

Assessment of pollution levels and human health risk of heavy metals in dust deposited on Yerevan's tree leaves (Armenia)

N. Maghakyan¹ · G. Tepanosyan¹ · O. Belyaeva¹ · L. Sahakyan¹ · A. Saghatelyan¹

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Abstract The total concentrations of Cd, As, Pb, Cr, Ni, Co, Zn, Cu, Ag, Hg, and Mo were determined in the atmospheric dust of the city of Yerevan by atomic absorption spectrometry (AAAnalyst PE 800). Heavy metal pollution levels were evaluated by calculating geo-accumulation (I_{geo}) and summary pollution (Z_c) indices. Potential human health risk was assessed using the United States Environmental Protection agency's human health risk assessment model. The results show that mean contents of all elements tested except Ni and Cr were substantially higher than local geochemical background values. According to the I_{geo} , Yerevan territory is strongly-to-extremely polluted by As, Ag, Hg, Mo, and Cd. The Z_c assessment indicated that very high pollution was detected in 36 % of samples, high in 32 %, average in 12 %, and low in 20 %. The health risk assessment revealed a non-carcinogenic risk ($HI > 1$) for children at 13 samplings sites and for adults at one sampling site. For children the risk was due to elevated levels of Mo, Cd, Co, and As, while for adults, only Mo. Carcinogenic risk ($> 1:1,000,000$) of As and Cr via ingestion pathway was observed in 25 and 14 samples, respectively. This study, therefore, is the base for further detailed investigations to organize problematic site remediation and risk reduction measures.

Keywords Urban dust · Heavy metals · Pollution levels · Health risk assessment

✉ N. Maghakyan
nairuhi.maghakyan@cens.am

¹ Department of Environmental Geochemistry, Center for Ecological-Noosphere Studies of the National Academy of Sciences, Abovian-68, 0025 Yerevan, Republic of Armenia

1 Introduction

Dust, one of the basic atmospheric pollutants, is an aggregation of naturally occurring and anthropogenic solid particles. Dust can have a negative impact on human health (Al Jallad et al. 2013; Zhou et al. 2014; Lu et al. 2015). The character and degree of basic impacts of dust depend on particle size, composition, and duration of exposure. Atmospheric dust is known as a carrier of toxic substances, especially heavy metals (Duzgoren-Aydin et al. 2006; Chaudhari et al. 2012). Heavy metals in dust may penetrate the human organism through inhalation, ingestion, and skin absorption and induce negative effects such as hematogenesis disorders and problems in the central nervous, cardiovascular, and urogenital systems (Li et al. 2013). Moreover, individual heavy metals are known to trigger specific diseases such as Alzheimer's and Parkinson's (Oves et al. 2012).

Pollution by dust and heavy metals is of particular concern in urban areas because of high population density and numerous sources of pollution—motor transport, industrial plants, domestic refuse, corrosion of roadway surfaces, etc. (Charlesworth and Lees 1999; Sharma et al. 2008; Wei et al. 2010; Cai et al. 2013). Extensive recent research has sought to estimate pollution levels, identify sources, and assess potential health risks—both to children and adults—associated with heavy metals in dust. An essential element of such studies has been the investigation of street dust and its heavy metal contents (Lu et al. 2009, 2015; Kong et al. 2011; Du et al. 2013; Zhang et al. 2013; Li et al. 2014; Wang et al. 2014). Another way to study urban atmospheric dust is to use biomonitors such as higher plants. Although higher plants are not ideal biomonitors like mosses and lichens, in industrialized and urban areas that are missing these vegetation types, higher

plants can be used as well. Airborne particles including dust and heavy metals deposit on the surface of tree leaves via wet and dry atmospheric precipitation (Mingorance and Oliva 2006; Pavlík et al. 2011). According to the Tomašević et al. (2005) study, tree leaf deposits directly reflect the level of atmospheric pollution by heavy metals.

Yerevan is an old city and, being an industrial center with dense population and heavy traffic, it has been exposed to high levels of atmospheric pollution for years (Saghatelyan and Arevshatyan 2003; Saghatelyan 2004; Sahakyan 2006; Saghatelyan et al. 2014). During the Soviet period, the spatial planning of the city was quite ordinary, and there were more heavily polluted industrial pockets of the city. After the collapse of the Soviet Union, during social and economic transformations in the 1990s and now, during recovery of industry, the spatial distribution of industrial units throughout Yerevan reflects a more mosaic character, i.e. irregularly spread across the city. This complicated the process of identification of pollution sources for exact contaminants. Although geochemical investigations have been conducted for many decades, it should be stressed that assessment of dust and heavy metal-induced health risks to Yerevan's residents has never been done before. The goal of this research was to assess levels of heavy metals pollution in urban dust using tree leaves as dust accumulators and assessing health risks to different groups of the population (children and adults).

2 Materials and methods

2.1 Study site

Yerevan (latitude 40°10'40"N, longitude 44°30'45"E), Armenia's capital, covers an area of 223 km² with a population of just over one million people. The relief is rather diverse and is represented by plains, plateaus, foothills, and the River Hrazdan canyon. The city is situated at a height of 850–1420 m a.s.l. The climate is typically dry continental; the amount of annual precipitation is 250–400 mm. Mean air temperature varies from 22 to 26 °C in summer and –4 to –6 °C in winter. Persistent snow cover occurs in January and February, but not regularly. Northeastern winds dominate the city year-round, but the air cycle is substantially complicated because of the topography (intermountain trough) and specificity of site development. Thermal inversions occur during winter. Dry steppe and semi-desert natural landscapes are common.

