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Origin identification and potential ecological risk assessment of potentially toxic inorganic elements in the topsoil of the city of Yerevan, Armenia

Gevorg Tepanosyan *, Lilit Sahakyan, Olga Belyaeva, Armen Saghatelyan

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

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ABSTRACT

The total concentrations of Ti, Fe, Ba, Mn, Co, V, Pb, Zn, Cu, Ni, Cr, Mo, Hg and As were determined in 1356 topsoil samples collected from the area of the city of Yerevan in order to: (1) determine the spatial distribution peculiarity and the origin of potentially toxic inorganic elements in Yerevan soils; and (2) assess the potential ecological risk of potentially toxic inorganic elements. The spatial distribution features of these elements were illustrated by environmental geochemical mapping. Pollution indexes (PIs) of As, Ti, Mn, Fe, Ba, and Co were between the range of 0.9–1.1, while PI of Cu, Zn, Ni, Cr, V, Hg, Mo (1.5–6.8) and especially Pb (22.9) was higher. Multivariate geostatistical analyses suggested that the concentrations of Pb, Cu, Zn, Hg, Cr, Ni and Mo observed in the topsoil bore the influence of anthropogenic and industrial activities. Moreover, according to the main findings of Principal component analysis (PCA) Pb and Zn have two distinct sources of origin: (1) vehicle emission and social activities (PC2); and (2) industrial activities (PC3). The potential ecological risk was quantitatively estimated for each sampling site and a risk map for the assessment was created. Among the investigated elements, Pb and Hg showed a higher potential ecological risk, than the others.

1. Introduction

Due to rapid industrialization and urbanization, significant concerns regarding urban soil pollution were raised in the past decades (Alekseenko and Alekseenko, 2014; Johnson et al., 2011; Morel and Heinrich, 2008; Wong et al., 2006). Being a complex mixer of soil parent materials and various inputs of exogenous materials (Morel and Heinrich, 2008), soils actually act as a pollutant sink and, if undisturbed, preserve the cumulative history of pollution. Especially topical in urban sites is contamination of soils by various potentially toxic inorganic elements (PTIE) (Charlesworth et al., 2011; Johnson et al., 2011; Luo et al., 2012; Wong et al., 2006). The long-term input of PTIE could result in a decreased buffering capacity of soil (Ljung et al., 2006) and groundwater contamination (Krishna and Govil, 2007; Ljung et al., 2006). Pollution of soils by PTIE has recently become a subject of many studies because of the risk both for the environment and human health (Albanese and Cicchella, 2012; Filippelli et al., 2012; Luo et al., 2011; Zhang et al., 2011). Highly polluted urban soils have an adverse effect on human health because of their easy transportation into human body from suspended dust or by direct contact (Madrid et al., 2002; Wang and Qin, 2005), as well as through the food chain (Charlesworth et al., 2011).

Geochemical studies in urban sites serve as an efficient tool to investigate peculiarities of the spatial distribution of PTIE in soils, to calculate geochemical baseline (Johnson et al., 2011), to reveal contaminated sites, to assess risk levels (Charlesworth et al., 2011; Johnson et al., 2011), to identify hot-spots and pollution sources (Acosta et al., 2011; Carr et al., 2008; Cicchella et al., 2005; Lee et al., 2006; Madrid et al., 2002), to control soil chemistry and safety, and to create a science based soil monitoring system.

Pollution with PTIE of the study area-city of Yerevan has been topical for many decades. Yerevan has a total area of 223 km^2, 1.06 million population (4782 persons per square km). The major land use types of the city are primarily residential, industrial and commercial.

Geochemical studies on the territory of Yerevan, among other Soviet Union cities, began in 1979 in the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements (IMGRE, Moscow). Later on, since 1989, the Center for Ecological-Noosphere Studies (CENS) of National Academy of Science of Armenia took up pace and continued all activities. PTIE were detected in Yerevan soils by the soils surveys implemented in last decades; particularly in 1979 and 1989–1990; during the Soviet Union (Saghatelyan, 2004); and in 2002–2003 after the economic collapse (Saghatelyan, 2004; Sahakyan, 2008). During the entire period of geochemical investigations existence of PTIE was also recorded in snow and leaf dust (Saghatelyan et al., 2014; Sahakyan, 2006), urban river waters (Nalbandyan and Saghatelyan, 2002; Nalbandyan et al., 2003; Saghatelyan and Nalbandyan, 2005) and vegetables grown in home gardens (Hovhannisyan et al., 2012; Hovhannisyan, 2004).

* Corresponding author.
E-mail addresses: gevorg.tepanosyan@cens.am (G. Tepanosyan), lilit.sahakyan@cens.am (L. Sahakyan), olga.belyaeva@cens.am (O. Belyaeva), ecocentr@sci.am (A. Saghatelyan).

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The recorded high concentrations of PTIE are not typical for the territory of Yerevan, due to its natural and geological peculiarities (volcanic lavas, tuffs and the Quaternary sediments represent the geological base of the city (Saghatelyan, 2004)). Since Soviet time, being one of the industrialized (approx. 60% of the republics industry) cities of Armenia, Yerevan territory has remained significantly polluted by PTIE. Huge enterprises such as an Aluminum plant, the Electric bulb plant, the Experimental plant of milling machines, the Car and Worsted complex, Typography and a Polygraphic complex had operated in the city. Discharges from the abovementioned and other enterprises, as well as from urban transport, led to a continued stream of PTIE accumulating in the territory of the city (Nalbandyan and Saghatelyan, 2002; Saghatelyan, 2004; Saghatelyan et al., 2003; Sahakyan, 2006).

After the collapse of the Soviet Union and following socioeconomic transformations in 1990, radical changes occurred in the ecologically significant factors in the city's environment. Alongside the collapse, the level of industrial production simultaneously decreased and many of the industrial plants were closed (Saghatelyan, 2004; Sahakyan, 2008). Those socioeconomic transformations also have definite reflections on the quantitative and qualitative features of geochemical streams of PTIE. This manifested in changes of quantities of PTIE concentrations and priorities of pollutants, but being stable pollutants, they still existed in the territory of Yerevan.

Today, socioeconomic conditions are completely different: industry is in the recovery stage, with a wide range of industrial production in place. Spatial distribution of industrial units throughout the city has changed as well (Fig. 1) and obtained a more decentralized character, i.e. spread across the city irregularly.

The mosaic distribution of industrial enterprises, heavy traffic and historical pollution complicates the eco-geochemical status and reiterate the need to assess the present geochemical situation of the city's soils. To this end, the third geochemical soil survey was carried out in 2012. The present study is focused on determining the concentration levels and mapping of spatial distributions of PTIE in soils, revealing hot spots, and identifying the origin of PTIE in the soils. The potential ecological risk of PTIE for the first time in this territory is assessed as well.

2. Materials and methods

2.1. Study area

The natural landscape of Yerevan (latitude 40°10′40″N, altitude 44°30′45″E) territory is mainly semi-desert, arid steppe and steppe. The climate is continental with quite a broad amplitude of temperature (summer temperature ranges from +22 to +26 °C; winter temperature: −20 to -30 °C). Precipitation figures are 300–350 mm. The relief is rather diverse and is represented by plains, plateaus, foothills, and the River Hrazdan canyon. A geological composition of the territory is dominated by volcanic lavas, tuffs and Quaternary sediments. According to the geochemical classification of cities (Perelman and Kasimov, 1999), based on the lithogeochemical characteristics of parent rocks, Yerevan belongs to the background city type. The soil (mostly brown semi-desert) profile is rich in carbonates, to the lower horizon a presence of gypsum is common, thus evidencing a lack of chemical element washout and creating a good environment for PTIE accumulation on soil profiles (Saghatelyan, 2004).

