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Chapter 15

Risk Assessment of Heavy Metals Pollution in Urban Environment

Gevorg Tepanosyan, Lilit Sahakyan, David Pipoyan and Armen Saghatelyan

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Abstract

This chapter summarizes the results of heavy metal’s human health and ecological risk assessment of multipurpose ecogeochemical studies performed by the Center for Ecological-Noosphere Studies of the National Academy of Sciences of the Republic of Armenia in the young industrial cities of Yerevan and Gyumri and in an old mining region of the city of Kajaran. According to the results children non-carcinogenic risk values were greater than permissible limit of 1 indicating the possibility of an adverse health effect in the whole area of all studied cities. Among all studied elements, the riskiest were those previously identified as primary pollutants. It has also been shown that in biogeochemical provinces, where mining activities and agricultural land of rural communities are spatially juxtaposed, health risk assessment should include all possible exposure pathways. Otherwise, underestimation of possible health risk will take place. Heavy metals in soils of Yerevan and Gyumri are also an ecological risk factor and the riskiest elements having significant contribution to the overall risk and are those (Hg, Cd, and Pb) with the high level of toxicity.

Keywords: urban environment, heavy metals, pollution, soil, dust, risk assessment

1. Introduction

Soils and dust of urbanized and industrialized areas are a basis of environmental quality. Nevertheless, various pollutants of the environment, especially heavy metals, migrate linked to the complexes of dust particles [1] and finally accumulate in the soil layer. Moreover, heavy metals are known to be an ecological risk factor [2–4] and cause different disorders when entering into the human organism [1, 5].

In Armenia, risks estimation associated with the pollution of cities environment by heavy metals was included in the framework of environmental complex ecogeochemical studies,
which were done since 1989 by The Center for Ecological-Noosphere Studies (CENS) of the National Academy of Sciences [6].

The results of the studies [7] performed by CENS showed that in the cities of Armenia, man-made activities lead to the formation of anthropogenically polluted areas, which were mainly localized in old mining regions (i.e., city of Kajaran) and relatively young industrial cities (i.e., Yerevan and Gyumri). In both cases, the differences of geochemical peculiarities and anthropogenic sources of pollution are conditioning the uniqueness of heavy metal’s quantitative and qualitative features. In the city of Kajaran [8], which is the biggest mining center of country and houses the Zangezur Copper Molybdenum Combine (ZCMC), high contents of heavy metals are the result of the superposition of geogenic and anthropogenic components, whereas in the biggest industrial center of Yerevan and postindustrial city of Gyumri [9, 10], a significant input of heavy metals is mainly from anthropogenic sources of pollution. Although primary pollutants and the levels of anthropogenic contribution differ from city to city, the increased contents of heavy metals become a risk factor to urban ecosystems and human health.

The linking of monoelemental and multielemental pollution by heavy metals to the overall index of population prevalence, the rate of children’s chronic illnesses, gestosis, and to the number of premature birth [11–13] were done in the end of 1990 through the collation of monoelemental and multielemental pollution levels spatial distribution maps [14] with the disease incidences. Later on, studies [8, 15, 16] targeted the sampling of biosubstrate and evaluation of the microelemental status of the organism among identified risk groups.

Nowadays, the most common and widely used human health risk assessment method is developed by the US Environmental Protection Agency [5, 17, 18]. The method is based on four basic steps, including hazard identification, exposure assessment, dose-response assessment, and risk characterization [18]. In the case of ecological risk from heavy metals, method developed by the Hakanson [4] was used repeatedly [2, 3, 9].

In this chapter, the results of human health and ecological risk assessment of heavy metals contents in Yerevan, Gyumri, and Kajaran environment are summarized.

