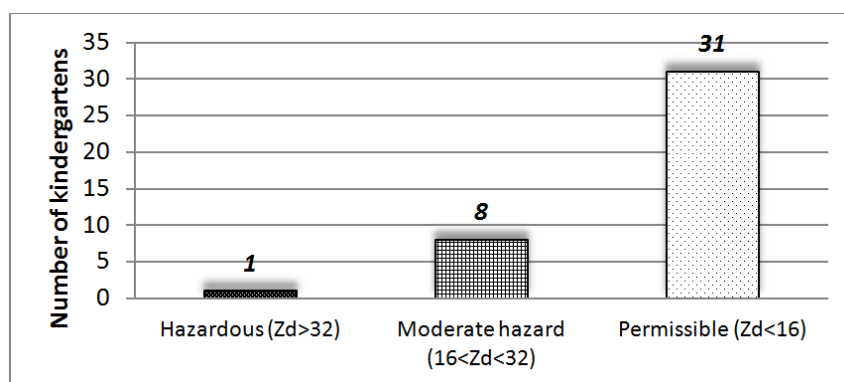


Fig. 4. The distribution of kindergartens by total contamination index (Z_d).

attributed to the soil contamination category.

The results of total contamination index: 77.5% (31 out of 40) of playgrounds of kindergartens are assigned to the category of permissible contamination ($Z_d < 16$), 20% (8 out of 40) of playgrounds of kindergartens are assigned to the moderate danger category ($16 < Z_d < 32$) and 2.5% (1 out of 40) - particularly dangerous ($32 < Z_d < 128$) (Fig. 4.).

All kindergartens attributed to moderate hazard level according to Z_d are located in Naujamiestis, Naujininkai, Antakalnis, Senamiestis, Snipiskes and Zirmunai sub-districts. One kindergarten ("Mazyliis", Vivulskis street) is attributed to hazardous level. Such territories can cause the overall increase of morbidity of adults and children also children suffering from chronic diseases that have cardio-vascular malfunctions (Lithuanian hygiene standard HN 60:2004).

3.4. Results of the interpolation

Geo-statistical analysis was carried out using IDW interpolator in "ArcMap" software. The distribution maps of Pb, Zn, Cu concentrations and total contamination index (Z_d) were created.

The distribution map of lead (Pb) concentrations indicates (Fig. 5.) one concentrated pollution point 210.51 ± 6.55 mg/kg) which is situated in the southern

part of analysed territory in industrial district. Concentrations decreases unevenly to the southeast and north. Pb concentrations are scattered unevenly in kindergartens situated in the northeast part of Vilnius (Snipiskes, Zirmunai, Antakalnis sub-districts). The higher concentrations of Pb were determined in soil samples of playgrounds of kindergartens that are situated closer to streets.

The highest concentrations of zinc (Zn) were determined in the southern part of Vilnius where concentrations are distributed unevenly. Single pollution sources were determined in western and eastern parts of city. The lowest concentrations were determined in northern and north-western parts of analysed territories.

The distribution map of Zn concentrations (Fig. 6.) shows one concentrated point (512.39 ± 19.18 mg/kg) of Zn concentration in the southern part of city (Vivulskis street, Naujamiestis sub-district). Two single points of quite high Zn concentrations are situated in the south-eastern part (M. Dauksa street, Senamiestis; Darius and Girenas street, Naujininkai). Also quite high concentrations are clearly visible in the eastern part (Antakalnis street), north-eastern part (Kalvariju street) and western part (Laisve avenue) of Vilnius city.

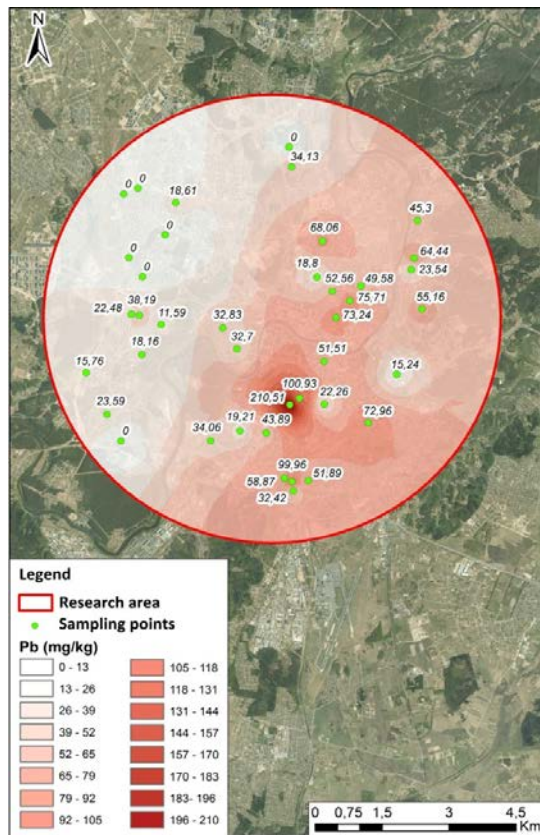


Fig. 5. The distribution of Pb concentrations in soil of play-grounds of kindergartens in Vilnius city.