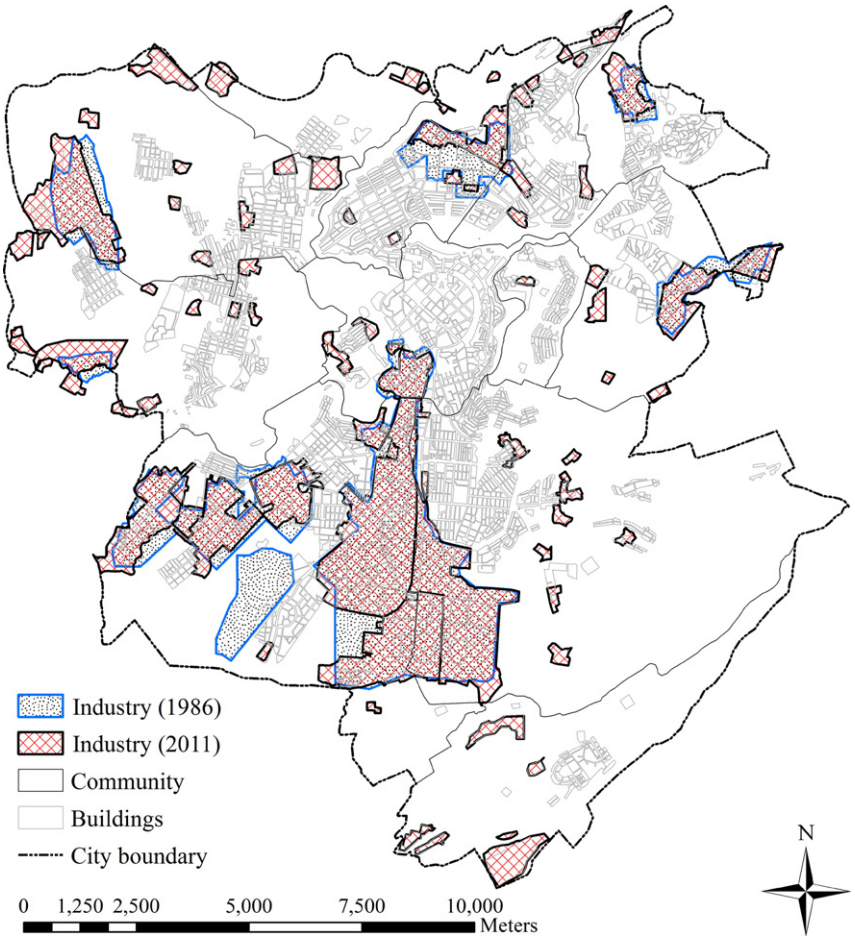

Fig. 1. Location of old (1986) and new (2011) industrial areas (Yerevan).

To establish local background values of the studied PTIE in Yerevan, a background site was selected outside of the city. The geological base of the latter was composed of alternated basalts and tuffs of Geghama Highland which is typical for northern, central and western parts of the city. The cumulative valley of Yerevan's southern part is comprised of fragmental debris of the same rocks (Vardanyan, 2006). The soils of the background site derived from lavas succeeded the main geochemical features of basalts and tuffs and characterized by low contents of chalcophile elements (Saghatelyan, 2004).

2.2. Topsoil sampling

Topsoil sampling (2012) was carried out in the urban area of Yerevan. A total of 1356 samples (Fig. 2) were collected (topsoil, 0–5 cm). Sampling was done in compliance with the uniform sampling strategy. Densely populated urban and industrial areas were sampled using a 0.25×0.25 km grid (16 samples per 1 km^2). Sampling density varied in some areas due to the location of buildings, roads and other structures. In some cases, sampling was performed using a 0.5×0.5 km

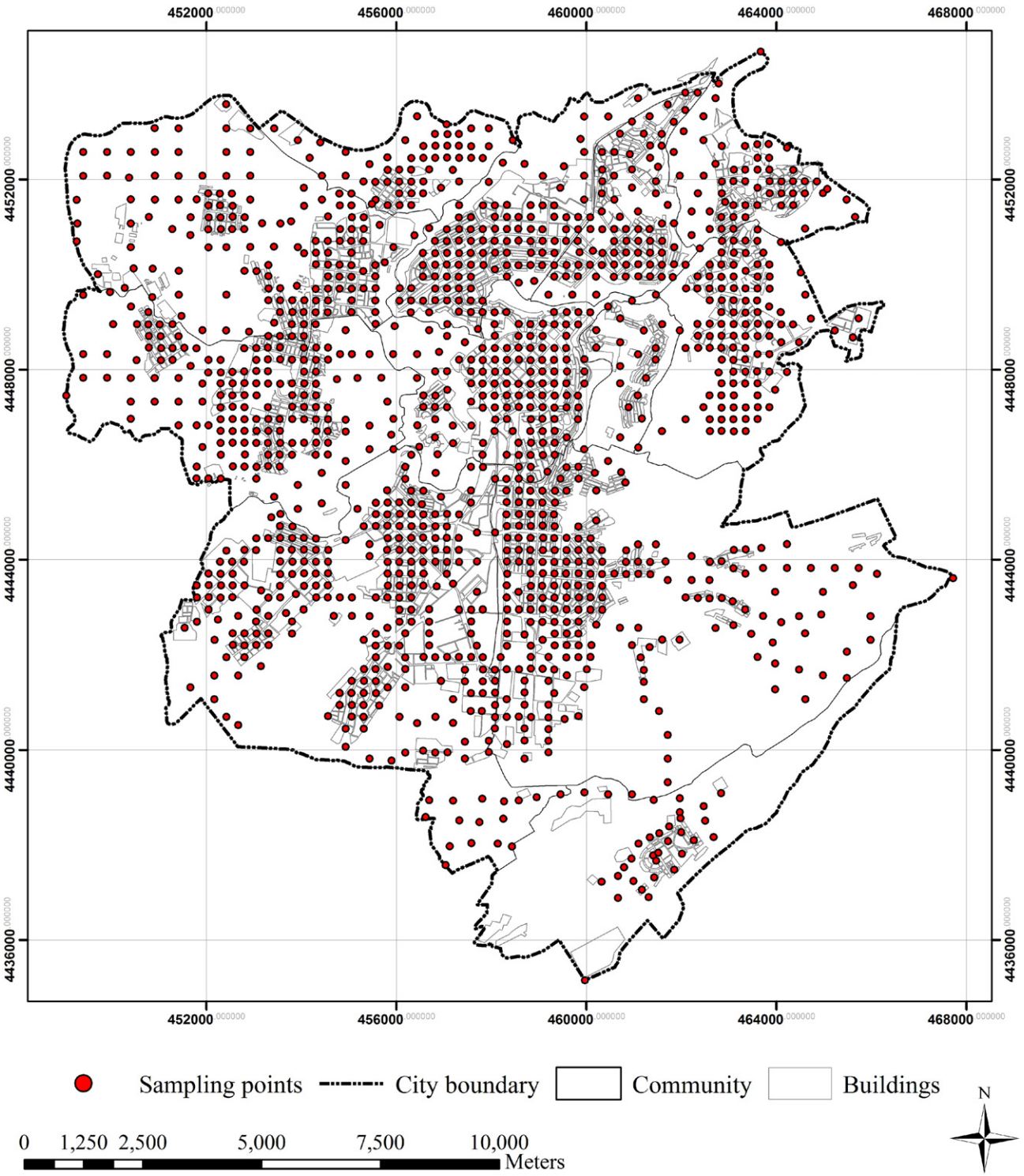

Fig. 2. Location of the topsoil samples (Yerevan).

Table 1
Detection limits, accuracy error and precision.

Elements	Detection limit	Accuracy (%)	Precision (%RPD)
Ti	2	12.1	4.4
Fe	4	13.9	4.3
Mn	2	8.0	2.7
V	1	5.8	0.4
Co	5	3.2	2.1
Ba	20	8.6	2.8
Cu	10	15.7	1.5
Zn	5	10.4	3.8
Ni	7.3	3.1	1.6
Cr	1.4	1.2	2.0
Pb	5	2.6	5.9
Mo	0.2	–[a]	6.3
Hg	0.01	15.6	5.7
As	0.1	12.9	2.4

Concentration mg/kg for all elements
The laboratory accuracy error and precision were determined by calculating Relative percent difference (RPD%) of duplicate samples and Percent difference (PD%) of standard reference materials (Cicchella et al., 2008; US EPA Method 6200, 2007).
[a] No certified value for Mo.

grid (4 samples per 1 km^2) (Fig. 2). To establish Yerevan topsoils background values of studied PTIE 51 background samples from the unpopulated and unpolluted external part (background site) of the city were collected following 0.5 × 0.5 km grid (4 samples per 1 km^2). A stainless steel hand auger was used. 3–5 randomly collected subsamples were mixed thoroughly to obtain a bulk sample. Bulk samples were stored in polyethylene bags for transportation and storaging purposes. Soils were air-dried, homogenized and sieved (<2 mm), milled in the laboratory according ISO-11464 (US EPA Method 6200, 2007) and then stored in sealed bags until the analysis stage.