2. Materials and methods

2.1. Study sites

Cities presented in this study are spatially located in different parts of Armenia (Figure 1). Particularly, the capital and industrial center of the country in the city of Yerevan (40°10’39.53”N and 44°30’45.10”E) is situated in the central part, whereas the cities of Gyumri (40°47’6.84”N and 43°50’29.97”E) and Kajaran (39°9’5.20”N and 46°9’12.02”E) in north-western and southern parts, respectively.

2.1.1. The city of Yerevan

Yerevan has a total area of 223 km² and 1.06 million population (4782 persons per square km) [19]. The city is located in the intermountain trough, and the natural landscape of city territory is mainly semidesert, arid steppe, and steppe. Yerevan’s area is dominated by tuffs, volcanic
lavas, and quaternary sediments, and the relief of the city is represented by plains, foothills, plateaus, and the River Hrazdan Canyon. The soil (mostly brown semidesert) profile of Yerevan is rich in carbonates, and at the lower horizon, the presence of gypsum is conditioning the lack of chemical element washout, thus creating a favorable environment for heavy metal accumulation on soil profiles [7].

Pollution with heavy metals in the city environment has been observed for many decades. Particularly, heavy metals were detected during the soil surveys conducted in 1979, 1989 [7], 2002 [7, 20], and 2012 [9, 21, 22], with ecogeochemical investigations of city snow cover and leaf dust [23, 24], Hrazdan river waters [25, 26], and homegrown vegetables [27, 28].

During the Soviet Union, the main sources [7, 24, 29] of heavy metal pollution in Yerevan were enterprises such as an electric bulb plant, the aluminum plant, the Car and Worsted complex, the experimental plant of milling machines, the polygraphic complex, and typography, as well as vehicular emission.

After the collapse of the Soviet Union, the socioeconomic transformations in 1990 lead to the changes in heavy metal geochemical streams’ quantitative and qualitative features as many of the abovementioned industrial plants were closed. Moreover, in 2001, leaded gasoline ceased to be used in Armenia.

Nowadays, the potential sources [9] of heavy metals in Yerevan territory are urban transport and industrial units including molybdenum concentrate smelting and processing plant, Ferro-concrete constructions plant, accumulator’s production, mechanical reconstruction plants, and industrial complex of metallic covers and corks, etc.

2.1.2. The city of Gyumri

Gyumri has a total area of 44.4 km² and 117.7 thousand population (2651 persons per square km) [16]. In the city, arid steppe and mountain steppe landscapes dominated and the city territory
was characterized by accumulative relief of plains, lake, and alluvial-diluvial sedimentation, sometimes mixed with lavas and tuffs. Brown and mountain steppe chernozem soils dominated in Gyumri area.

During the Soviet Union period, the potential sources of heavy metals in Gyumri were forge-and-press, universal grinding machines, instrument engineering, electrotechnical, household electrical appliances, refrigerator compressors and ferro-concrete constructions plants, microelectromotor “Strommashina” plant, and foundry of machine-tool construction plant [30], which were operated till the devastating earthquake of 1988 and did not resume after the collapse of the Soviet Union. Unfortunately, there is a lack of information about the heavy metal emission from the abovementioned plants in city territory.

Nowadays, the Gyumri and its industrial sector are in reconstruction stage and there are no significant potential sources of heavy metals. In the polluted areas identified during 2013, Gyumri ecogeochemical complex investigations [10] were mainly linked to the historical pollution.

2.1.3. The city of Kajaran

The city of Kajaran has a total area of 2.74 km$^2$, 8.4 thousand population (3066 persons per square km) [16], and is located in the valley of river Voghchi, where two types of the erosion landforms are distinguished: U-shaped river valleys in the middle and lower course of the river and V-shaped river valleys in the riverheads. Up to 1800 m, brown soils and 1800–2400 m chestnut soils predominated. The northern slope of Kajaran territory is covered with the gray mountain-forest skeletal soils [31]. The geological base of Kajaran includes volcanogenic sedimentary and intrusive rocks of the tertiary period, particularly monzonites and porphyry granites. The Kajaran sulfide copper-molybdenum deposit is timed to the monzonites, and the main ore minerals are molybdenite and chalcopyrite and the accessory minerals are pyrite, magnetite, hematite, sphalerite, tetrahedrite, bismuthine, wulfenite, vanadinite, galena, as well as native Te and Au. Besides, ore contains Re, Se, and Ag [8].