The main industrial branch is processing. The city contains metallurgical plants, manufacturing enterprises (production of concrete, wood- and metalware, food, medicines, paper, etc.), and stone- and woodworking workshops. In the area of Yerevan and its outskirts there are active sandpits

and quarries of basalt, tuff, and clay. Presently, the city area is under intense construction; in most cases, construction sites are not properly isolated.

2.2 Sampling and analysis

Sampling density in local-scale projects does not follow any exact rules, as it mainly depends on the objectives of the project and available funds (Demetriades et al. 2015). In the case of multifunctional cities having mosaic distribution of pollution sources such as Yerevan, this issue becomes more complicated; collection and analysis costs can restrict sampling scale and sample size.

In this study, sampling sites were based on the geomorphological features and the peculiarities of the spatial distribution of urban green areas which cover 5.6 % (12.5 km²) of the territory of Yerevan. The number of samples was determined taking into account available funds and the long-term air monitoring points of the Center for Ecological-Noosphere Studies (CENS) NAS RA in order to ensure continuity of research.

In the summer 2011, 25 tree-leaf samples were collected from the city. Samples were collected from the most widespread tree species having relatively good dust absorption properties (Kretinin and Selyanina 2006): white elm (*Ulmus laevis*), Chinese elm (*Ulmus parvifolia*), Persian walnut (*Juglans regia*), oriental plane tree (*Platanus orientalis*), common lilac (*Syringa vulgaris*), white poplar (*Populus alba*), and white mulberry tree (*Morus alba*) (Fig. 1).

Leaves were sampled at a height of 1.5–2 m above the ground from at least three trees of the same species per sampling site then placed in paper bags and transported to the Central Analytical Laboratory CENS accredited by ISO-IEC 17025.

After the sampled leaves had been dried at room temperature, they were washed with de-ionized water (MilliQ). The generated liquid underwent filtration using a weighed ash free filter (retention limit 2–3 µm).

Dry residue was dissolved in nitric acid (1:1), then the acid was evaporated and MilliQ water was added to the residual solution until 20 ml was achieved.

In the filtrated matter the contents of eleven elements—Cd, As, Pb, Cr, Ni, Co, Zn, Cu, Ag, Hg, and Mo—were determined by AAnalyst 800 AAS PE, USA.

Concentrations below detection levels of the employed analytical method were given a value half of the detection limit as proposed by Reimann et al. (2008).

2.3 Assessment of pollution with heavy metals in dust

Based on the concentrations of heavy metals in Yerevan's atmospheric dust, single-element and multi-element

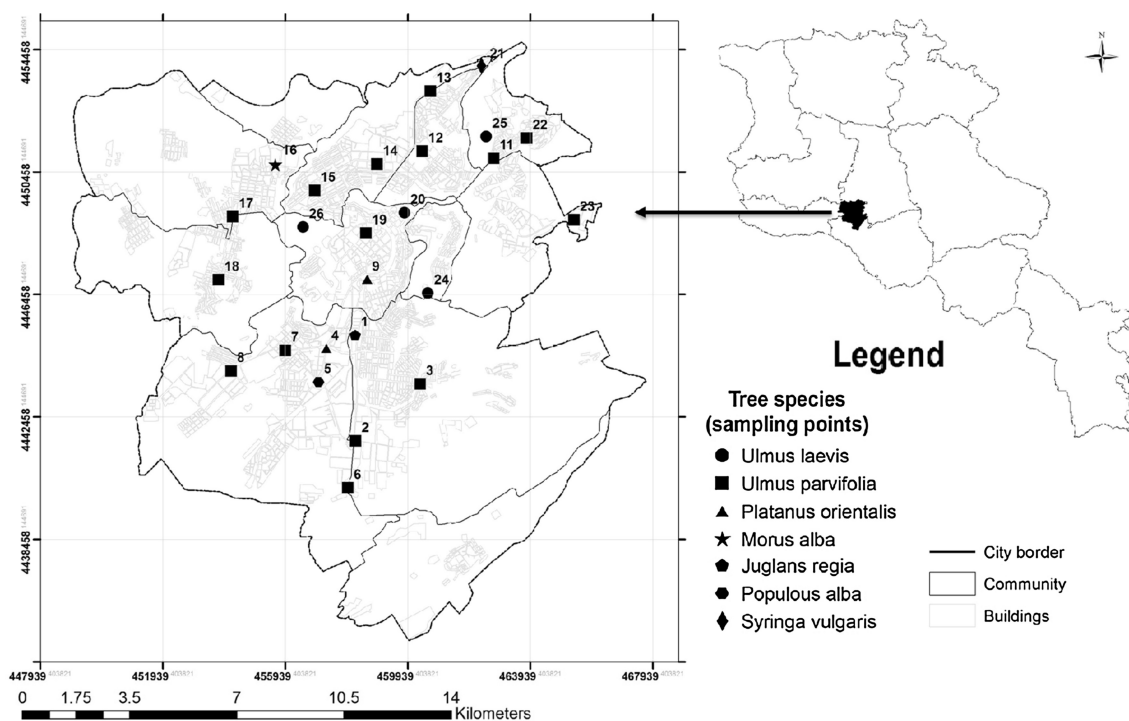


Fig. 1 Position of Yerevan in Armenia's area, sampling points and sampled tree species

pollution level assessments were done. Particularly, the degree of each heavy metal contaminant in the dust was characterized by geoaccumulation index (I_{geo}) (Muller 1969; Lu et al. 2009; Johnson et al. 2011):

$$I_{geo} = \log_2 \frac{C_i}{1.5B_i} \quad (1)$$

where C_i is the concentration of element i in dust, while B_i is the local geochemical background concentration from Tepanosyan et al. (2016) of the i th element in Yerevan's soil. The following classification is given for the I_{geo} : unpolluted ($I_{geo} \leq 0$), unpolluted to moderately polluted ($0 < I_{geo} \leq 1$), moderately polluted ($1 < I_{geo} \leq 2$), moderately to strongly polluted ($2 < I_{geo} \leq 3$), strongly polluted ($3 < I_{geo} \leq 4$), strongly to extremely polluted ($4 < I_{geo} \leq 5$), and extremely polluted ($5 < I_{geo}$) (Muller 1969; Lu et al. 2009; Johnson et al. 2011).