2.3. Analytic methods and QA/QC

The total concentrations of Ti, Fe, Ba, Mn, Co, V, Pb, Zn, Cu, Ni, Cr, Mo, Hg and As in the soils were determined by X-ray fluorescence spectrometry employing Olympus Innov-X-5000 (USA) according to EPA standard method 6200 (US EPA Method 6200, 2007) in CENS. Standard reference materials (NIST 2711a and NIST 2710a, USA) and blank (SiO_2) obtained from the National Institute of Standards and Technology of the USA were analyzed as part of the quality assurance and quality control (QA/QC) procedures. Analysis of the samples was performed in triplicate, and the standard deviation was within 5%. Laboratory analytical precision was determined on the basis of laboratory duplicates analyses results and Relative percent difference (RPD) of 70 pairs of duplicates was within 0.4–6.3% (Table 1). The accuracy error of analyses was checked by evaluating Percent difference (PD) between measured and certified values. PD was within the acceptable range of 20%. X-ray analysis results showed that Mo (589.7%), Pb (210%), Cu (179%) and Zn (292%) have significant variability. Hence, for this purpose PTIE comparative sample analysis was done. Generally, according to the EPA Method 6200 (US EPA, 2007) confirmatory analysis should be done for a minimum of 1 sample for each 20 XRF-analyzed samples but due to the financial limitations of this study only ≈1.5% (20 samples) were selected and analyzed for Mo, Pb, Cu and Zn by atomic absorption spectrometry (Perkin Elmer AAnalyst 800, Method ISO 5725–1 (ISO, 1994)) at a certified (ISO-17025) analytical laboratory of the CENS. XRF vs. laboratory data comparison showed that the correlation coefficients for all 4 elements were >0.7, particularly Mo ($r = 0.88$), Pb ($r = 0.97$), Cu ($r = 0.84$) and Zn ($r = 0.96$), indicating that even with such a big variability XRF results of Mo, Pb, Cu and Zn can be considered screening level data.

In the present work, element concentrations below detection limits were given a value 1/2 of the detection limit (Johnson et al., 2011; Reiman et al., 2008).

2.4. Data analysis and geochemical mapping

Descriptive statistics were calculated for PTIE contents. To identify the relationship between PTIE in urban soil and their possible sources, multivariate statistical analyses, such as principal component analysis (PCA) and cluster analysis (CA), were performed (SPSS 20). As environmental data are usually strongly right-skewed and are characterized by the existence of outliers, and the element concentrations varied greatly among the major, minor and trace elements (Johnson et al., 2011; Reiman et al., 2008), in this study, the raw data were log-transformed prior to PCA and CA. The software used for the mapping and spatial analysis was ArcGIS. IDW method was used as a quicker interpolative method that accurately identifies the overall spatial pattern (Preston et al., 1996; Zhou et al., 2007) of geochemical data. The power of 2 and the number of neighboring samples of 12 were chosen. Intervals of 5%, 25%, 50%, 75%, 95%, 99% and 100% were used in mapping of distribution of PTIE. The produced geochemical maps reflect spatial distributions of the studied PTIE and allow for the implementation of a visual control of the processed data.

The background concentrations were determined according to the combined method (Matschullat et al., 2000; Reimann et al., 2005;

Table 2
Descriptive statistics of studied elements concentrations in topsoil (mg/kg) in the city of Yerevan.

Elements	Mean	Median	SD	Min	Max	CV (%)	Maximum acceptable concentrations (RA Government decision, 2015)	Yerevan background	Pollution index[a]
Fe	36,400	36,726	4252	17,936	71,853	11.7	–	38,304	1.0
Ti	4115	4129	529	2169	6835	12.9	–	4646.6	0.9
Mn	776.2	775.0	112.4	401.0	2036.0	14.5	1500	788.0	1.0
Ba	427.6	420.0	64.3	265.0	1070.0	15.0	–	407.8	1.1[b]
Zn	261.9	193.6	764.6	41.9	26,736.0	292.0	220	78.4	3.3[b]
Cr	122.0	113.8	64.2	25.7	1522.0	52.6	90	71.1	1.7[b]
Pb	109.9	70.8	230.9	2.5	5524.4	210.0	65	4.8	22.9[b]
Cu	103.4	68.2	185.0	25.9	3635.0	179.0	132	40.0	2.6[b]
V	90.30	91.00	11.57	48.60	168.00	12.8	150	45.80	2.0[b]
Ni	61.90	60.10	50.60	3.60	1639.80	81.8	80	30.40	2.0[b]
Co	13.70	13.70	1.63	6.90	23.90	11.9	–	15.60	0.9
Mo	2.60	1.08	15.29	0.11	420.84	589.7	132	1.75	1.5[b]
As	0.780	0.750	0.230	0.050	4.900	30.1	10	0.690	1.1[b]
Hg	0.115	0.117	0.050	0.010	0.270	44.0	2.1	0.017	6.8[b]

"–" No MAC available.
[a] Pollution index is the ratio of the mean concentration of element in the topsoil to the background values.
[b] Pollution indexes >1.

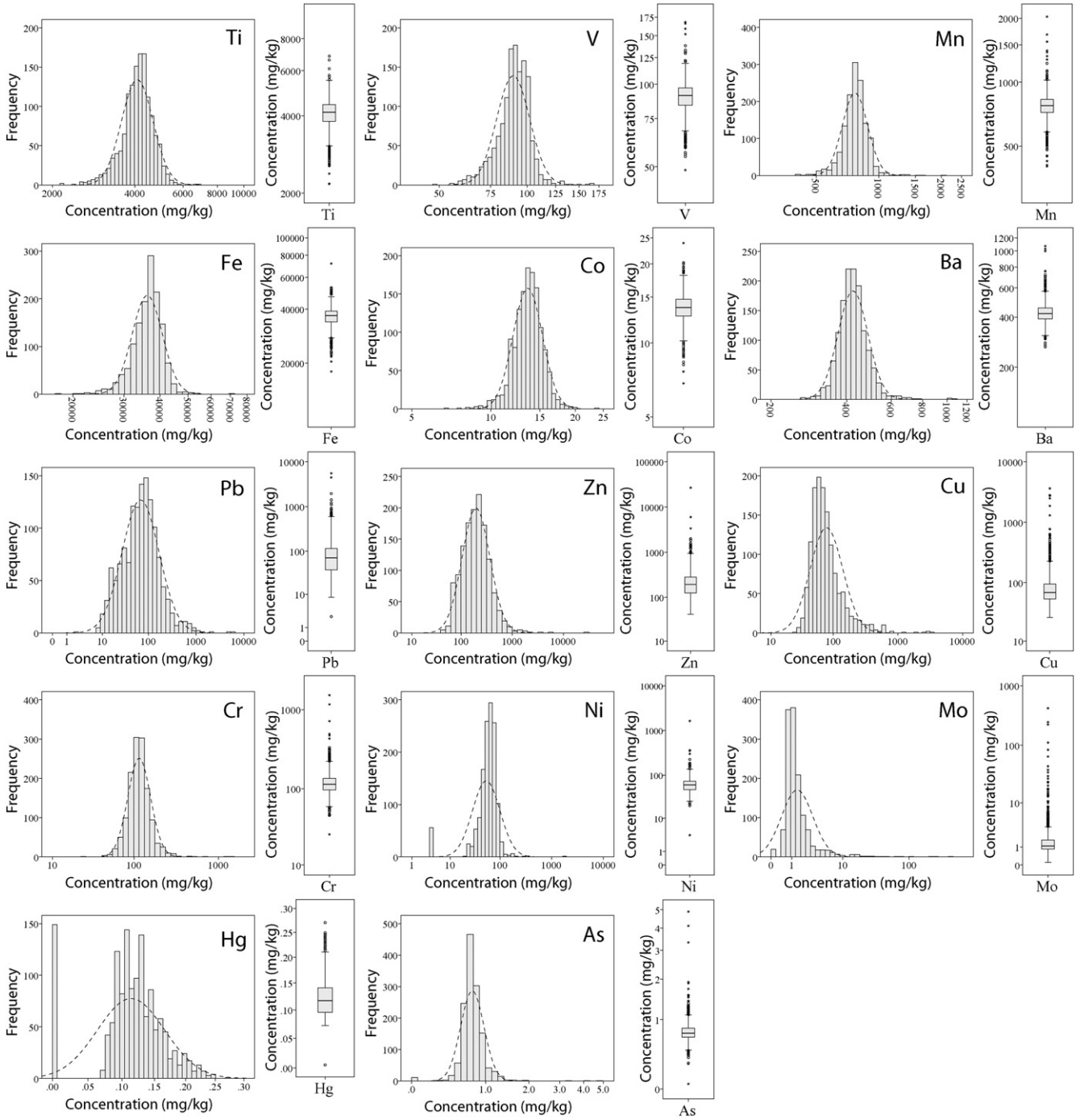

Fig. 3. Histograms and box-plots of PTIE in the topsoil (n = 1356).