The main pollution source of Kajaran is ZCMC, including Cu-Mo opencast mine. ZCMC complex also includes ore crushing and milling, as well as ore dressing plants and active Artsvanic tailing repository. In addition, abandoned tailing repositories of Voghchi, Darazami, and Pkhrut are also significant sources of dust and heavy metals in it [8].

2.2. Soils, dust, and food sampling and analysis

Soil, dust, and food sampling and pretreatment were done according to the SOPs developed in compliance with methodological guidelines [32–34], international ISO [35–38] standards, and US EPA [39] guidelines. Totally, 1356, 443, and 76 soils and 25, 22, and 15 dust have been collected in Yerevan, Gyumri, and Kajaran, respectively.

Food sampling was done and 68 samples were collected from the agricultural lands of Kajaran and rural communities located near ZCMC Artsvanic tailing repository. Soils, dust, and food samples have been placed in special clean bags for transportation and storing purposes. Prior to the analysis, samples laboratory pretreatment was done.
The total contents of heavy metals (Table 1) were determined using X-ray fluorescence spectrometry (Innov-X 5000, USA) [40] and atomic absorption spectrometry (AAnalyst 800 AAS PE, USA).

The analysis was done in the environmental geochemistry department and at the Central Analytical Laboratory of CENS, accredited by ISO-IEC 17025.

Detailed information concerning Yerevan’s, Gyumri’s, and Kajaran’s soils, dust, and food sampling, samples’ pretreatment, and analysis can be found in a number of manuscripts [7–10, 20–23].

2.3. Health risk assessment

Human health risk assessment [5] was done based on the contents of HM in soils and dust of city Yerevan, Gyumri, and Kajaran. In the case of Kajaran, health risks arising from the HM content in the food products grown near the city, ZCMC query, and its tailing storages were also studied. Health risk assessment model proposed by US EPA was used. As a preferential exposure pathway of HM for humans, soil and dust ingestion was chosen.

Noncarcinogenic health effects from the soils, dust, and food heavy metals contents was assessed using the following Eqs. [5, 17, 18].

\[
\text{CDI}_{\text{ing}} \left( \frac{\text{mg}}{\text{kg day}} \right) = \frac{C \times \text{IngR} \times \text{EF} \times \text{ED} \times 10^{-6}}{\text{AT} \times \text{BW}},
\]

\[
\text{HQ}_{\text{ing}} = \frac{\text{CDI}_{\text{ing}}}{\text{RfD}_{\text{ing}}},
\]

\[
\text{HI} = \sum \text{HQ}.
\]

where CDI is the chronic daily intake of metal, C is the element concentration in studied medium (mg/kg), EF is the exposure frequency: 350 day/year for soil and dust, ED is the

<table>
<thead>
<tr>
<th>City</th>
<th>Medium</th>
<th>Heavy metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yerevan</td>
<td>Soil</td>
<td>Hg, Pb, As, Ni, Cu, Zn, Mo, Cr, Co, Mn, Ba, and V</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>Hg, Pb, Mo, Cd, Zn, Cu, Ni, Ag, Co, Cr, and As</td>
</tr>
<tr>
<td>Gyumri</td>
<td>Soil</td>
<td>Hg, Pb, As, Cd, Cu, Zn, Mo, Fe, Co, Mn, and Ba</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>Pb, Cr, Ni, Zn, Cu, and Mo</td>
</tr>
<tr>
<td>Kajaran</td>
<td>Soil</td>
<td>Ti, Mn, Fe, Co, Cu, Zn, Mo, and Pb</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>Cu, Pb, Mo, Mn, Ni, Cr, V, Zn, and Sn</td>
</tr>
<tr>
<td></td>
<td>Food</td>
<td>Cu, Mo, Ni, Cr, Zn, Pb, Hg, As, and Cd</td>
</tr>
</tbody>
</table>