For an integral description of heavy metal pollution, the summary pollution level was assessed and a contamination index (Z_c) was calculated (Perelman and Kasimov 2000; Johnson and Demetriades 2011) according to formulas (2) and (3).

$$K_c = \frac{C_i}{C_f} \quad (2)$$

$$Z_c = \sum_{i=1}^n K_c - (n - 1) \quad (3)$$

where K_c is a concentration coefficient, C_i is the content of i th metal in dust, C_f is local background content of the i th element in soil from Tepanosyan et al. (2016), and n is the number of elements in the same sample with $K_c > 1$. The summary pollution level was classified as low ($Z_c < 16$), moderately hazardous ($16 < Z_c < 32$), high/hazardous ($32 < Z_c < 128$), or very high/extremely hazardous ($Z_c > 128$) (Perelman and Kasimov 2000).

Finally, to obtain qualitative and quantitative characteristics of heavy metals in soil, decreasing geochemical series were created.

2.4 Risk assessment

Taking into account toxic and carcinogenic effects of heavy metals, calculations of both non-carcinogenic and carcinogenic risks were done. Two pathways of exposure of humans to dust heavy metals—direct ingestion of dust particles and dermal absorption of dust heavy metals (Lu et al. 2009; RAIS 2014)—were considered for non-carcinogenic risk assessment. Risk from inhalation was not assessed as undifferentiated dust was investigated.

Health risks to children and adults posed by heavy metals in dust were calculated in a manner consistent with a health risk model developed by the US Environmental Protection Agency (US EPA 1989, 2002; RAIS 2013).

2.5 Non-carcinogenic risk

Non-carcinogenic risk was calculated with respect to all the detected heavy metals: Hg, Pb, Mo, Cd, Zn, Cu, Ni, Ag, Co, Cr, and As.

Per metal chronic daily intake (CDI) per pathway of exposure was calculated by formulas (4) and (5) (US EPA US 1989, 2002; RAIS 2013).

$$CDI_{ing} \left(\frac{mg}{kg \text{ day}} \right) = \frac{C * IngR * EF * ED * 10^{-6}}{AT * BW} \quad (4)$$

$$CDI_{dermal} \left(\frac{mg}{kg \text{ day}} \right) = \frac{C * EF * ED * SA * AF * ABS_d * 10^{-6}}{AT * BW} \quad (5)$$

Non-carcinogenic hazard quotient per element via each pathway was calculated by formulas (6) and (7):

$$HQ_{ing} = \frac{CDI_{ing}}{RfD_{ing}} \quad (6)$$

$$HQ_{dermal} = \frac{CDI_{dermal}}{RfD_{dermal}} \quad (7)$$

Description and values of factors used in formulas (4–7) are given in Tables 1 and 6.

RfD values (Table 1), which underpinned the assessment of non-carcinogenic risk, were taken from the risk assessment information system (RAIS 2013). There exists no Oral RfD value for Pb, so this research used the value from the WHO guidelines for drinking water quality (WHO 1998).

RAIS lacks dermal RfD values, so instead, with respect to all the elements, oral chronic RfD_{ing} values multiplied by respective gastrointestinal absorption factors (US EPA 2002, 2004; RAIS 2013) were used.

The sum of all HQ values represents a Hazard Index $HI = \sum HQ_i$. In addition, a single-element HI including ingestion and dermal absorption pathways was calculated to reveal priority of elements, while multi-element HI of all studied elements via two pathways was evaluated to describe total human health risk. $HI < 1$ indicates the absence of harmful effect on the health, whereas $HI > 1$ denotes a possibility of adverse health effects.

2.6 Carcinogenic risk

Carcinogenic risk is defined as occurrence probability for any type of cancer during the whole lifetime in case of exposure to a carcinogenic element. The allowable risk limits are defined as 10^{-6} – 10^{-4} (Lu et al. 2009). Particularly, in the case of a single element, allowable carcinogenic risk limit is 10^{-6} , while for multi-element carcinogenic risk the allowable limit is $< 10^{-4}$ (TCEQ Regulatory Guidance).

According to the International Agency for Research on Cancer, Cr, Cd, As, Ni, and Co are considered to have a carcinogenic effect (Cao et al. 2014). Taking into consideration the existence of slope factors, the carcinogenic risks of Cr and As through ingestion were assessed.

The lifetime (LT = 70) average daily dose was calculated for the ingestion pathway by formula (8) (US EPA 1989, 2002; RAIS 2013):

$$LADD_{ing} = \frac{C * EF * 10^{-6}}{AT * LT} \times \left(\frac{ED_{child} * IngR_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) * IngR_{adult}}{BW_{adult}} \right) \quad (8)$$

Carcinogenic risk from ingestion for each element was assessed by formula (9) (RAIS 2013), while multi-element

