MERCURY SOIL CONTENTS AND ASSOCIATED ECOLOGICAL AND HEALTH RISKS IN KINDERGARTENS AND FUNCTIONAL AREAS OF THE CITY OF VANADZOR (ARMENIA)

ABSTRACT. Mercury is a widespread environmental pollutant becoming a crucial health concern as a result of natural and anthropogenic releases. Understanding Hg distribution pattern between different functional urban areas is needed for urban pollution control and health impact assessment. Therefore, in this paper urban soil Hg spatial distribution, pollution level evaluation, and mercury-induced health risks were studied, for different urban functional areas (355 samples) and kindergartens (18 samples) of Vanadzor. Geospatial mapping and the geostatistical analysis suggest that Hg concentration in the entire area of Vanadzor and its kindergartens has a natural origin, besides a certain anthropogenic impact on some urban sites. According to geoaccumulation index (Igeo), uncontaminated or moderately contaminated levels were detected only in 2 samples from industrial area and 5 samples from residential area, the remaining samples were classified as uncontaminated. In all kindergartens and the 22.15 sq.km of the city (270 samples) are characterized by low level potential ecological risk, whereas 3.85 sq.km (85 samples) correspond to moderate and for 1 sampling site high level of potential ecological risk. A non-carcinogenic health risk assessed for children and adults indicates health hazards neither in Vanadzor entire areas nor in kindergartens. The hazard index (HI) in each urban functional area is less than allowable level (HI <1) for children and adults. Obtained results are indicative and offer the ability for better management of urban soil and urban planning in terms of Hg pollution regulation in different functional areas.

KEY WORDS: Mercury, Soil pollution, Urban functional area, health risk, kindergartens

INTRODUCTION

Mercury is one of the metals which pose a grave environmental threat worldwide (Yanin 1992; B.J. Alloway 2013; Driscoll et al. 2013). Due to its chemical and ecotoxicological properties, this element is listed among persistent bioaccumulative toxic elements (PBTs) producing negative effects on both living organisms and the environment (Yanin 1992).

On a global scale, the mercury contamination issue is determined primarily by a complex geochemical cycle of this element (Li et al. 2009; Rice et al. 2014) which includes accumulation of naturally occurring mercury in the earth crust, its emission to the atmosphere (Beckers and Rinklebe 2017), deposition in soil and water, evaporation from these environments (Selin 2009) and consequent accumulation in soil substrates (AMAP/UNEP 2013). In biogeochemical cycle of mercury, soil has an essential part in distribution and accumulation of this element in different environments (Nezhad 2014; Kelepertzis and Argyraki 2015) thus serving as a key indicator of environmental contamination with mercury (Szymon Różański 2015). In soil, mercury is most commonly encountered in organic (Hg–C) and inorganic (Hg2+) forms (Lymberidi 2005; UNEP 2013), the presence of which affects the soil quality characteristics including natural soil profile and soil fertility values (Laker 2005).

Since recent years the mercury contamination issue has become increasingly topical in regard to urban soils (Li et al. 2010; Szymon Różański 2015; Gray et al. 2015; Wan et al. 2016; Kumar et al. 2017; Moller et al. 2018).

Globally, Hg concentrations in the soil range between 0.01 and 0.2 mg/kg, with a mean of 0.03 mg/kg (Reimann and de Caritat 1998). According to Pan et al. 2018, in urban soils from 32 Chinese cities, Hg concentration ranges from 0.02-0.93 mg/kg, with the median of 12.05 mg/kg, and in all studied cities non-carcinogenic health risks of Hg were within threshold values (HI < 1) (Pan et al. 2018). The lowest median value was found in Aveiro (0.055 mg/kg), and the highest- in Glasgow (1.2 mg/kg) (Rodrigues et al. 2006).

The issue of urban soil contamination with mercury is prioritized due to serious risks this element poses to human health (Ajmone-Marsan and Biasioli 2010; Wip et al. 2013; Kotova et al. 2017; Li et al. 2017).

Through direct or indirect ingestion, inhalation or skin absorption mercury and its compounds travel from soil into the organism (Steffan et al. 2018), causing thus acute and chronic diseases including dysfunction of locomotive and nervous systems, toxic effects on the respiratory system (Bernhoft 2012; AMAP/UNEP 2013) and in some severe cases kidney and liver failure.

Different groups of the population depending on physiological, biological and social conditions respond to mercury contamination in different ways (Mamtani et al. 2011). In this respect, a special emphasis is placed on children since their organisms and immune system are still immature. Another fact to explain the sensitivity of children is that for them is more likely to come into contact with soils/soil-derived materials and that due to low stature they inhale topsoil weathering-induced contaminants more intensively than adults (Mielke 2011; Kumpiene and Brännvall 2011; Tepanosyan et al. 2017a). Also, it needs to take into consideration so-called main venues, which for children commonly are kindergartens (Sun et al. 2013; Zheng et al. 2015), for adults – certain functional urban areas (Jing et al. 2012).