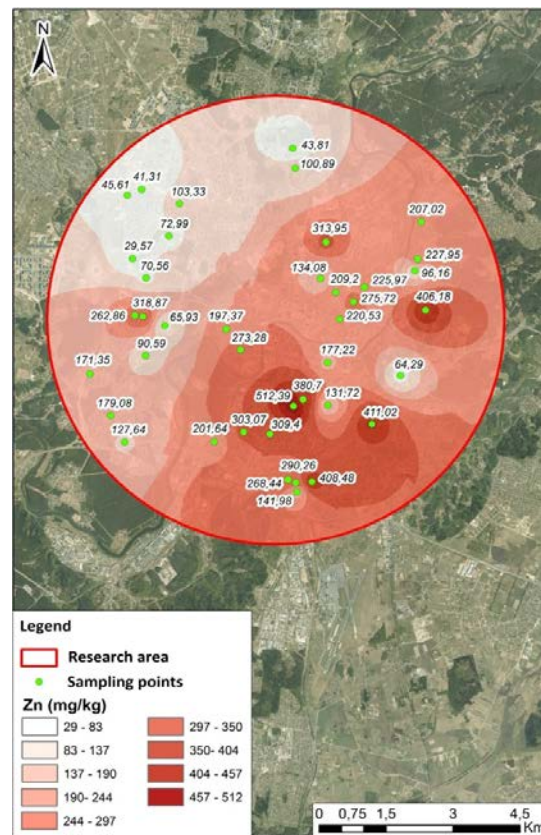


Fig. 6. The distribution of Zn concentrations in soil of play-grounds of kindergartens in Vilnius city.

The highest concentrations of copper (Cu) were determined in the southern and south-eastern part of Vilnius city while the lowest concentrations (limit of detection) of Cu were mostly determined in the north-western and south-western part of city.

The distribution map of Cu concentrations (Fig. 7.) clearly shows one concentrated point (95.61 ± 2.91 mg/kg) in the southern territory. Such concentrations of copper gradually decreases in other parts of analysed area. Also it can be noticed that there is one higher concentration of copper in the eastern part.

All of interpolated concentrations of heavy metals (Pb, Zn and Cu) are similarly distributed in Vilnius city territory. The highest concentrations of lead, zinc

and copper were determined in the southern part of the city. This part of the city is industrial district, Naujamiestis sub-district, the same Vivulskis street where concentrations of heavy metals were the highest.

The distribution map of total contamination index Z_d shows that dangerously polluted ($Z_d > 32$) soil is located in the southern part (Fig. 8.) of the city (Naujamiesti sub-district). Moderate hazard ($Z_d > 16$) level of Z_d is attributed to the central part of the city (Senamiestis) and surrounding districts (Snipiskes, Zirmunai, Antakalnis and Naujininkai sub-districts). Higher than permissible Z_d values according hygiene standard are due to the high concentrations of zinc,

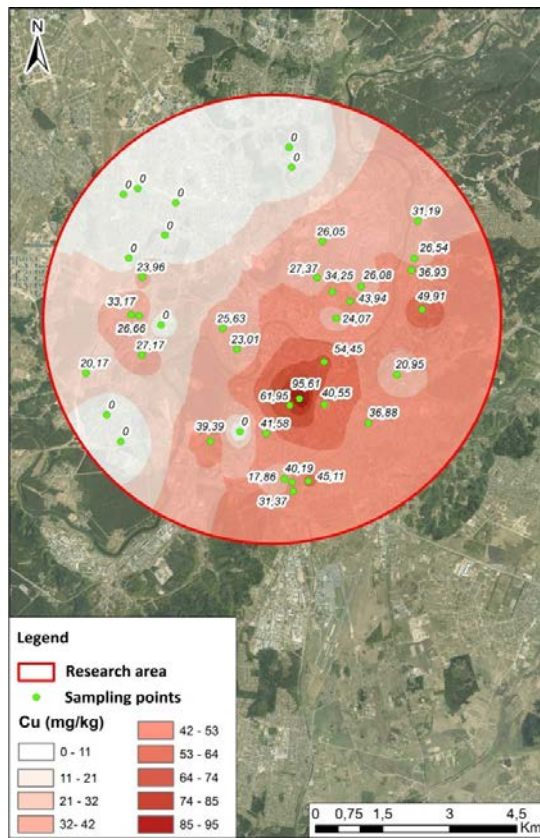


Fig. 7. The distribution of Cu concentrations in soil of play-grounds of kindergartens in Vilnius city.