Table 1 Description and values of factors used in the risk assessment equations

Factors (measurement unit)	Description	Value		Source
		Adults	Children	
IngR (mg/day)	Ingestion rate	100	200	(US EPA 2002)
EF (day/year)	Exposure frequency	90*	90*	—*
ED (year)	Exposure duration	30	6	(US EPA 2002)
BW (kg)	Average body weight	70	15	(US EPA 1989)
SA (cm ²)	Skin area	5700	2800	(US EPA 2002)
AF (mg/cm ²)	Skin adherence factor	0.07	0.2	(US EPA 2002)
AT	Average time	In the case of non-carcinogenic exposure $AT = 365 * ED$		(US EPA 2002)
ABS _d	Dermal absorption	(ABS = 0.03 for As, ABS = 0,001 for the rest of elements.		(RAIS 2013)
RFD _{ing} (mg/kg-day),	Chronic reference dose	Chemical specific		(RAIS 2013)
SF(mg/kg-day) ⁻¹	Cancer slope factor	Chemical specific		(RAIS 2013)

*Values used for this particular research

carcinogenic risk (RI) was calculated by summing single element carcinogenic risk values.

$$\text{Oral Risk} = \text{LAAD}_{\text{ing}} \times \text{SF} \quad (9)$$

Description and values of the coefficients are given in Tables 1 and 7, while carcinogenic risk level classification is given in Table 2 (Rapant et al. 2010).

3 Results and discussion

3.1 Contents of heavy metals in atmospheric dust

Ni, Co, Ag, Cr, Pb, Mo, Cd, Zn, and Cu were detected in all samples, whereas As in two samples and Hg in six samples had concentrations below the detection limit. A value of half of the detection limit was given in these cases as proposed by Reimann et al. (2008).

Descriptive statistical parameters and local geochemical background values of heavy metals are given in Table 3.

As demonstrated in Table 3, asymmetry and excess values of all the elements differ from 0 which proves deviation from normal distribution.

The standard error (λ) of the mean of studied heavy metals at the level of 5 % ($p < 0.05$) reflects the representativeness of the 25 samples' studied. Mean standard errors (Table 3) of heavy metals in dust deposits of Yerevan territory's tree leaves show that studied heavy metals categorized into the following three groups: (1) Ni, Cr, Zn, and Co ($\lambda < 20$ %); (2) Ag, Hg, Cu, and Pb (20 % $< \lambda < 50$ %); and (3) As, Mo, and Cd ($\lambda > 50$ %). The highest standard mean errors were observed for As, Mo, and Cd: 24.38 (155.2 %), 1914.43 (188.7 %) and 60.51 (124.3 %), respectively. After removing some extreme values of these elements which were thought to be the results of discharges from point pollution sources, the standard mean error values became As 39.2 %, Mo 40.2 %, and Cd 44.1 %. According to Revich et al. (1982), allowable standard mean error to be considered background sites (or natural) is $\lambda \leq 30$ %. For this study $\lambda < 50$ % can be considered sufficient, but further detailed investigations

should be carried out to reveal sources and spatial distribution peculiarities of As, Mo, and Cd.

Meanwhile, Ni, Co, and Zn may be regarded as having an approximately normal distribution according to the rule of ± 3 (Beus et al. 1976). Also, typical of Ni, Co, and Zn are relatively low values of the coefficient of variation (CV): 26, 47 and 40, respectively. Relatively low CV was determined for Cr, Ag, Hg, Pb, and Cu. However, their distribution significantly deviated from normal distribution, which might be due to the presence of outliers and extreme values of manmade contents. CV values of As, Mo, and Cd were 396, 481, and 317, respectively. This is attributed to extremely high manmade contents of heavy metals detected in some dust samples.

Mean contents of almost all elements except Cr and Ni exceeded background contents (Tables 3, 4). As seen from the arranged geochemical series (Table 4), mean contents of Mo, Cd, Hg, and Ag are manifold excessive versus the background: by 579.8, 155.9, 33.5, and 26.8 times, respectively. At their highest contents Mo, Cd, As, and Hg showed the highest excesses versus the background: by 13,974.86, 2510.9, 453.5 and 139.4 times, respectively.

It should be noted that collation of statistical characteristics of Ni, Co, and Zn with results obtained during comparison of mean of these elements versus local background values suggests that Ni may have a natural origin, while Co and Zn come from both natural and anthropogenic sources. The known source for heavy metals, especially Mo, in the Yerevan area is Mo concentrate smelting and processing in plants located in the south of Yerevan, where all studied elements with the exception of Ni exceeded local background values. In addition, for Cd, vehicle tire wear is supposed to be one of the main sources of pollution. For Hg, sources include combustion of diesel, jet fuel, medical waste disposal facilities, dental offices, and some consumer products. Arsenic may have come from metal smelting, glass, textiles, and paper production.

At the lowest contents Hg, Ag, Pb, Zn, and Cu are also excessive versus the background (Tables 3, 4).

3.2 Heavy metal pollution assessment

3.2.1 Geoaccumulation index

The calculated results of I_{geo} of heavy metals in dust are presented in Table 5. The mean values of I_{geo} decrease in the order of Cd > Mo > Ag > Hg > Pb > Cu > Zn > Co > As > Ni > Cr. The I_{geo} ranges from -1.56 to 0.07 with a mean value of -0.70 for Ni (unpolluted); -7.96 to 2.1 with a mean value of 0.68 for Co (moderately polluted); -4.88 to 8.24 with a mean value of 0.56 for As (unpolluted to moderately polluted); 2.06 to 6.35 with a mean value of

Table 2 Carcinogenic risk level classification (Rapant et al. 2010)

Risk level	Calculated cases of cancer occurrence	Cancer risk
I	$<10^{-6}$	Very low
II	10^{-6} – 10^{-5}	Low
III	10^{-5} – 10^{-4}	Medium
IV	10^{-4} – 10^{-3}	High
V	$>10^{-3}$	Very high

Table 3 Mean contents of heavy metals, descriptive statistical parameters, and background values