Since targeting careful studies with regard to mercury pollution in soils havenot been performed in Armenia, in 2016 the Center for Ecological-Noosphere Studies of the National Academy of the Republic of Armenia (CENS) implemented a first-ever complex research aimed at mercury contamination in city of Vanadzor (former Kirovakan) - one of Armenia’s biggest industrial centers. Although according to Vanadzor’s geological base, Hg natural concentrations are not typical for the city, however, due to intense industrial activity of Vanadzor’s Kimprom chemical plants, hydroelectric power stations, an electrotechnical plant, a number of...
chemicals and chemical fiber manufacturing enterprises, the city was notable for mercury pollution of its environment. At present, the major contamination source to the city is the Vanadzor-Kimprom (Nazaryan 2009). In 1978 as the result of an accident at the chemical plant, significant amounts of mercury were emitted into the city environment. Afterward, massive destruction of thousands of structures during the catastrophic Spitak earthquake of 1988 led to the origination of huge quantities of debris and toxic leakage from the plant’s tailing dump (Karakhanian et al. 2004).

Thus, to understand the current city state of Hg pollution, this particular research was initiated with a purpose of 1. detecting mercury contents in Vanadzor’s functional areas and kindergartens, 2. establishing regularities of mercury distribution and 3. assessing mercury-induced health risks.

MATERIAL AND METHODS

Study area

Vanadzor (40°48´46´´N,44°29´18´´E) is Armenia’s third-biggest city located in the north of the country in intermountain basin at a height of 1350 m a.s.l. The city covers an area of 26 sq.km and has a population of 80.7 thousand inhabitants. Vanadzor city is surrounded by wooded slopes. The central part of the city mainly occupied by residential, public and industrial buildings while on the outskirts of the city the abandoned manufacturing buildings and small houses (sometimes metal made) for low-income families are located.

The climate is temperate: hot, moderately mild summer and mild winter. The average annual precipitation is 600mm, the average temperature in summer varies from +4°C to +24°C, in winter -3.2 °C to -18°C. The cardinal direction of the Vanadzor wind rose is southerly and (State Committee of the Real Estate Cadastre 2007). To the city carbonate rocks and debris, forest cinnamon and limestone loam and black soils are common. The city sits in the forest-steppe landscape belt. The geological structure of the city is complex and involves alluvial, diluvial sediments and basalts, tuffs and other conglomerates (State Committee of the Real Estate Cadastre 2007).

Soil sampling and pretreatment of soil samples

In the frames of this research in August-September 2016 18 soil samples were collected from Vanadzors’ kindergartens as well 355 soil samples were collected from the entire area of Vanadzor (Fig. 1), of which 64 were spatially located within industrial area, 19-

Fig. 1. A map of spatial distribution of soil samples in different functional areas in Vanadzor
in the green belt, 82- on a roadside section, 184- in the residential area of the city (6 samples overlapped). In order to determine a local geochemical background of Hg, 20 soil samples were collected from a background plot (about high of 1750m) in 17km away to the west of the city which can be regarded as being uncontaminated. Background soils are mainly characterized by forest cinnamon and limestone loam and black soils, which are also similar to the city soils. In order to obtain a bulk soil sample, 3-5 subsamples were collected with a stainless steel spade from 0-5 cm deep soil layer, then labeled, placed into plastic zip-lock containers and transported to the CENS lab. Then the samples were air-dried at 20°C, sieved through a 2mm sieve, then crushed and homogenized in compliance with standard operation procedures (SOPs) developed at CENS in compliance with international ISO (ISO 10381-2 2002), US EPA (US EPA 2001), and other international standards (Stauffer 2008).

Analytical method and QA/QC

Total mercury in the soil samples was determined by X-ray fluorescent spectrometry (Olympus Innov-X-5000 (USA)) consistent with the US EPA 6200 method. Detection limit for Hg in the soil is 0.0003 mg/kg. The quality of analytical work was assured based on a SiO2 blank sample certified by the National Institute of Standards and Technologies USA and reference substances NIST 2710a and NIST 2711a.

Statistical treatment and geochemical mapping

Statistical treatment of data was performed (IBM SPSS 21). Normal distribution of data was tested by the Shapiro-Wilk test. In order to visualize mercury contents in different urban functional areas, respective box plots were constructed. The geochemical background of mercury was calculated in compliance with an integral method of determining the background contents of chemical elements in soil (Tepanosyan et al. 2017b). Geochemical mapping of data was implemented in ArcGIS 10.1 program environment by the IDW interpolation method of mapping.