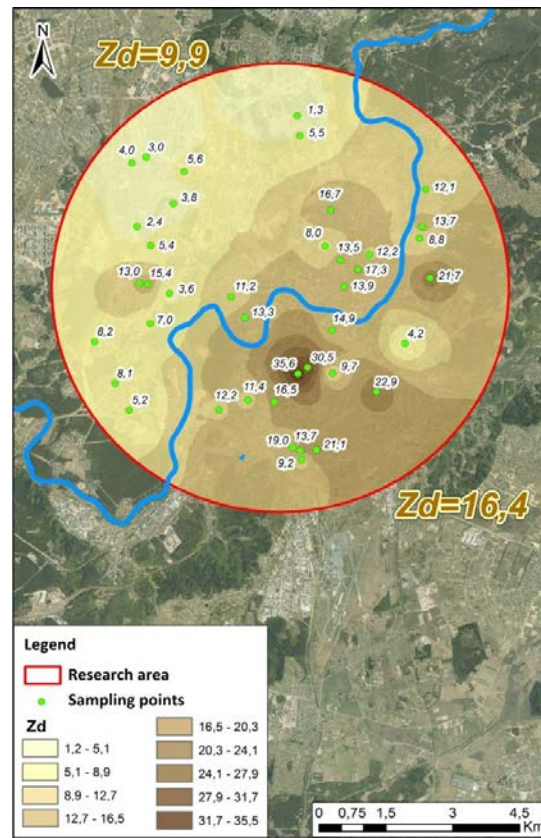


Fig. 8. The distribution map of total contamination index (Z_d) in soil of playgrounds of kindergartens located in southern and northern part of the city.

lead and copper. These heavy metals indicates the impact of anthropogenic activity and impact on urban territories especially soil.

To summarize the spatial distribution of contamination in Vilnius city total contamination index Z_d was calculated separately for the southern and northern part of the city (Fig. 8.). Z_d in the southern part of the city is permissible and reaches 9.9 of Z_d value. Meanwhile Z_d in the southern part of the city reaches 16.4 therefore soil is attributed to the moderate hazard category. All playgrounds of kindergartens should be monitored in this part of the city due to the anthropogenic load in this territory.

4. Conclusions

1. Four of heavy metals (Zn, As, Pb, Co) exceeded the maximum allowable concentrations ($K_0 > 1$) in playgrounds of kindergartens in Vilnius city. Zn exceeded MAC in 8 playgrounds up to 1.71 times, As - in 3 playgrounds up to 3.9 times, Pb - in 2 playgrounds up to 2.11 times and Co - in 1 playground up to 5.26 times exceeded the MAC.

2. According to the geo-hygienic evaluation on the maximum contamination coefficient K_0 : 65% (26 playgrounds) of playgrounds are attributed to the permissible ($K < 1$) category, 30% (12 playgrounds) of playgrounds are attributed to the moderate hazard

($1 < K_0 < 3$) category and 5% (2 playgrounds) are attributed to the dangerous contamination category ($3 < K_0 < 10$).

3. Concentrations of Zr, Sr, Zn, Rb, Pb, Cu, Mn, Ti in playgrounds of kindergartens in Vilnius city were mostly higher than background levels. Zn 16.58 times exceeded the background level, Pb - 13.5 times and Cu 10.86 times exceeded background values.

4. Geo-chemical assessment according total contamination index (Z_d) showed that 22.5% (9) playgrounds does not meet the hygiene standard ($Z_d > 16$), 8 (20%) of them were attributed to moderate hazard level ($16 < Z_d < 32$). The only soil (2.5%) of playground of kindergarten which was dangerously contaminated is "Mazylis" kindergarten in Vivulskis street.

5. The distribution maps of lead, zinc and copper showed that concentrations distribute evenly and the highest Pb, Zn, Cu concentrations were determined in the southern, industrial part of the city in Naujamiestis sub-district, kindergartens that are located in Vivulskis street.

6. Soil of southern part of the city does not meet the hygiene standard ($Z_d = 16.4$). Soil of this city territory is attributed to the moderate hazard category meanwhile soil in the northern part is attributed to the permissible contamination level ($Z_d = 9.9$).

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