Value	Ni	Co	As	Ag	Hg	Cr	Pb	Mo	Cd	Zn	Cu
Mean ^a	29.09	62.26	15.71	6.68	0.57	54.23	32.43	1014.68	48.66	281.93	294.65
Std. error (p < 0.05), λ	2.91	11.50	24.38	2.93	0.23	10.05	8.10	1914.43	60.51	44.36	90.47
Median ^a	28.65	70.66	2.05	3.40	0.43	48.03	30.15	24.89	12.84	288.73	261.05
SD	7.44	29.34	62.19	7.49	0.59	25.64	20.67	4883.76	154.36	113.17	230.80
Skewness	0.27	-1.14	4.93	2.30	1.43	2.45	2.30	5.00	4.87	0.56	0.83
Std. error of skewness	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46
Kurtosis	0.19	0.43	24.52	4.96	2.18	7.63	7.08	25.00	24.07	-0.53	-0.60
Std. error of kurtosis	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Minimum ^a	15.48	0.09	0.04	1.56	0.03	23.11	12.10	1.54	0.09	129.01	60.24
Maximum ^a	47.77	100.90	312.94	30.63	2.37	149.81	108.47	24456.00	783.43	511.45	757.70
CV, %	26	47	396	112	102	47	64	481	317	40	78
Background ^b	30.4	15.65	0.69	0.25	0.017	71.1	4.8	1.75	0.312	78.38	40.03

^a values are described in mg/kg; n = 25

^b Tepanosyan et al. (2016)

Table 4 Geochemical series arranged according to highest, mean, and lowest contents

Contents	Geochemical series
Highest	Mo _(13974.9) >Cd _(2510.9) >As _(453.5) -Hg _(139.4) -Ag _(122.5) >Pb _(22.6) -Cu _(18.4) >Zn _(6.5) -Co _(6.5) -Cr _(2.1) -Ni _(1.6)
Mean	Mo _(557.7) -Cd _(151.6) >Hg _(42.9) -Ni _(28.9) -Ag _(26.8) -As _(23.8) >Cu _(7.5) -Pb _(6.7) -Co _(4.0) -Zn _(3.6)
Lowest	Ag _(6.3) -Pb _(2.5) -Hg _(1.8) -Zn _(1.7) -Cu _(1.5)

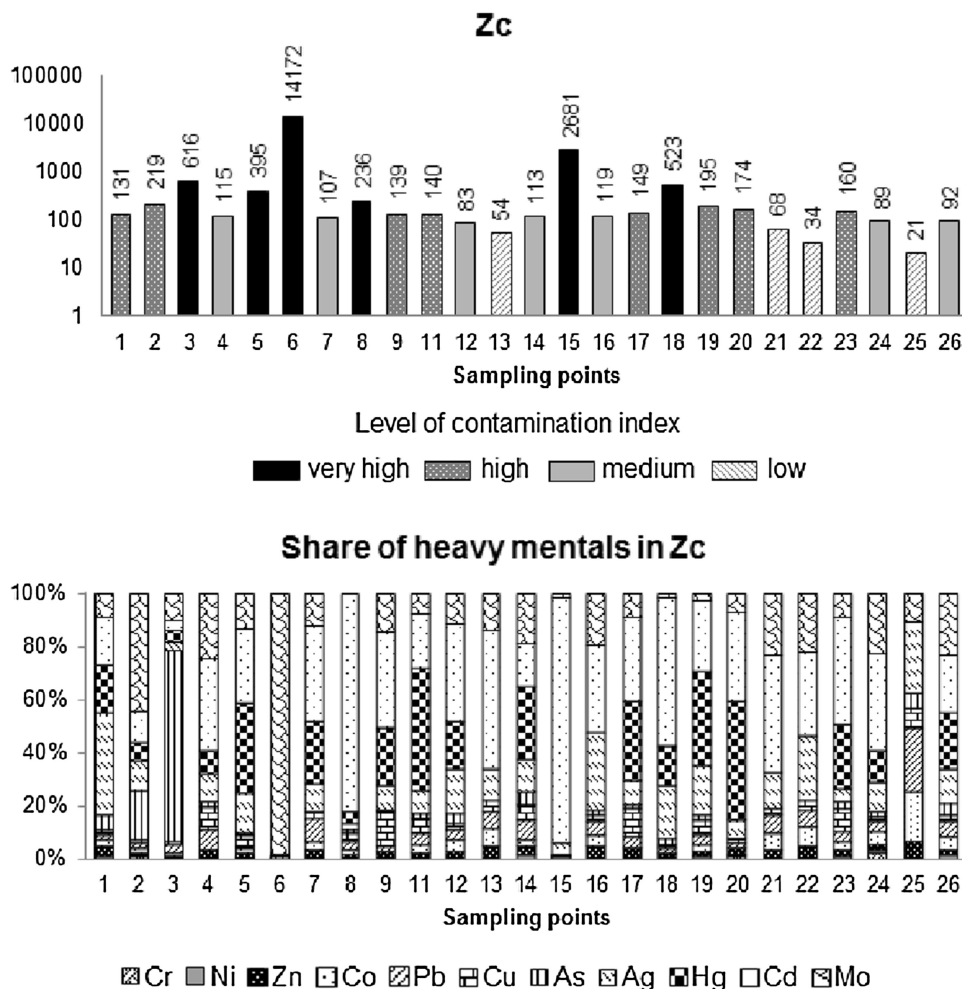
Table 5 Values of I_{geo} and single-element pollution levels