Contamination level assessment

The concentration coefficient (Kc) is a criteria of abnormality of an element denoting an excess of the substance against the background and determined through the ratio between its actual contents (Kosheleva et al. 2003). The concentration coefficient is calculated by a formula (1)

$$K_c = \frac{C_{Hg}}{C_f}$$

(1)

where $K_c$ is the concentration coefficient; $C_{Hg}$ - mercury contents in the study environment (mg/kg); $C_f$ – background contents of mercury. Different soil contamination levels are determined by Kc values as follows: Kc<4 corresponds to allowable, 4-8 to moderately hazardous, 8-16 hazardous, 16-32 highly hazardous, >32 extremely hazardous level (Golovin 2000).

Assessment of geoaccumulation index

The geoaccumulation index (Igeo) employed for assessing the intensity of manmade contamination, was first suggested by Müller (Müller 1969) as a method for determining metal contamination of soils through collation between background contents and detected concentrations of the element (Barbieri 2016). Igeo is determined by the following formula (2):

$$I_{geo} = \log_2 \left( \frac{C_{Hg}}{1.5 \times B_{Hg}} \right)$$

(2)

where $C_{Hg}$ is mercury content of soils, $B_{Hg}$ -background contents of mercury (Tepanosyan et al. 2017b). The 1.5 factor is used because of possible variations of the background data due to lithological variations and it helps analyze natural fluctuations of mercury in the environment and determine small anthropogenic impacts (Müller 1969). A descriptive classification of $I_{geo}$ values suggested by Müller is provided in Table 1.

Assessment of potential ecological risk

In order to describe a potential hazard caused by toxicity of mercury assessment was done of the ecological risk of Vanadzor soils. This risk was identified in compliance with the Potential Ecological Risk Index (PERI) suggested by
Hakanson (Hakanson 1980) and intended for contamination assessment in sedimentology. However, many researchers widely employ this method for assessing ecological risks of soil and dust as well (Sun et al. 2010; Yuan et al. 2014; Soliman et al. 2015; Zhao et al. 2015).

PERI ($E_{Hg}$) is determined by the formula (3) and (4) as follows:

$$C_{r}^{Hg} = \frac{C_{r}^{Hg}}{C_{n}^{Hg}}$$  \hspace{1cm} (3)

$$E_{r}^{Hg} = T_{r}^{Hg} \times C_{r}^{Hg}$$  \hspace{1cm} (4)

where $T_{r}^{Hg}$ is a mercury toxicity-response factor ($T_{r}^{Hg} = 40$); $C_{r}^{Hg}$ – contamination factor; $C_{r}^{Hg}$ mercury content of soil; $C_{n}^{Hg}$ background content of mercury.

### Non-carcinogenic risk assessment

Non-carcinogenic health risk was assessed by the formula suggested by US EPA, according to which non-carcinogenic risk assessment can be done through calculation of three mercury exposure routes: inhalation, ingestion, skin absorption (US EPA 2002a). Based on the three routes of exposure chronic daily intake (CDI) for mercury was calculated by formulae 5-7 (RAIS 2018):

$$CDI_{ing} = \frac{C \times IngR \times CF \times EF \times ED}{BW \times AT}$$ \hspace{1cm} (5)

$$CDI_{inh} = \frac{C \times IngR \times EF \times ED}{BW \times AT \times PEF}$$ \hspace{1cm} (6)

A whole set of CDI calculation parameters is given in Table 2. Hazard Quotient (HQ) for non-carcinogenic risk is calculated through an

$$HQ = \frac{CDI}{RfD}$$ \hspace{1cm} (8)

where $CDI$ is daily intake from $i$ –route: the sum of HQ value calculated for each of three routes represents $HI$ – a hazard index, $HI = \Sigma HQ$ (US EPA 1989).

### RESULTS AND DISCUSSION

The entire area of Vanadzor

Mercury content of soil samples collected from the entire area of Vanadzor varies from 0.001mg/kg to 0.29 mg/kg, with a mean value of 0.043 mg/kg. A map of spatial distribution of mercury contents of Vanadzor soils provided in Fig.3 shows that the city area is dominated by a field of 50-75% mercury contents ranging between 0.039
and 0.05 mg/kg. Relatively high content of mercury (95%, 0.064 mg/kg) exceeds the local background value (0.05 mg/kg) and is characterized by patch-like distribution in form of point-source anomalies throughout the city, whereas the most intensive of these anomalies are spatially located close to the chemical plant and once active but presently inactive industrial centers in the northwest and north of the city. In the entire area of the city, Hg content does not exceed MAC (2.1 mg/kg).