Zglobicki et al., 2011). The latter included geochemical and statistical methods simultaneously.

2.5. Potential ecological risk assessment

The potential ecological risk assessment was done according to the Potential Ecological Risk Index (PERI) method (Håkanson, 1980) for Hg, As, Pb, Cu, Ni, Cr and Zn as "toxic-response" factors list is limited. Although the potential ecological risk index (PERI) method was introduced by Håkanson (1980)) to valuate PTIE contamination from the perspective of sedimentology it was applied by many other authors (Sun et al., 2010; Yuan et al., 2014; Zhao et al., 2015) to assess the ecological risks from PTIE in soils. PERI was computed using (1), (2) and (3) formulas:

$$\boldsymbol{C_r^i} = C^i_{topsoil}/C^i_n \tag{1}$$

$$\boldsymbol{E_r^i} = T^i_r * C^i_r \tag{2}$$

$$\boldsymbol{RI} = \sum_{i=1}^{n} E^r_i \tag{3}$$

where ***RI*** is integrated potential ecological risk index and it represents

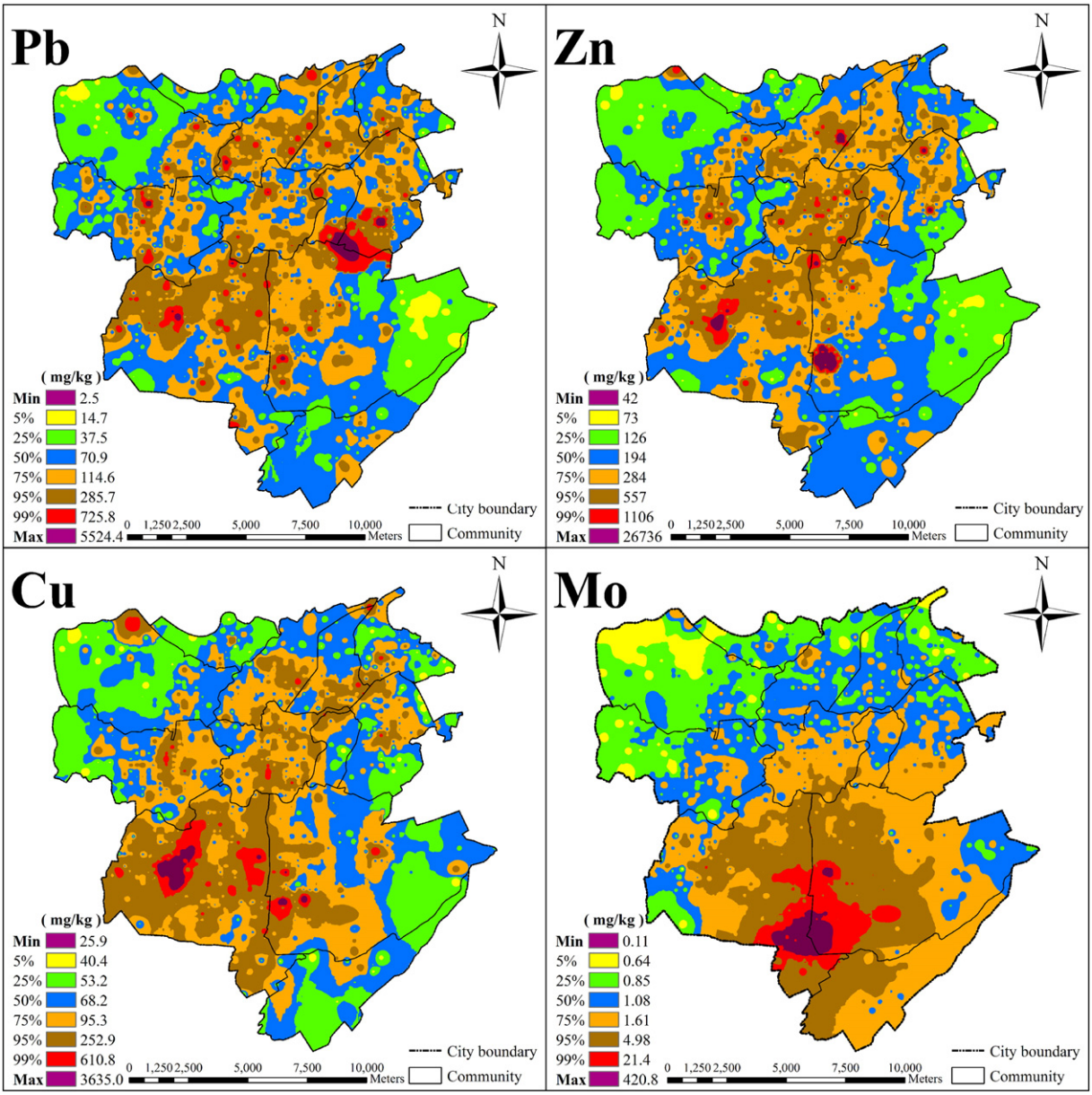

Fig. 4. Spatial distribution of Pb, Zn, Cu and Mo in the topsoil (n = 1356).

the sensitivity of various biological communities to harmful elements and illustrates the potential ecological risk, E_r^i is potential ecological risk index of single element, T_r^i is "toxic-response" factor for the given element (i.e. Hg = 40, As = 10, Pb=Cu=Ni = 5, Cr = 2 and Zn = 1), C_r^i is the pollution factor of the given element, $C_{topsoil}^i$ is the concentration of the given element in the topsoil and C_n^i is the reference value of the given element (local background).

3. Results and discussion

3.1. Data analyses and PTIE concentrations in the topsoil

The descriptive statistics of PTIE concentration are summarized in Table 2. In addition, Yerevan soil background values (BV) of PTIE are also listed for reference and for a calculation of pollution index (PI). Herein, PI is the ratio of the mean value of the element concentration in the topsoil to the BV.

The mean concentrations of Mo, Pb, Zn, and Cu (Table 2) are significantly higher than their respective median values. This indicates right-skewed distributions of these elements (Fig. 3). For all other studied elements, the difference between mean and median concentrations was not as high. Ti, V and Fe have left-skewed distribution and Cr, Ba, Mn and Co have approximately normal distribution (Fig. 3). Although Hg, Ni and As means and medians are approximately equal, these elements also have right-skewed distribution (Fig. 3). It could be explained that for Hg, Ni and As below detection limit concentrations were recorded.

PI of Ti, Fe, Mn, Co, Ba and As 0.9–1.1 (Table 2) indicates relatively low concentration of these elements in the topsoil studied. These could be the result of less accumulation time and a lower rate of accumulation. PI of Cr, Ni, Mo, V, Cu, Zn were higher (1.5–3.3). Hg and Pb have significantly high PI (6.8 and 22.9 respectively) indicating that they may be affected strongly by exogenous substances. The collation of mean contents of elements with maximum acceptable concentrations (MAC) approved by the RA Government (RA Government decision, 2015) showed that only Pb, Zn and Cr mean concentrations exceeded MAC by 1.7; 1.2 and 1.4 times, respectively.