I_{geo}	Elements										
	Ni	Co	As	Ag	Hg	Cr	Pb	Mo	Cd	Zn	Cu
Max	0.07	2.10	8.24	6.35	6.54	0.49	3.91	13.19	10.71	2.12	3.66
Min	-1.56	-7.96	-4.89	2.06	0.23	-2.21	0.75	-0.77	-2.41	0.13	0.005
Mean	-0.70	0.68	0.56	3.59	3.46	-1.09	1.96	3.65	4.82	1.15	1.83
SD	0.38	2.46	2.91	1.18	2.09	0.55	0.77	2.44	2.15	0.59	1.22
Samples (%)											
$I_{geo} \leq 0$	96.0	16.0	24.0	0.0	0.0	96.0	0.0	4.0	4.0	0.0	0.0
$0 < I_{geo} \leq 1$	4.0	0.0	28.0	0.0	24.0	4.0	12.0	4.0	0.0	44.0	32.0
$1 < I_{geo} \leq 2$	0.0	76.0	28.0	0.0	0.0	0.0	36.0	8.0	0.0	48.0	16.0
$2 < I_{geo} \leq 3$	0.0	8.0	8.0	32.0	12.0	0.0	44.0	20.0	0.0	8.0	32.0
$3 < I_{geo} \leq 4$	0.0	0.0	4.0	36.0	12.0	0.0	8.0	36.0	16.0	0.0	20.0
$4 < I_{geo} \leq 5$	0.0	0.0	4.0	16.0	28.0	0.0	0.0	12.0	40.0	0.0	0.0
$5 > I_{geo}$	0.0	0.0	4.0	16.0	24.0	0.0	0.0	16.0	40.0	0.0	0.0

3.59 for Ag (strongly polluted); 0.23 to 6.54 with a mean value of 3.46 for Hg (strongly polluted); -2.21 to 0.49 with a mean value of -1.09 for Cr (moderately polluted); 0.75 to 3.91 with a mean value of 1.96 for Pb (moderately polluted); -0.77 to 13.18 with a mean value of 3.65 for Mo

(strongly polluted); -2.4 to 10.7 with a mean value of 4.82 for Cd (strongly to extremely polluted); 0.13 to 2.12 with a mean value of 1.15 for Zn (moderately polluted); and 0.005 to 3.66 with a mean value of 1.83 for Cu (moderately polluted).

Fig. 2 Levels of the contamination index and shares of individual elements in it (%)



The concentrations of Ni, Co, As, Cr, Mo, and Cd register at the unpolluted level ($I_{geo} \leq 0$) in 96 %, 16 %, 24 %, 96 %, 4 %, and 4 % of all samples, respectively. The unpolluted to moderately polluted ($0 < I_{geo} \leq 1$) level was determined in 4, 28 %, 24 %, 4 %, 12 %, 4 %, 44 %, and 32 % of all samples for Ni, As, Hg, Cr, Pb, Mo, Zn, and Cu, respectively. The moderately polluted ($1 < I_{geo} \leq 2$) level included 76 %, 28 %, 36 %, 8 %, 48 %, and 16 % of all samples for Co, As, Pb, Mo, Zn, and Cu, respectively. The moderately-to-strongly polluted ($2 < I_{geo} \leq 3$) level was observed in 8 %, 8 %, 32 %, 12 %, 44 %, 20 %, 8 %, and 32 % of all samples for Co, As, Ag, Hg, Pb, Mo, Zn, and Cu respectively. The strongly polluted ($3 < I_{geo} \leq 4$) level was detected in 4 %, 36 %, 12 %, 8 %, 36 %, 16 %, and 20 % of all samples for As, Ag, Hg, Pb, Mo, Cd, and Cu, respectively. The concentrations of As, Ag, Hg, Mo, and Cd belong to the strongly-to-extremely polluted ($4 < I_{geo} \leq 5$) level in 4%, 16%, 28%, 12%, and 40 % of all samples, and to the extremely polluted ($I_{geo} > 5$) level in 4 %, 16 %, 24 %, 16 %, and 40 % of all samples, respectively. Only for Ni, Co, Cr, and

Zn were concentrations belonging to the strongly polluted to extremely polluted levels not observed.

3.2.2 Summary pollution level

The summary pollution levels (Z_c) are given in Fig. 2. The contamination index value varied from 21 to 14,172, averaging 805.5 (extremely hazardous level). According to the contamination index, 36 % of samples exhibited a very high level of pollution, i.e. extremely hazardous; 32 % a high level of pollution, i.e. hazardous degree; 12 % a mean level, i.e. moderately hazardous degree; and 20 % a low level of pollution. Very high and high levels of pollution were detected in the southern (industrial) and central (densely populated and exposed to heavy traffic load) districts of Yerevan.

As seen from Fig. 2, a relatively large share in the contamination index of almost all the samples belongs to Mo, Cd, Hg, and Ag. In addition, Cd approximating 93 % and 83 % of the contamination index falls on sampling points N8 and N15 located in the north and west of the city.