According to descriptive statistics parameters (Table 3) as well as box-plots (Fig. 2) the mean value of mercury contents throughout the city is higher than the median, while the skewness differs from 0, being thus indicative of right asymmetry (＜1) and deviation from normal distribution. According to the Shapiro-Wilk test, mercury contents are abnormally distributed, which can possibly be due to presence of outlier values, and after their excluding abnormal distribution is observable again. However, after logarithmic transformation of data and exclusion of outliers, consistent with the Shapiro-Wilk test log-normal distribution is derived.

In 83.9% of Vanadzor area (21.81 sq.km - 305 samples) the detected Hg contents of soil do not reach the background values. In 16% of the city area (4.16 sq.km – 49 samples) the detected Hg contents exceed the background 1.2 - 2.15 times. Calculated contamination coefficient (Kc) is less than 4, which is indicative of low-level mercury contamination; however, for the only sample (0.086% of the city area, 0.02 sq.km) which exceed the background 5.8 times, Kc is 4-8, corresponding to a moderate mercury contamination level.

Mercury contents detected in Vanadzor are typical of other cities of the world (McGrath 1995; Birke and Rauch 2000; Manta et al. 2002; Tijhuis 2002; Crnković et al. 2006; Szymon Różański 2015). For instance, in Berlin and Tallinn, where the local background value is close to that in Vanadzor (0.05 mg/kg), mean mercury contents of soils are assessed to be
Table 3. Parameters of descriptive statistics, MAC and geochemical background of mercury contents (mg/kg) of soils in different functional areas in Vanadzor

<table>
<thead>
<tr>
<th>Descriptive statistics</th>
<th>Entire area</th>
<th>Industrial area</th>
<th>Green area</th>
<th>Residential area</th>
<th>Roadside area</th>
<th>Kindergartens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.043</td>
<td>0.0423</td>
<td>0.044</td>
<td>0.043</td>
<td>0.041</td>
<td>0.037</td>
</tr>
<tr>
<td>Median</td>
<td>0.039</td>
<td>0.042</td>
<td>0.047</td>
<td>0.038</td>
<td>0.038</td>
<td>0.034</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.019</td>
<td>0.013</td>
<td>0.013</td>
<td>0.023</td>
<td>0.013</td>
<td>0.010</td>
</tr>
<tr>
<td>Min.</td>
<td>0.0015</td>
<td>0.024</td>
<td>0.025</td>
<td>0.0015</td>
<td>0.024</td>
<td>0.025</td>
</tr>
<tr>
<td>Max.</td>
<td>0.290</td>
<td>0.095</td>
<td>0.064</td>
<td>0.290</td>
<td>0.080</td>
<td>0.049</td>
</tr>
<tr>
<td>Coefficient of variation %</td>
<td>44.22</td>
<td>31.14</td>
<td>29.14</td>
<td>53.4</td>
<td>31.65</td>
<td>26.73</td>
</tr>
<tr>
<td>Skew</td>
<td>6.60</td>
<td>1.528</td>
<td>-0.298</td>
<td>6.929</td>
<td>0.830</td>
<td>0.205</td>
</tr>
<tr>
<td>Quantity of samples</td>
<td>355</td>
<td>64</td>
<td>19</td>
<td>184</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>MAC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Background</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Box-plots of mercury contents in industrial, green, residential, roadside areas and kindergartens in Vanadzor
0.42 mg/kg and 0.24 mg/kg, respectively (Birke and Rauch 2000; Bityukova et al. 2000). In Palermo, where the local background content (0.06 mg/kg) is similar to Vanadzor, Hg mean content is 0.68 mg/kg (Manta et al. 2002). In Warsaw, where the local background value is twice as high as it is in Vanadzor (0.1 mg/kg), Hg mean content is 0.13 mg/kg. The same contents are typical for Oslo, where the local background is 0.03 mg/kg (Tijhuis 2002). So, mean Hg contents of soils in Berlin, Tallin, Oslo (where the local background is lower than it is in Vanadzor (0.05 mg/kg)), max 8 times (Berlin) and min 2.5 times (Oslo) are higher than in Vanadzor.

$I_{geo}$ values are provided in Table 4, which shows that $I_{geo}$ for Vanadzor varies from 1.56 to 1.9, with a mean value of ~0.9. For 96.9% of samples (344 samples), $I_{geo}$ corresponds to uncontaminated level ($I_{geo} \leq 0$), for 2.81% of samples (10 samples) – to uncontaminated or moderately contaminated level ($0 < I_{geo} < 1$) and for the only sample – to the moderately contaminated level ($1 < I_{geo} < 2$). Summarizing the descriptive statistic data as well as $K_c$ and $I_{geo}$ values allows to conclude that in different parts of Vanadzor ambiguous contents of mercury are found, the origin and potential sources of which were identified through determining mercury contents of soils in separate functional urban areas.