Table 1. Heavy metals determined in soils, dust, and food.
exposure duration: 30 years for adult [17] and 6 years for children [5]. IngR is the ingestion rate: 100 mg/day$^{-1}$ for adults and 200 mg/day$^{-1}$ for children average time (AT) (AT = 365 × ED) [5], and average body weight (BW, kg): 70 kg for adults [17] and 15 kg in the case of children [5].

Taking into consideration the fact that unlike Yerevan and Gyumri where there is no local food production and consumption, in Kajaran, mining region’s contribution of local plant-origin food in overall diet is significantly higher. Therefore, dietary intakes of heavy metals via consumption of selected vegetables and fruits may also be a risk factor to health.

Noncarcinogenic risk of heavy metals in food was assessed by the abovementioned formulae (1)–(3) using the following parameters: EF: 183 days/year for all investigated fruits and vegetables, except potato (365 days/year). ED was set to 63.6 for males and 69.7 for females based on the average life expectancy, starting from 8 years of age. IRS: food consumption rate was evaluated based on the result of standardized food frequency questionnaires filled by 200 males and females residing in Kajaran mining impact area. According to our polling survey in studied region, BW for males and females were considered to be 70 and 60 kg, respectively.

The reference doses (RfDs) of studied heavy metals were taken from RAIS and US EPA Human health risk assessment guidance [5, 17]. Only the RfD of Pb was taken from the WHO guideline [41]. Hazard index (HI-multielement) is the sum of all HQ (monoelement). When HI and/or HQ is less than one, there is no harmful effect to the health, whereas when HI and/or HQ values are greater than one, there is a possibility of adverse health effects.

To get overall adults health risk ($\text{HI}_{\text{sum}}$) from soils, dust ingestion, and food consumption in Kajaran, the obtained mean values of HI were summed.

### 2.4. Potential ecological risk assessment

Potential ecological risk assessment (PERI) was performed using the method proposed by Hakanson [4]. From the studied elements, only Hg, Cd, As, Pb, Cu, Ni, Cr, and Zn have “toxic-response” factors 40, 30, 10, 5, 5, 5, 2, and 1, respectively. Taking into consideration the fact that soils are the sink of city pollutants, ecological risk assessment was done based on the contents of heavy metals in soils. As the city of Kajaran is spatially located within the biogeochemical province, high contents of heavy metals are intrinsic to the city environment. Here, ecosystems have their own distinctive features and there is a deviation from common environmental patterns. Therefore, the city of Kajaran was excluded from the ecological risk assessment. RI was calculated using (4)–(6) formulas:

$$C'_r = \frac{C^i_{\text{topsoil}}}{C^i_{\text{ref}}}$$

(4)

$$E'_r = T'_r \times C'_r$$

(5)

$$\text{PERI} = \sum_{i=1}^{n} E'_r$$

(6)

where PERI is potential ecological risk index, $E'_r$ is PERI of single element, $T'_r$ is “toxic-response” factor for the selected element (i.e., Hg = 40, As = 10, Pb = Cu = Ni = 5, Cr = 2, and
Zn = 1), \( C_i \) is the pollution factor of the element, \( C_{\text{soil}}^i \) is the concentration of element in the topsoil, and \( C_{\text{ref}}^i \) is the reference value of the selected element (local background [9, 10]). The PERI levels are classified as low (<150), moderate (150–300), considerable (300–600), and very high (>600) [4].

3. Results

Health noncarcinogenic risk assessment of adults and children was performed based on the contents of studied heavy metals (Table 1) in soils and dust of the city of Yerevan and Gyumri and in soils, dust, and food in the city of Kajaran.