Table 6 Non-carcinogenic health risk of heavy metals in dust

Element	Group	HQ _{ing}			HQ _{derm}			HI = ∑HQI			RFDing (mg/kg day ⁻¹)
		min	max	mean	min	max	mean	min	max	mean	
Hg	Child	6.16E-04	4.87E-02	1.17E-02	1.73E-06	1.36E-04	3.26E-05	6.18E-04	4.88E-02	1.17E-02	1.60E-04
	Adult	6.60E-05	5.22E-03	1.25E-03	2.64E-07	2.08E-05	4.98E-06	6.63E-05	5.24E-03	1.25E-03	
Pb	Child	1.14E-02	1.02E-01	3.06E-02	2.12E-04	1.90E-03	5.71E-04	1.16E-02	1.04E-01	3.12E-02	3.50E-03
	Adult	1.22E-03	1.09E-02	3.28E-03	3.24E-04	2.90E-03	8.72E-04	1.54E-03	1.38E-02	4.15E-03	
Mo	Child	1.01E-03	<i>1.61E+01</i>	6.67E-01	2.84E-06	4.50E-02	1.87E-03	1.02E-03	<i>1.61E+01</i>	6.69E-01	5.00E-03
	Adult	1.08E-04	<i>1.72E+00</i>	7.15E-02	4.33E-07	6.87E-03	2.85E-04	1.09E-04	<i>1.73E+00</i>	7.18E-02	
Cd	Child	2.89E-04	2.58E+00	1.60E-01	3.24E-05	2.88E-01	1.79E-02	3.22E-04	2.86E+00	1.78E-01	1.00E-03
	Adult	3.10E-05	2.76E-01	1.71E-02	4.95E-06	4.40E-02	2.74E-03	3.59E-05	3.20E-01	1.99E-02	
Zn	Child	1.41E-03	5.60E-03	3.09E-03	3.96E-06	1.57E-05	8.65E-06	1.42E-03	5.62E-03	3.10E-03	3.00E-01
	Adult	1.51E-04	6.01E-04	3.31E-04	6.04E-07	2.40E-06	1.32E-06	1.52E-04	6.03E-04	3.32E-04	
Cu	Child	4.95E-03	6.23E-02	2.42E-02	1.39E-05	1.74E-04	6.78E-05	4.97E-03	6.25E-02	—	4.00E-02
	Adult	5.30E-04	6.67E-03	2.59E-03	2.12E-06	2.66E-05	1.04E-05	5.33E-04	6.70E-03	2.61E-03	
Ni	Child	2.54E-03	7.85E-03	4.78E-03	1.78E-04	5.50E-04	3.35E-04	2.72E-03	8.40E-03	5.12E-03	2.00E-02
	Adult	2.73E-04	8.41E-04	5.12E-04	2.72E-05	8.39E-05	5.11E-05	3.00E-04	9.25E-04	5.63E-04	
Ag	Child	1.03E-03	2.01E-02	4.39E-03	7.18E-05	1.41E-03	3.07E-04	1.10E-03	2.16E-02	4.70E-03	5.00E-03
	Adult	1.10E-04	2.16E-03	4.70E-04	1.10E-05	2.15E-04	4.69E-05	1.21E-04	2.37E-03	5.17E-04	
Co	Child	1.03E-03	<i>1.11E+00</i>	6.82E-01	2.88E-06	3.10E-03	1.91E-03	1.03E-03	<i>1.11E+00</i>	6.84E-01	3.00E-04
	Adult	1.10E-04	1.18E-01	7.31E-02	4.40E-07	4.73E-04	2.92E-04	1.11E-04	1.19E-01	7.34E-02	
Cr	Child	2.53E-02	1.64E-01	5.94E-02	2.84E-03	1.84E-02	6.66E-03	2.82E-02	1.83E-01	6.61E-02	3.00E-03
	Adult	2.71E-03	1.76E-02	6.37E-03	4.33E-04	2.81E-03	1.02E-03	3.15E-03	2.04E-02	7.38E-03	
As	Child	3.84E-04	<i>3.43E+00</i>	1.72E-01	3.22E-05	2.88E-01	1.45E-02	4.16E-04	<i>3.72E+00</i>	1.87E-01	3.00E-04
	Adult	4.11E-05	3.67E-01	1.84E-02	4.92E-06	4.40E-02	2.21E-03	4.60E-05	4.11E-01	2.07E-02	

In italics >1 values are given

Fig. 3 Multi-elemental risk to children and adults according to sampling point

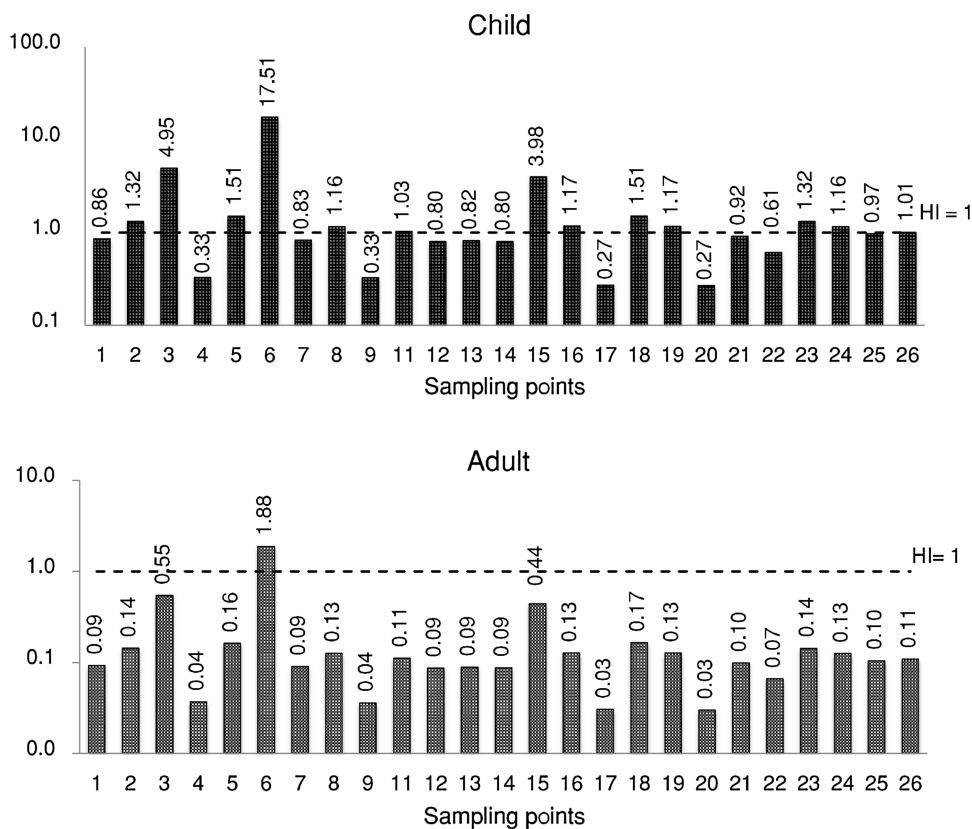


Table 7 Summary of carcinogenic risk via ingestion and inhalation exposure of dust, based on min., max., and mean concentrations