### Industrial area

Mercury contents of 64 soil samples collected from the Vanadzor industrial area range between 0.024 and 0.095 mg/kg, with a mean value of 0.042 mg/kg. The mean mercury contents of these samples are almost identical to the mean value obtained for almost the entire area of the city (0.043 mg/kg). As seen from Table 3 and the diagram (Fig. 2), mean and median values are similar (0.0423 and 0.0420), however, the skewness differs from 0, which is indicative of some deviation from normal distribution. According to the Shapiro-Wilk test, in the industrial area of the city abnormal distribution of mercury ($p<0.05$) is observable, whereas after logarithmic transformation ($p=0.061>0.05$) lognormal distribution is derived. Having regard to low values of the coefficient of variation (31.14%) as well as lognormal distribution of mercury, one may suppose that mercury contents in this area of the city are mainly of natural origin. Nonetheless, according to the box-plots (Fig. 2) in the industrial area of the city two mercury outliers are found which are 1.7 and 1.9 times higher against the background value. One of two mentioned samples is spatially adjacent to a welding plant site which accommodates huge amounts of domestic garbage and waste.

#### Table 4. $I_{geo}$ values for different functional areas in Vanadzor

<table>
<thead>
<tr>
<th>$I_{geo}$ value</th>
<th>Entire area</th>
<th>Industrial area</th>
<th>Green area</th>
<th>Residential area</th>
<th>Roadside area</th>
<th>Kindergartens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>-0.903</td>
<td>-0.885</td>
<td>-0.821</td>
<td>-0.923</td>
<td>-0.928</td>
<td>-1.044</td>
</tr>
<tr>
<td>Min</td>
<td>-5.640</td>
<td>-1.64</td>
<td>-1.580</td>
<td>-5.640</td>
<td>-1.64</td>
<td>-1.580</td>
</tr>
<tr>
<td>Max</td>
<td>1.950</td>
<td>0.340</td>
<td>-0.22</td>
<td>1.950</td>
<td>0.070</td>
<td>-0.600</td>
</tr>
<tr>
<td>SD</td>
<td>0.574</td>
<td>0.413</td>
<td>0.462</td>
<td>0.679</td>
<td>0.438</td>
<td>0.353</td>
</tr>
</tbody>
</table>

| $I_{geo}$ classes | | | |
|-------------------| Uncontaminated | | |
| $I_{geo} \leq 0$  | 97.18%        | 96.8%           | 100%       | 96.2%           | 100%          | 100%          |
| 0 < $I_{geo} < 1$ | Uncontaminated to moderately contaminated | 2.53%         | 3.12%      | -               | 3.26%         | -             |
| 1 < $I_{geo} < 2$ | Moderately contaminated | 0.281%        | -          | -               | 0.54%         | -             |
metals; the second sample is spatially located on the abandoned industrial site with survived metal warehouses. Hence, high mercury contents of these samples could presumably be due to large amounts of metals on the mentioned sites (Sastry et al. 2001). 14% of samples (9 samples) exceed the background value 1.1-1.9 times (0.05 mg/kg), whereas the contamination coefficient varies 0.48 to 1.9, with a mean value of 0.84. For all the samples Kc is less than 4, which corresponds to the allowable level of mercury contamination on these urban sites. Igeo values range between 1.67 - 0.34, with a mean value of -0.88. Only for two samples Igeo > 0 which, according to Igeo classification (Table 1), corresponds to uncontaminated or moderately contaminated level. Considering the value of the coefficient of variation (31.14%) as well as lognormal distribution of mercury, one may suppose that mercury detected in these parts of the city is mainly of natural origin.

In comparison with Hg concentrations from different areas of various cities (Table 6), Hg mean value in Vanadzor industrial area is 5.4 and 5 times lower than in Zima (Russia) and Changchun (China) cities respectively, Hg Max content is 4 and 5.8 times, min content - 8 and 5 times lower than in above cities, respectively.

### Green area

Mercury contents of 19 soil samples collected from the green area of the city vary 0.025 to 0.064 mg/kg, with a mean value of 0.044 mg/kg, which insignificantly exceeds the mean value obtained for the entire area of the city (0.043 mg/kg). The skewness value for this part of the city is negative, mean value is lower than median, thus pointing to left-side deviation from normal distribution. However, according to the Shapiro-Wilk test, the green area of the city is characterized by normal distribution of mercury. 36.8% of samples (7 samples) exceed the background contents (0.05 mg/kg) 1.1-1.05 to 1.29 times (Table 3). The contamination coefficient Kc varies from 0.5 to 1.29, with a mean value of 0.8. For all the samples Kc<4, corresponding to the allowable level of mercury contamination, whereas Igeo value ranges between -158 and 0.21, with a mean value of -0.82, which is indicative of the absence of contamination.

Hence, collation between statistical parameters, insignificant excess against the background contents and the low coefficient of variation (29.14%) points to the natural origin of mercury in the green area of Vanadzor.