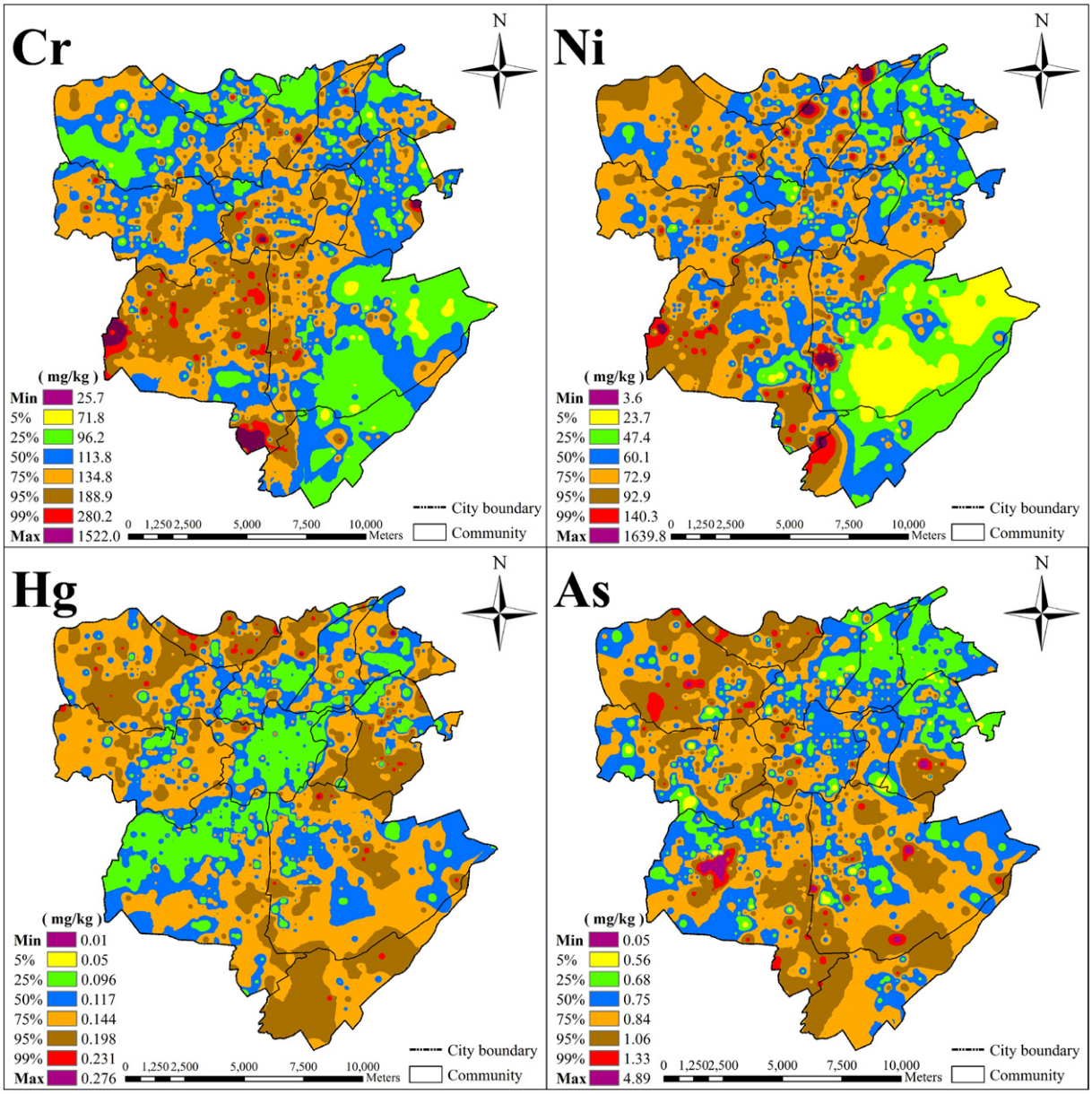

Fig. 5. Spatial distribution of Cr, Ni, Hg and As in the topsoil (n = 1356).

The SD and CV% (Table 2) of Mo, Zn, Cu and Pb were significantly high, suggesting that they had the greatest variation among the studied elements and thus would have a high possibility of anthropogenic origin. SD and CV% observed for Cr and Ni were moderate, while other studied elements have lower SD and CV%. The box-plots show (Fig. 3) that all PTIE have some outliers and extreme values, which are mainly caused by pollution with exogenous substances.

3.2. Spatial distribution of PTIE in urban topsoil

Geochemical maps are very important tools from which a lot can be extracted (Johnson et al., 2011; Reiman et al., 2008; Reimann, 2005). The maps generated for Yerevan (Figs. 4, 5 and Supplementary materials Figs. S1–S6 in the online version at http://dx.doi.org/10.1016/j.gexplo.2016.04.006.) showed that Fe, Ti, V, Mn, Co and Ba concentrations above 95th percentile values had point shape and randomly appeared in different parts of the city. The distributions of Pb, Zn, Cu, Ni and Cr had some similar features (Figs. 4 and 5): particularly concentrations above the 75th percentile were mainly located in dense populated and industrial parts of the city. Concentrations between the 25th and 50th percentile had outline dense populated and industrial areas of the city, while concentrations below the 25th percentile were mainly located in the south east (for Pb, Zn, Cu, Ni and Cr) and north west (for Pb, Zn, Cu) not residential parts of the city. High values (>95th percentile) of Hg and As (Fig. 5) were fixed in densely populated and industrial parts of the city, and as opposed to Pb, Zn, Cu, Ni and Cr distributions, in the form of randomly distributed hot spots appeared in north west and south east parts of the city.

Spatially, "hot spots" of the studied PTIE mainly coincide with historical industrial zones and spatial location of present-day pollution sources (Fig. 1).

Nonetheless, mosaic and uneven distribution of PTIE pollution sources throughout the city hampers the identification of responsible pollution sources.

Only the spatial distribution of Mo was unique as it had a significant "hot spot", which is located near Mo concentrate smelting and processing plants. Generally, the spatial distribution and the shapes of the studied PTIE "hot spots" indicated that in the territory of Yerevan there were

Table 3
Pearson correlation matrix of studied elements data in topsoil samples.

Elements	Correlation coefficient												
	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ba	Hg
Ti	1												
V	0.764[a]	1											
Cr	0.298[a]	0.256[a]	1										
Mn	0.709[a]	0.582[a]	0.314[a]	1									
Fe	0.764[a]	0.631[a]	0.339[a]	0.683[a]	1								
Co	0.645[a]	0.509[a]	0.258[a]	0.536[a]	0.865[a]	1							
Ni	−0.014	−0.122[a]	0.413[a]	0.045	0.007	−0.095[a]	1						
Cu	0.055[b]	0.158[a]	0.347[a]	0.173[a]	0.280[a]	0.244[a]	0.138[a]	1					
Zn	0.024	0.145[a]	0.365[a]	0.195[a]	0.122[a]	0.103[a]	0.221[a]	0.599[a]	1				
As	−0.134[a]	−0.066[b]	−0.145[a]	−0.151[a]	−0.045	−0.011	0.004	−0.019	−0.209[a]	1			
Mo	−0.186[a]	0.058[b]	0.125[a]	−0.008	0.048	0.049	−0.075[a]	0.394[a]	0.302[a]	0.066[b]	1		
Ba	0.230[a]	0.521[a]	0.037	0.302[a]	0.224[a]	0.197[a]	−0.186[a]	0.177[a]	0.367[a]	−0.101[a]	0.182[a]	1	
Hg	−0.154[a]	>−0.198[a]	−0.180[a]	−0.249[a]	−0.151[a]	−0.021	−0.086[a]	−0.270[a]	−0.544[a]	0.171[a]	−0.057[b]	−0.273[a]	1
Pb	−0.077[a]	0.062[b]	0.265[a]	0.070[b]	0.019	0.017	0.163[a]	0.489[a]	0.722[a]	−0.286[a]	0.294[a]	0.278[a]	−0.382[a]

Correlation is significant at the
[a] 0.05 level (2-tailed)
[b] 0.01 level (2-tailed)

two types of "hot spots": (1) single element point shape "hot spots" which appeared in the most densely populated areas of the city; and (2) multi-element intense "hot spots" which were spatially allocated near huge industrial enterprises.

3.3. Correlation and Principal component analysis for PTIE in the topsoil

A correlation matrix and PCA was used to study the correlations between PTIE, properties and their grouping into a few factors. PCA was conducted using factor extraction with an eigenvalue >1 after varimax rotation with Kaiser normalization, which allows for an easier interpretation of the principal component loadings and the variance explained by the extracted factors.

Significant negative correlation (0.01 and 0.05 level of significance) (Table 3) observed between: Hg and Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ba, Pb; As and Ti, Cr, Mn, Zn, Ba, Pb; Ni and V, Co, Mo, Ba; Ti and Mo, Pb. This significant negative correlation suggests that these elements came from different sources. Correlation was not significant between Ni and Ti, Mn, Fe, As; Mo and Mn, Fe, Co; As and Fe, Co, Cu; Ti and Zn; Cr and Ba; Co and Hg. In all other cases, significant positive correlations exist at the level of 0.01 and 0.05.

PCA was used to identify the origin of PTIE in the topsoil. Kaiser-Meyer-Olkin (KMO) and Bartlett's test of sphericity were used to check the measures of sampling adequacy. In this study, the KMO (0.721) and Bartlett's test ($p < 0.001$) results indicated that PCA was suitable for analysis of the data set.

According to the PCA results first four principal components (PC) showed >1 eigenvalues (PC1–4.38; PC2–2.70; PC3–1.47 and PC4–1.27). Eigenvalue of PC5 was 0.87. The first four components varimax rotation results are shown in Table 4 and the 3D loading plot of PC1, PC2 and PC3 is presented in Fig. 6. PC1, PC2, PC3 and PC4 explained 70.14% of the total variance.