Element	Value	Oral risk	SF(mg/kg-day) ⁻¹
Cr	min	4.42E-06	5.00E-01
	max	2.86E-05	
	mean	1.04E-05	
As	min	2.01E-08	1.50E+00
	max	1.80E-04	
	mean	9.01E-06	
<i>RI_{ing}</i>	min	4.44E-06	
	max	1.89E-04	
	mean	1.94E-05	

In italics $>10^{-6}$ values are given for single-element carcinogenic risk, $>10^{-4}$ for multi-element carcinogenic risk values

Rather a large share of Mo (98 % of the contamination index) falls on a sampling point in the south of the city near the Mo concentrate smelting and processing plants.

3.3 Non-carcinogenic risk assessment

Results of assessment of non-carcinogenic risk of heavy metals in leaf dust are given in Table 6. Both to children and adults, the major route of exposure from multi-elemental risk is ingestion followed by skin absorption. For

children, major (HQ >1) risk is determined for Mo, Cd, Co, and As; in adults, for Mo only. In the case of children, the single-elemental HI for Mo varies from 0.001 to 16.1; for Cd, 0.0003 to 2.86; for Co, 0.001 to 1.11; and for As, 0.0004 to 3.72, with means of 0.67, 0.18, 0.68, and 0.19, respectively. Moreover, for children, single-elemental HI was greater than 1 in one sample in the cases of Mo, Cd, and As, and in three samples in the case of Co. Single-elemental HI for adults for Mo varies from 0.0001 to 1.73, with a mean of 0.072, and HI greater than 1 was detected in one sample.

Mean single-elemental HI values of studied metals are represented by the following decreasing series for both children and adults:

$$Co > Mo > As > Cd > Cr > Pb > Cu > Hg > Ni > Ag > Zn$$

Multi-elemental HI varies from 0.27 to 17.51 for children and 0.03 to 1.86 for adults with means of 1.89 and 0.2, respectively. Moreover, a probable heavy metal-induced non-carcinogenic risk to children and adults is posed by thirteen and one dust samples, respectively (Fig. 3).

3.4 Carcinogenic risk assessment

To assess carcinogenic risk of Cr and As, appropriate SF values were taken from RAIS (2013). However, RAIS

contains no values for ingestion pathway for the rest of the detected elements.

The results of the carcinogenic risk calculation are given in Table 7.

It is evident (Table 7) that minimum carcinogenic risk values of Cr via ingestion pathway belong to the low risk level, while mean and maximum carcinogenic risk values of Cr belong to the medium risk level. In the case of As, carcinogenic risk was detected only for mean (low risk level) and max (high risk level) values. From all 25 samples, a low level ($>10^{-6}$ and $<10^{-5}$) of Cr and As carcinogenic risk was detected in seventeen and twelve samples, respectively; and a medium level ($>10^{-5}$ and $<10^{-4}$) in eight and one samples, respectively. A high level ($>10^{-4}$ and $<10^{-3}$) of carcinogenic risk was observed only in the case of As in one sampling site. Multi-element carcinogenic risk ($>10^{-4}$) via ingestion pathway has been observed only by the maximum RI_{ing} value.

4 Conclusions

The concentrations, pollution levels, and health risks of heavy metals (Cd, As, Pb, Cr, Ni, Co, Zn, Cu, Ag, Hg, and Mo) in tree leaf dust deposits from Yerevan territory were studied. The obtained results show that mean contents of all studied elements, except Cr and Ni, exceed background values. A geochemical series of mean contents of heavy metals is represented as $Mo_{(579.8)}-Cd_{(155.9)}>Hg_{(33.5)}-Ag_{(26.8)}-As_{(22.8)}>Cu_{(7.4)}-Pb_{(6.7)}-Co_{(4.0)}-Zn_{(3.6)}$. Statistical descriptions of the contents indicate that high contents of As, Mo, and Cd detected in Yerevan are due to man-made sources, while Ni has a natural origin, and Co and Zn originate from both natural and anthropogenic sources. This fact was also complemented by low levels of I_{geo} for these elements. Summary pollution levels based on the contamination index show that 36 % of all samples exhibited a very high level of pollution; 32 %, high; 12 %, mean; and 20 %, low.

The results of risk analysis suggest that both in children and adults the major pathway of risk is ingestion of dust particles. Children, as compared with adults, are at a higher risk, and such a level of air pollution with heavy metals can trigger serious health problems. A probable cause of non-carcinogenic risk to children was found to be Mo, Cd, Co, and As; to adults, Mo only. From very low to high levels of carcinogenic risk were observed for single-element and medium levels for multi-element ingestion of Yerevan dust.

It should be stressed that there are some limitations in the used risk assessment model: (1) all employed coefficients are set for US citizens, (2) lack of respective coefficients for individual pathways of some elements, (3) dust

particle size and rate of penetration are not taken into account, (4) seasonal variations are not taken into account, and (5) calculations are based on total concentrations of heavy metals. Despite this, application of the described risk model helped us get a better vision of probable health risks to Yerevan's residents.

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