### Table 6. Literature data on Hg concentrations (mg/kg) in urban different areas from various cities around the world

<table>
<thead>
<tr>
<th>City</th>
<th>Urban area</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mexico(Mexico)</td>
<td>Residential</td>
<td>0.017</td>
<td>0.061</td>
<td>-</td>
<td>(Morton-Bermea et al. 2016)</td>
</tr>
<tr>
<td>Bydgoszcz(Poland)</td>
<td>Green</td>
<td>0.009</td>
<td>1.114</td>
<td>0.210</td>
<td>(Szymon Różański 2015)</td>
</tr>
<tr>
<td>Palermo(Italy)</td>
<td>Green</td>
<td>0.040</td>
<td>5.600</td>
<td>0.070</td>
<td>(Manta et al. 2002)</td>
</tr>
<tr>
<td>Kavalas(Greece)</td>
<td>Roadside</td>
<td>Not detected</td>
<td>3.300</td>
<td>0.100</td>
<td>(Christoforidis and Stamatis 2009)</td>
</tr>
<tr>
<td>Changchun (China)</td>
<td>Industrial</td>
<td>0.140</td>
<td>0.479</td>
<td>0.208</td>
<td>(Fang et al. 2004)</td>
</tr>
<tr>
<td>Beijing(China)</td>
<td>Roadside</td>
<td>0.022</td>
<td>1.500</td>
<td>0.210</td>
<td>(Chen et al. 2010)</td>
</tr>
<tr>
<td>Beijing(China)</td>
<td>Residential</td>
<td>0.034</td>
<td>2.800</td>
<td>0.350</td>
<td>(Chen et al. 2010)</td>
</tr>
<tr>
<td>Beijing(China)</td>
<td>Green</td>
<td>1.100</td>
<td>9.400</td>
<td>2.900</td>
<td>(Chen et al. 2010)</td>
</tr>
<tr>
<td>Zima city(Russia)</td>
<td>Industrial</td>
<td>0.100</td>
<td>0.810</td>
<td>0.230</td>
<td>(Butakov et al. 2017)</td>
</tr>
</tbody>
</table>
In comparison with Hg concentrations from different areas of various cities (Table 6), we can conclude, that in Vanadzor’s green area Hg mean content is 72, 5 and 1.75 times lower than the mean reported for Beijing (China), Bydgoszcz (Poland) and Palermo (Italy), respectively. Hg max content is 146, 17.8 and 87.5 times lower than in above cities respectively, Hg min content - 44 and 1.6 times lower than in Beijing (China) and Palermo (Italy), but approximately the same with Bydgoszcz (Poland).

Residential area

As evidenced by descriptive statistic data (Table 3), mercury contents of 184 soil samples collected from Vanadzor residential area vary from 0.0015 to 0.29 mg/kg, with a mean value of 0.043 mg/kg, which is equal to mean values obtained for the entire area of the city. Of all soil samples collected throughout the city, minimal and maximal contents of mercury were established for those taken from the residential area. In this area mean contents of mercury are higher than median, this being indicative of skewness, which, as visualized by a box plot (Fig 2), is right-sided. The skewness value differs from 0, this fact pointing to the presence of some deviation from normal distribution as evidenced by a large amount of outlier values. The Shapiro-Wilk test shows abnormal distribution and even after exclusion of outliers and log transformation of data the pattern does not change.
22.8% of samples (42 samples) exceed the background contents (0.05 mg/kg) 1.5-5.8 times. According to the coefficient of contamination varying within 0.03-5.8 in this area with the exception of the only sample, Kc<4, which corresponds to the allowable level of mercury contamination. Only for one sample Kc value is in the range of 4-8 (Kc=5.8), thus corresponding to moderate contamination level. The sample was taken from the surroundings of private houses located close to one of the main roads. As such a high content of mercury was not detected in the rest of samples taken from this area (VS-220 =0.051 mg/kg, VS-217=0.036 mg/kg), so one may conclude that mercury contents in the mentioned sample can possibly be due to manmade point-source contamination: combustion of fuel, broken thermometers, or other anthropogenic activities.

Igeo values vary from -5.64 to 1.95, with a mean value of -0.92. Only 5 out of 185 samples taken from this area have Igeo>5, corresponding thus to uncontaminated or moderately contaminated level (0<Igeo<1), while moderately contaminated level (1<Igeo<2) was established for a single sample only.

According to Hg concentrations in different areas of various cities (Table 6), in Vanadzor’s residential area Hg mean content is 8 times lower than the mean reported for Beijing(China), but 4.8 times higher than Hg max content in Mexico(Mexico). Hg Min content is 15 and 22 times lower than in Beijing(China) and Mexico(Mexico), respectively.