PC1 (31.27% of the total variance) showed strong positive loading for Ti, V, Mn, Fe and Co. This suggests that they may have natural origin, which is also confirmed by low values of PI and CV.

PC2 (19.32% of total variance) showed negative loadings for As and Hg and strong positive loadings for Zn and Pb. The latest have moderate positive loading also in PC3 (10.50% of the total variance), indicating quasi-independent behavior within the group. A strong positive loading for Cu and Mo was observed in PC3. Meanwhile, there were high PI and CV values of Pb, Zn, Cu and Mo in urban topsoil (Table 2), which implies that these PTIE in the topsoil may have originated from anthropogenic sources. The distribution maps showed that the high-value areas of these elements were mainly located in dense populated and industrial

Table 4
Factor loadings for varimax rotated PCA of studied elements data in topsoil samples.

Elements	Component			
	1	2	3	4
Ti	0.91[a]	0.10	−0.20	0.05
V	0.81[a]	0.20	0.06	−0.21
Cr	0.35	0.20	0.23	0.66[b]
Mn	0.79[a]	0.22	−0.03	0.08
Fe	0.92[a]	−0.04	0.13	0.11
Co	0.83[a]	−0.13	0.18	0.03
Ni	−0.07	0.10	0.00	0.83[a]
Cu	0.17	0.22	0.75[a]	0.24
Zn	0.06	0.68[b]	0.56[b]	0.20
As	−0.05	−0.64[b]	0.28	−0.05
Mo	−0.04	−0.05	0.80[a]	−0.14
Ba	0.34	0.47	0.26	−0.49
Hg	−0.12	−0.69[b]	−0.13	−0.04
Pb	−0.07	0.66[b]	0.50[b]	0.15
Eigenvalue	4.38	2.70	1.47	1.27
Variance %	31.27	19.32	10.50	9.06
Cumulative %	70.14			

[a] Strong (>0.7) loading.
[b] Moderate (0.5 − 0.7) loading.

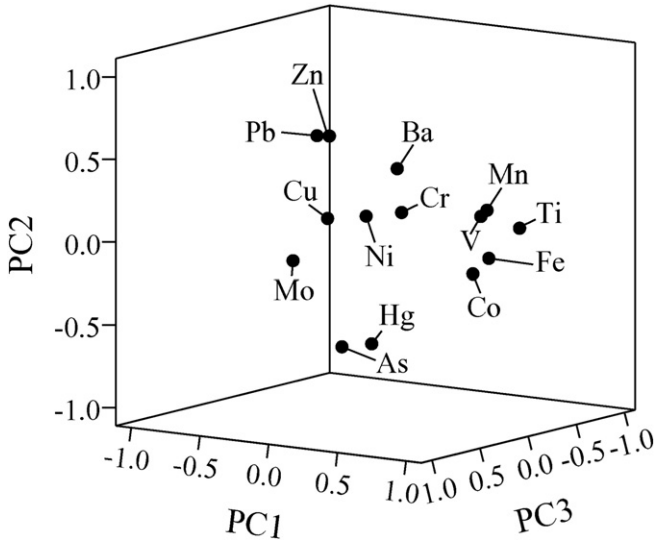

Fig. 6. PCA loading plots for the rotated components.

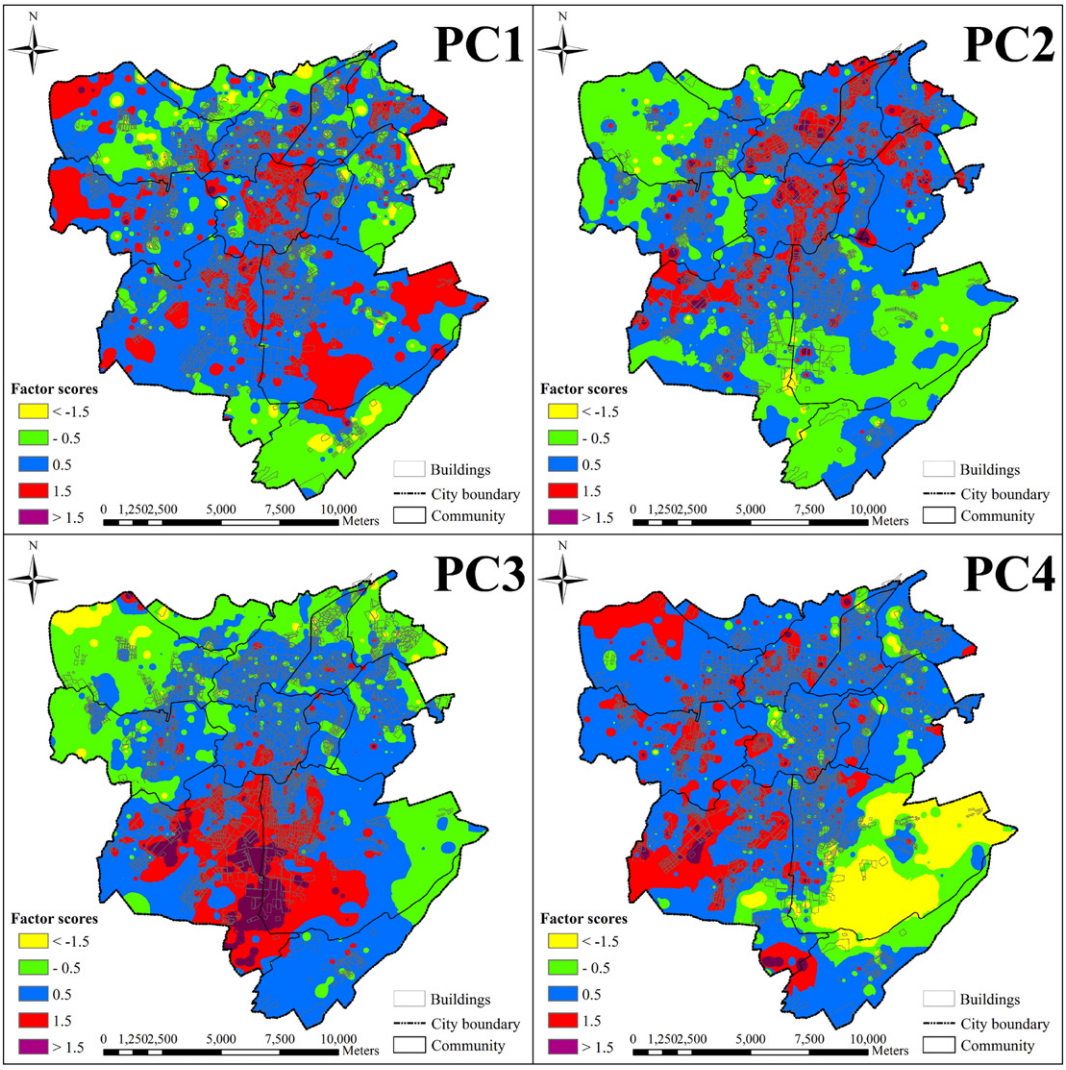

Fig. 7. Spatial distribution of the factor score (PC1; PC2; PC3 and PC4).

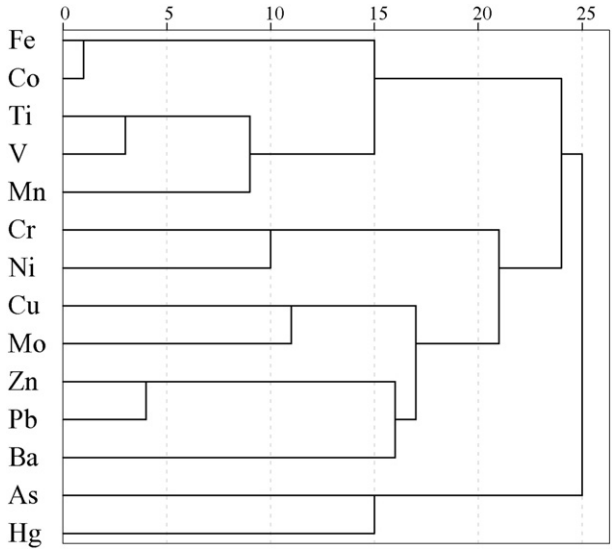

Fig. 8. Results of hierarchical cluster analysis of PTIE in the topsoil in the form of dendrogram (centroid clustering).

part of the city. For Pb, Zn and Cu, similar results were observed in other studies (Chabukdhara and Nema, 2013; Guo et al., 2012; Sun et al., 2010; Yuan et al., 2014). Previous studies showed that vehicle emissions were the principal source of Pb in the city of Yerevan (Saghatelyan, 2004; Sahakyan, 2008). After 2001, leaded gasoline ceased to be sold in Armenia. Other sources of Pb could be the road transport (i.e. brake lining) (Winther, 2010), Pb-based paints, coal burning, plastics and rubber production, and car batteries (Steinnes, 2013). As there is no other known essential source of Pb in the city, nowadays high concentrations of Pb are the result of the redistribution of historical pollution (Chabukdhara and Nema, 2013; Johnson et al., 2011). Cu might come from vehicle brake lining (Lindström, 2001), and Zn from the traffic emission, especially from the vehicle tires (Li et al., 2001). Except for road transport, the possible sources of Zn and Cu could be the plants located in industrial parts of the city. The highest concentration of these

Table 5
Statistics of potential ecological risk index of single element (E_r^i) and integrated potential ecological risk index (***RI***).