3.1. Noncarcinogenic risk in Yerevan

The results obtained showed that in the case of Yerevan soils, monoelemental risk to adults was detected only for the contents of Pb in two sampling sites.

Multieelemental noncarcinogenic risk range from 0.12 to 2.37 with the mean of 0.25, and risk was observed in four sampling sites (Figure 2). Monoelemental noncarcinogenic risk from dust heavy metals was observed in a single sampling site and is associated with the high contents of Mo. Multieelemental risk ranges from 0.02 to 1.87 with the mean of 0.2, and risk was observed in one sampling site (Figure 2) situated in the southern part of the city. For

Figure 2. Spatial distribution of soils and dust noncarcinogenic risk to children and adults health in Yerevan.
both soils and dust, the observed risky sites are spatially allocated in or near the industrial units of Yerevan (Figure 1).

Children monoelement noncarcinogenic risk for Ni, Cu, Zn, Mo, Co, and Mn in a single sampling point while for Cr and Pb risk was observed in 28 and 72 sampling sites (Figure 3), respectively. The study revealed [21] that riskiest contents of Pb in Yerevan are the result of the redistribution of historically polluted soils. HI values of soil’s heavy metal contents range from 1.1 to 22.1 with the mean of 2.31, indicating an adverse health effect to children (Figure 2) in whole territory of the city. In case of dust, HQ values greater than 1 were observed from Mo, Cd, Co, and As in 1, 1, 2, and 1 sampling sites, correspondingly. Dust HI values (Figure 2) range from 0.25 to 17.45 with the mean of 1.82, and risk was detected in 12 sampling sites located in Yerevan’s residential areas and near the industrial units (Figures 1 and 2).

3.2. Noncarcinogenic risk in Gyumri

Noncarcinogenic risk assessment showed that in Gyumri’s territory, soils and dust heavy metal’s HQ and HI values were less than 1, suggesting the absence of adverse health effects to adults. Risk from the dust heavy metal contents was also not detected in case of children. Soil’s heavy metal HQ values greater than 1 were detected for Cu and Pb contents in 1 and 17 sampling sites, respectively. Moreover, Pb risky sites are spatially located in residential parts of the city and near its industrial units (Figures 1 and 4). Soil’s heavy metal multielemental risk in Gyumri range from 0.85 to 7.42 with the mean of 1.56, and risk was observed in 439 of 443 sampling locations (Figure 4).
3.3. Noncarcinogenic risk in Kajaran

Noncarcinogenic risk assessment based on the detected contents of heavy metals in soils and dust of Kajaran territory showed that the HQ values of adults greater than one were detected only in four soil sampling sites for the contents of Mo. HI values of soil heavy metals range from 0.23 to 5.46 with the mean of 0.64 and risk was observed in seven sampling sites (Figure 5), whereas HI values of dust were all less than 1.

In the case of children, noncarcinogenic risk observed Mn, Fe, Co, Pb, Cu, and Mo in 6, 49, 18, 1, 2 and 34 sampling sites out of the 76, respectively. Soils HI values range from 2.11 to 51.0 with the mean of 5.94 and suggested an adverse health effect to children in whole area of the city. For both Fe and Mo (Figure 6), the risky sites are spatially located in the residential part of Kajaran and near the ZCMC ore crushing, milling, and ore dressing plants. Moreover, in the same areas of city, Mo poses a noncarcinogenic risk to children (7 of 15 dust samples).