Roadside area

Mercury contents of the roadside samples vary 0.024 - 0.08 mg/kg, with a mean value of 0.041 mg/kg, which is lower than mean contents throughout the city (0.043 mg/kg). As seen in Table 3, the skewness value differs from zero, which is indicative of a certain deviation from normal distribution. The Shapiro-Wilk test points to abnormal distribution, but after log transformation of data lognormal distribution is derived. A conclusion drawn from this is that roadside mercury is naturally occurring. However, mercury contents in these roadside area samples exceed the background, which can possibly be due to heavy road traffic.

18.3% of samples (15 samples) exceed the background (0.05 mg/kg) 1.2-1.6 times. The concentration coefficient (Kc) ranges between 0.48-1.58, therefore Kc<4, thus corresponding to the allowable level of mercury contamination. In the roadside area, Igeo values vary from -1.64 to 0.075, with a mean value of 0.92. For all the samples Igeo values are below zero, this corresponding to the absence of mercury contamination in the given area.

In comparison with Hg concentrations from various city areas (Table 6), in Vanadzor’s roadside area Hg mean content is 2.5 and 5.2 times lower than in Kavalas (Greece) and Beijing (China), respectively. The max content is 41 and 30 times lower than in the above cities respectively, but Hg min content is approximately the same with Beijing(China).

Kindergartens

Mercury contents of soil samples collected from 18 kindergartens in Vanadzor vary 0.025 to 0.049 mg/kg, with a mean value of 0.037 mg/kg, which is lower than mean contents of the element throughout the city (0.043 mg/kg). As visualized in Table 3 and Fig. 2, mean and median values differ insignificantly (0.037 and 0.034, respectively), whereas the skewness value differs from zero, which points to right-side asymmetry (<1) and deviation from normal distribution. According to the Shapiro-Wilk test, kindergarten soils exhibit normal distribution of mercury, but after log transformation of data and exclusion of outlier values log normal distribution is derived.

Considering a low value of the coefficient of variation (26.73-24.5%) as well as lognormal distribution of mercury, one may suppose that the detected mercury contents in the given area are mainly of natural origin.

In Vanadzor kindergartens no MAC and
background exceeding contents were established. According to the concentration coefficient (Kc) which varies 0.5 to 0.98, Kc<4 correspondings to the low level of Hg contamination. Igeo values for the mentioned kindergartens range between -1.58-0.6, with a mean value of -1.04. Igeo values for all the samples are below zero, which is indicative of the absence of contamination.

Assessing potential ecological risk

The index of potential ecological risk of mercury exposure from Vanadzor soils including classification of ecological risk levels is given in Fig 4. $E_{Hg}$ value for Vanadzor soils varies from 1.2 to 85.6, with a mean value of 33.73. Only one out of 355 samples exhibits $E_{Hg}=232$, thus corresponding to high potential ecological risk. For 76.05% of samples (270 samples) $E_{Hg}$ value is below 40, which corresponds to low level potential ecological risk; however, the remaining 23.38% of samples (83 samples) correspond to moderate and the only sample to high potential ecological risk (Fig. 4). The sample exhibiting high contamination level was collected from the residential area, at the intersection of main roads close to private houses. It is noteworthy that as compared with this sample Er values for other samples collected from the given area are relatively low (VS-218- 39.2; VS-217-28.8). Hence, one may conclude that high mercury contents of the mentioned sample can presumably...

![Legend](image)

Fig. 4. Spatial distribution of mercury potential ecological risk levels (Er) in Vanadzor soils
be due to point-source contamination: broken thermometers, combustion of fuel, or can result from other activities of a man. Contrastingly, for all Vanadzor kindergartens a mean value of $E_{\text{Hg}}$ is 29.92, which is <40 i.e. corresponds to low level potential ecological risk.

**Assessing non-carcinogenic risk of mercury exposure**

Assessment data on non-carcinogenic risk of mercury exposure from Vanadzor soils are provided in Table 5. HQ values for children and adults were calculated in respect of main mercury exposure routes: ingestion, inhalation, dermal absorption. Ingestion risk to Vanadzor adult population ranges between $1.37 \times 10^{-5}$ and $2.64 \times 10^{-3}$, with a mean value of 3.91$\times 10^{-4}$. HQ for inhalation varies 2.25$\times 10^{-9}$ to 4.36$\times 10^{-7}$, with a mean value of 6.45$\times 10^{-8}$. HQ for dermal absorption - 3.97$\times 10^{-6}$ to 7.6$\times 10^{-4}$, with a mean value of 1.13$\times 10^{-4}$. In general, a mean value of HI is 5.04$\times 10^{-4}$, minimal 1.77$\times 10^{-5}$, maximal 3.4$\times 10^{-3}$ (Table 5). In adults and children, alike HQ values for all functional urban areas have the following decreasing order HQ$_{\text{inh}}$>HQ$_{\text{ing}}$>HQ$_{\text{dermal}}$, according to which the major route of non-carcinogenic risk of mercury exposure is ingestion.