Statistics	Elements							RI
	Pb (E_r^i)	*Cr* (E_r^i)	*Zn* (E_r^i)	*Ni* (E_r^i)	*Cu* (E_r^i)	*As* (E_r^i)	*Hg* (E_r^i)	
Mean	114.3	3.4	3.3	10.2	12.8	11.2	270.1	425.3
Maximum	5754.6	42.8	341.1	269.7	451.0	70.8	635.3	5793.2
Minimum	2.6	0.7	0.5	0.6	3.2	0.8	11.8	53

Table 6
Risk grades indexes and levels of potential ecological risk of toxic elements pollution (Håkanson, 1980).

E_r^i	*RI*	Potential ecological risk grade
<40	<150	Low
40–80	150–300	Moderate
80–160	300–600	Considerable
160–320	–	High
>320	>600	Very high

elements were observed in south west of the city and are spatially associated with the location of industrial complex of metallic covers and corks, Ferro-concrete constructions plant, plant of production of accumulators, and plant of mechanical reconstruction. The highest concentrations of Mo are spatially allocated with Mo concentrate smelting and processing plants.

PC4 (9.06% of total variance) showed strong loadings for Ni and Cr with high PI and moderate CV values (Table 2), indicating other anthropogenic sources differ from PC2 and PC3. However, the distribution maps showed that in the industrial part of the city some high-value areas of Ni and Cr spatially overlap with those in case of Zn, Cu and Pb.

PC's spatial distribution is shown in Fig. 7 PC1 (including Ti, Fe, Co, V and Mn) high values are distributed in whole city area. High values of PC2 (including Pb, Zn, Hg and As) were manly located in the residential part of the city. In case of PC3 (including Pb, Zn, Cu and Mo) high values observed in the industrial part of the city. PC4 (including Ni and Cr) high values, besides south east part of the city, are distributed in entire city area.

3.4. Cluster analysis (CA)

Hierarchical CA was performed to check the results of the PC analysis for PTIE. The data were standardized to the Z score (with a mean of 0 and a standard variation of 1) and then classified using the Centroid clustering to avoid the influence of outliers of concentration. The distance measure used in CA was the Pearson correlation and results are represented in a dendrogram (Fig. 8).

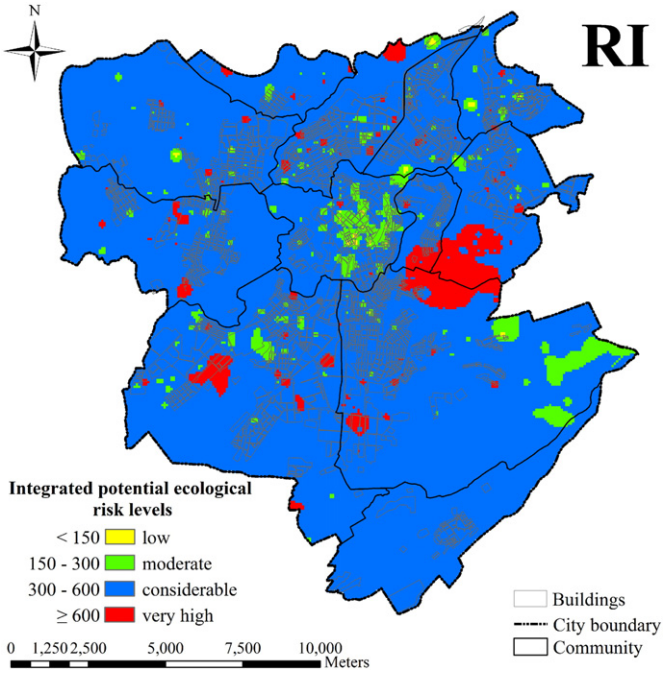

Fig. 9. Spatial distribution of the potential ecological risk indices (RI) for PTIE in the topsoil of the study area.

Three distinct clusters were observed from the dendrogram for the elements in the topsoil. Cluster I contained Ti, Fe, Co, V and Mn. Cluster II contained Pb, Cu, Zn, Mo, Cr, Ni and Ba. Besides Ba, all of these elements showed high PI values in the studied area. Cluster II comprises two sub clusters. The first sub cluster contained Cr and Ni, and the second Cu, Mo, Zn, Pb and Ba. Aside from Ba, all the elements in the Cluster II have previously been interpreted as anthropogenic.

Cluster III consisted of Hg and As, indicating that the properties of Hg and As in the topsoil were generally various from those of the elements in Cluster II. It is evident that the source of Hg and As in the soil was different from that of Zn, Pb, Cu, Ni, Cr. The CA also verified the PCA.

3.5. Potential ecological risk assessment

Single element (Hg, As, Pb, Cu, Ni, Cr, Zn) ($\boldsymbol{E_r^i}$) potential ecological risk indexes and integrated potential ecological risk index (***RI***) in the topsoil were computed (Table 5). $\boldsymbol{E_r^i}$ and ***RI*** indexes and classification of ecological risk levels are presented in Table 6.

Hg, As, Pb, Cu, Ni, Cr, and Zn $\boldsymbol{E_r^i}$ (Table 5) mean values in topsoil were classified by severity of potential ecological risk as Hg> > Pb> > Cu > As > Ni > Cr > Zn. Single element ($\boldsymbol{E_r^i}$) mean values of Cr, Zn, Ni, Cu and As was <40 and represent the low level of potential ecological risk. By the way, the maximum $\boldsymbol{E_r^i}$ values of Zn, Ni and Cu (341, 269.7 and 451.0 respectively) belong to the considerable potential ecological risk level, while for As and Cr: moderate potential ecological risk level (42.8 and 70.8 respectively). Hg and Pb had higher $\boldsymbol{E_r^i}$ mean values (Hg: 270.1; Pb: 114.3). Hg posed a high potential ecological risk in 62.6% and a very high potential ecological risk in 32.2% of all samples. Pb posed a considerable, high and very high potential ecological risk in 32.7%, 8.7% and 3% of all samples respectively.

Integrated potential ecological risk assessment of PTIE (Hg, As, Pb, Cu, Ni, Cr and Zn) showed that ***RI*** values in 14.2% of sampling sites were <300 (low to moderate ecological risk). The ***RI*** values between 300 and 600 were in 78.8% of sampling sites, indicating considerable potential ecological risk. In 7.0% topsoil samples ***RI*** values were >600; these areas were exposed to a very high potential ecological risk from PTIE. Highest ***RI*** values were located in the dense populated and plant areas (Fig. 9), which was consistent with the PC's scores spatial distribution (Fig. 7). Thus, industrial discharge and human activities were thought to be responsible for the highest potential ecological risk from pollution by multiple PTIE.

4. Conclusion

PI of As, Ti, Mn, Fe, Ba, Co is between 0.9–1.1. PI of Cu, Zn, Ni, Cr, V, Hg, and Mo were between 1.5–6.8. PI of Pb (22.9) was especially higher. Similar features of spatial distribution were observed for Pb, Cu, Zn, Ni and Cr. Generally, the "hot spots" observed in the territory of Yerevan could be separated into two types: (1) point shaped "hot spots" of single element; and (2) multi-element "hot spots" of PTIE. "Hot-spots" of all PTIE were spatially allocated in densely populated and industrial areas. Multivariate geo-statistical analyses suggested that Pb, Cu, Zn, Hg, Cr, Ni and Mo topsoil concentrations were influenced by anthropogenic and industrial activities. PCA showed that there were two distinct sources of origin for Pb and Zn: (1) vehicle emissions and social activities; and (2) industrial activities. Hg, As, Pb, Cu, Ni, Cr, Zn by the mean values of $\boldsymbol{E_r^i}$ were ranked as follows: Hg> > Pb> > Cu > As > Ni > Cr > Zn. Pb and Hg showed a higher potential ecological risk than the others. 14.2% of the samples were exposed to low and moderate, 78.8% to considerable and only 7% to very high RI.