Health risk assessment of food product consumption showed that HQ for Cu was more than 1 in maize, potato, and bean both for males and females, whereas for Mo, HQ range from 0.05 to 5.79 for males and 0.05 to 8.63 for females. Particularly, in carrot, potato, and

![Figure 4. Spatial distribution of soils, dust, and soil Pb contents noncarcinogenic risk to children in Gyumri.](http://dx.doi.org/10.5772/intechopen.70798)
onion leaf, HQ value is more than 5, which proves that risks are obvious. For maize consumption, the HQ is higher than 1 for males and females (3.94 and 4.40, respectively). None of the studied vegetables and fruits has a HQ > 1 for Ni, Cr, Zn, Pb, As, and Cd beside the case of Ni in maize for females. In case of Hg, beet and grape indicated HQ more than 1 both for males and females. From all studied elements, only Mo HI values from all studied vegetables and fruits were greater than 1, indicating an adverse health effect both for males and females.

The results of health risk assessment in Kajaran showed that HI$_{sum}$ were greater than 1, indicating an adverse health effect to adults from soils, dust ingestion, and food consumption. Therefore, it should be highlighted that in biogeochemical provinces where industrial activities are closely related to the agricultural lands, the risk assessment including only environmental abiotic mediums may lead to the underestimation of risk level.

Overall, heavy metals in the Yerevan, Gyumri, and Kajaran environment are a primary concern to children health. Moreover, risk assessment showed that the riskiest elements in the cities environments are those previously identified as primary pollutants.
3.4. Potential ecological risk in Yerevan and Gyumri

In Yerevan, PERI was evaluated based on the contents of Hg, As, Pb, Cu, Ni, Cr, and Zn and the mean values of single ecological risk indices decreased in the following order: Hg > Pb > Cu > As > Ni > Cr > Zn. The results of Yerevan’s soils potential ecological risk assessment showed (Figure 7) that PERI ranges from 53 to 5793.2 with the mean value of 425.3. The latter belongs to the considerable risk level, which was also observed in 1068 (78.8% of all samples) sampling sites. The low level (Figure 7) of ecological risk was detected in 38 (2.8% of all samples) and the moderate level in 155 (11.4% of all samples) sampling sites. The very high level of ecological risk was detected in 95 (7.0% of all samples) sampling sites. From all elements included in Yerevan soil’s ecological risk assessment, significant contribution to the considerable and very high levels of PERI was mainly from the single ecological risk indices of Pb and Hg.

In the case of the city of Gyumri, PERI was evaluated based on the contents of Hg, Cd, As, Pb, Cu, and Zn, and the mean values of single ecological risk indices decreased in the following
order: Cd > Hg > Pb > As > Cu > Zn. PERI ranges from 48.2 to 1892 with the mean of 252, which belongs to the moderate ecological risk level. The latter was also observed in 128 (28.9% of all samples) sampling sites. The low level (Figure 7) was detected in 183 (41.3% of all samples), considerable level in 111 (25.1% of all samples), and very high level of ecological risk in 21 (4.7% of all samples) sampling sites. In Gyumri, significant contribution to the very high levels of PERI was mainly from the single ecological risk indices of Cd, Pb, and Hg.

4. Conclusions

The result of human health risk assessment showed that soils multielemental noncarcinogenic risk (HI > 1) to adults observed in a few sampling sites both for Yerevan and Kajaran, while in Gyumri HI < 1. For children, noncarcinogenic risk values indicated possible adverse health effects approximately in the whole area of all studied cities. Also for dust, risks have been detected mainly for children in the cities of Yerevan and Kajaran. In Kajaran, risk assessment showed possible adverse health effects for the population from food, as well. The riskiest elements were Pb and Cr for Yerevan, Pb for Gyumri, and Mo for Kajaran. It should be stated that unlike anthropogenic contents of Pb in Yerevan and Gyumri, the high Mo concentrations in Kajaran can be the result of geogenic input as well. According to the results of PERI in cities of Yerevan and Gyumri, considerable and very high levels of ecological risk were observed and the riskiest elements were those (Pb, Hg, and Cd) included in the first group of toxicity. Both human health and ecological risk assessment results highlight the need for further detailed studies, especially in those areas with the highest level of identified risk.
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