Ingestion risk in Vanadzor kindergarteners varies within 5.3$\times 10^{-4}$ to 1.05$\times 10^{-3}$, with a mean value of 7.97$\times 10^{-4}$. HQ for inhalation is 1.04$\times 10^{-7}$ to 2.06$\times 10^{-7}$, mean 1.56$\times 10^{-7}$; HQ for dermal absorption 4.06$\times 10^{-5}$ to 8.03$\times 10^{-3}$, with a mean value of 7.10$\times 10^{-3}$.

In contrast to the functional areas of Vanadzor, kindergartens HQ values have the following decreasing order: HQ$_{\text{inh}}$>HQ$_{\text{ing}}$>HQ$_{\text{dermal}}$, according to which the major route of non-carcinogenic risk of mercury exposure is inhalation.

As evidenced by research results, in the entire area of Vanadzor and its kindergartens HQ value is below the safe level (HQ<1), which is indicative of the absence of non-carcinogenic risk in Vanadzor soils.

**Conclusion**

The mean contents of soil samples throughout Vanadzor city range from 0.025-0.04 mg/kg which are common to urban soils. However, in comparison with Hg concentrations from different areas of various cities, the mean value of Hg in Vanadzor’s functional areas is much lower than reported data.

Mercury content of kindergarten soil does not exceed MAC and the background; that of city soils does not exceed MAC, however, the contents of this element in 50 soil samples collected from separate functional urban areas exceed the background in the range from 1.2 to 5.8. According to research outcomes, after the exclusion of 2 samples collected from the industrial area, 1 sample – from the roadside area and 6 samples – from residential area normal distribution was derived for the entire area of Vanadzor, this being indicative of the natural origin of mercury. However, mercury contents on excluded sites can probably be due to a certain anthropogenic impact.

The natural origin of mercury in Vanadzor kindergartens and the entire area of the city is also evidenced by I$_{\text{geo}}$ values below zero for the majority of samples. According to geoaccumulation index, uncontaminated or moderately contaminated levels in the city soils were detected only in industrial (2 samples, 3.12%) and residential (5 samples, 3.2%) areas. The kindergartens and the major portion of the city (76.05%, 270 samples) are characterized by low level potential ecological risk.

23.38% of Vanadzor soil samples (83 samples) correspond to moderate potential ecological risk. Those samples were mosaically distributed mainly in the industrial and residential areas, close to the welding plant site, near chemical plant
Table 5. Hazard quotient (HQ) of non-carcinogenic risk in children and adults in Vanadzor kindergartens and different functional areas

<table>
<thead>
<tr>
<th>Functional area</th>
<th>Value</th>
<th>Adults</th>
<th>Children</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>HQ\textsubscript{ing}</td>
<td>HQ\textsubscript{inh}</td>
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<td>Min</td>
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<td>3.61·10^{-8}</td>
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<td></td>
<td>Max</td>
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<td>3.86·10^{-4}</td>
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<tr>
<td>Residential area</td>
<td>Min</td>
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<td></td>
<td>Max</td>
<td>2.64·10^{-3}</td>
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<tr>
<td>Roadside area</td>
<td>Min</td>
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<td></td>
<td>Max</td>
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<td></td>
<td>Mean</td>
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<tr>
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<td>Min</td>
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<td></td>
<td>Max</td>
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<td></td>
<td>Mean</td>
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<tr>
<td>Entire area of Vanadzor</td>
<td>Min</td>
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<td>2.25·10^{-9}</td>
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<tr>
<td></td>
<td>Max</td>
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<td></td>
<td>Mean</td>
<td>3.91·10^{-4}</td>
<td>6.45·10^{-8}</td>
</tr>
<tr>
<td>Kindergartens</td>
<td>Min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>-</td>
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</tr>
<tr>
<td>HI</td>
<td>Min</td>
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<tr>
<td></td>
<td>Max</td>
<td>-</td>
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<tr>
<td></td>
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<td>HI (kindergartens)</td>
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</tr>
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<td></td>
<td>Max</td>
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</table>

surroundings and abandoned an industrial site. Only 1 sample taken from the residential area’s private house surroundings, located close to one of the main roads, corresponds to high potential ecological risk.

The obtained non-carcinogenic risk assessment data have indicated that mercury content detected in both kindergartens and Vanadzor soils is not a health risk factor in adults and children.

Finally, data generated from this research support the conclusion that mercury found in all of Vanadzor and its kindergartens has a natural origin, not excepting, however, a certain anthropogenic impact on some urban sites.
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