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References

Acosta, J.A., Faz, A., Martínez-Martínez, S., Zornoza, R., Carmona, D.M., Kabas, S., 2011. Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. J. Geochem. Explor. 109, 8–17. http://dx.doi.org/10.1016/j.gexplo.2011.01.004.

Albanese, S., Cicchella, D., 2012. Legacy problems in urban geochemistry. Elements 8, 423–428. http://dx.doi.org/10.2113/gselements.8.6.423.

Alekseenko, V., Alekseenko, A., 2014. The abundances of chemical elements in urban soils. J. Geochem. Explor. 147, 245–249. http://dx.doi.org/10.1016/j.gexplo.2014.08.003.

Carr, R., Zhang, C., Moles, N., Harder, M., 2008. Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. Environ. Geochem. Health 30, 45–52. http://dx.doi.org/10.1007/s10653-007-9106-0.

Chabukdhara, M., Nema, A.K., 2013. Heavy metals assessment in urban soil around industrial clusters in Ghaziabad, India: probabilistic health risk approach. Ecotoxicol. Environ. Saf. 87, 57–64. http://dx.doi.org/10.1016/j.ecoenv.2012.08.032.

Charlesworth, S., Miguel, E. De, Ordonez, A., 2011. A review of the distribution of particulate trace elements in urban terrestrial environments and its application to considerations of risk. Environ. Geochem. Health 33, 103–123. http://dx.doi.org/10.1007/s10653-010-9325-7.

Cicchella, D., De Vivo, B., Lima, A., 2005. Background and baseline concentration values of elements harmful to human health in the volcanic soils of the metropolitan and provincial areas of Napoli (Italy). Geochem. Explor. Environ. Anal. 5, 29–40. http://dx.doi.org/10.1144/1467-7873/03-042.

Cicchella, D., De Vivo, B., Lima, A., Albanese, S., McGill, R.A.R., Parrish, R.R., 2008. Heavy metal pollution and Pb isotopes in urban soils of Napoli, Italy. Geochemistry Explor. Environ. Anal. 8, 103–112. http://dx.doi.org/10.1144/1467-7873/07-148.

Filippelli, G.M., Morrison, D., Cicchella, D., 2012. Urban geochemistry and human health. Elements 8, 439–444. http://dx.doi.org/10.2113/gselements.8.6.439.

Guo, G., Wu, F., Xie, F., Zhang, R., 2012. Spatial distribution and pollution assessment of heavy metals in urban soils from Southwest China. J. Environ. Sci. 24, 410–418. http://dx.doi.org/10.1016/S1001-0742(11)60762-6.

Håkanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14, 975–1001. http://dx.doi.org/10.1016/0043-1354(80)90143-8.

Hovhannisyan, H.A., 2004. Ecological monitoring of vegetables grown in urban sites. Electron. J. Nat. Sci. 2, 10–13 (NAS RA).

Hovhannisyan, H.A., Nersisyan, G.S., Saghatelyan, A.K., 2012. Ecological assessment of heavy metal pollution of vegetable in Yerevan (Armenia). Safe Food, XVI International Eco-Conference, pp. 331–336.

ISO, 1994. ISO 5725-1:1994 - Accuracy (Trueness and Precision) of Measurement Methods and Results – Part 1: General Principles and Definitions [WWW Document]. URL http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=11833 (accessed 3.2.16).

Johnson, C.C., Demetriades, A., Locutura, J., Ottesen, R.T., 2011. Mapping the Chemical Environment of Urban Areas.

Krishna, A.K., Govil, P.K., 2007. Assessment of heavy metal contamination in soils around Manali industrial area, Chennai, Southern India. Environ. Geol. 54, 1465–1472. http://dx.doi.org/10.1007/s00254-007-0927-z.

Lee, C.S.-L., Li, X., Shi, W., Cheung, S.C., Thornton, I., 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Sci. Total Environ. 356, 45–61. http://dx.doi.org/10.1016/j.scitotenv.2005.03.024.

Li, X., Poon, C., Liu, P.S., 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. Appl. Geochem. 16, 1361–1368. http://dx.doi.org/10.1016/S0883-2927(01)00045-2.

Lindström, M., 2001. Urban land use influences on heavy metal fluxes and surface sediment concentrations of small lakes. Water Air Soil Pollut. 126, 363–383. http://dx.doi.org/10.1023/A:1005291611702.

Ljung, K., Otabbong, E., Selinus, O., 2006. Natural and anthropogenic metal inputs to soils in urban Uppsala, Sweden. Environ. Geochem. Health 28, 353–364. http://dx.doi.org/10.1007/s10653-005-9031-z.

Luo, X., Yu, S., Li, X., 2011. Distribution, availability, and sources of trace metals in different particle size fractions of urban soils in Hong Kong: implications for assessing the risk to human health. Environ. Pollut. 159, 1317–1326. http://dx.doi.org/10.1016/j.envpol.2011.01.013.

Luo, X., Yu, S., Zhu, Y., Li, X., 2012. Trace metal contamination in urban soils of China. Sci. Total Environ. 421-422, 17–30. http://dx.doi.org/10.1016/j.scitotenv.2011.04.020.

Madrid, L., Díaz-Barrientos, E., Madrid, F., 2002. Distribution of heavy metal contents of urban soils in parks of Seville. Chemosphere 49, 1301–1308. http://dx.doi.org/10.1016/S0045-6535(02)00530-1.

Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background - can we calculate it? Environ. Geol. 39, 990–1000. http://dx.doi.org/10.1007/s002549900084.

Morel, J.-L., Heinrich, A.B., 2008. SUITMA—soils in urban, industrial, traffic, mining and military areas. J. Soils Sediments 8, 206–207. http://dx.doi.org/10.1007/s11368-008-0023-3.

Nalbandyan, M.A., Saghatelyan, A.K., 2002. Ecotoxicological Characteristic of Yerevan Environment Pollution, In: Ecotoxicological Assessment of Pollution Risk of the Caucasus' Environment. pp. 166–171.

Nalbandyan, M.A., Grigoryan, L.M., Mikaelyan, M.G., 2003. Peculiarities of heavy metal pollution of water bodies in the bounds of Yerevan conglomeration. Mater. IV Repub. Youth Conf. "XXI Century Ecol. Sci. Armen. CENS NAS RA.

Perelman, A.I., Kasimov, N.S., 1999. Landscape Geochemistry.

Preston, J., Engel, B., Lalor, G.C., Vutchkov, M.K., 1996. The application of geographic information systems to geochemical studies in Jamaica. Environ. Geochem. Health 18, 99–104. http://dx.doi.org/10.1007/BF01771285.

RA Government decision, 2015. About the Order of Evaluation of Agricultural Activities – Caused Impact on Soil Resources. http://www.arlis.am/DocumentView.aspx?DocID=13401 (Armenia).

Reiman, C., Filzmoser, P., Garrett, R.G., Dutter, R., 2008. Statistical Data Analysis Explained: Applied Environmental Statistics With R. John Wiley & Sons, Ltd. http://dx.doi.org/10.1002/9780470987605.

Reimann, C., 2005. Geochemical mapping: technique or art? Geochem. Explor. Environ. Anal. 5, 359–370. http://dx.doi.org/10.1144/1467-7873/03-051.

Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Sci. Total Environ. 346, 1–16. http://dx.doi.org/10.1016/j.scitotenv.2004.11.023.

Saghatelyan, A.K., 2004. Peculiarities of Heavy Metal Distribution on the Territory of Armenia. CENS NAS RA, Yerevan.

Saghatelyan, A.K., Nalbandyan, M.A., 2005. A complex assessment of ecological status of River Hrazdan. Problems of River Monitoring and Ecological Safety of the South Caucasus, pp. 83–87.

Saghatelyan, A.K., Arevshatyan, S.H., Sahakyan, L.V., 2003. Ecological-geochemical assessment of heavy metal pollution of the territory of Yerevan. Electron. J. Nat. Sci. 1, 36–41 (NAS RA).

Saghatelyan, A., Sahakyan, L., Belyaeva, O., Maghakyan, N., 2014. Studying atmospheric dust and heavy metals on urban sites through synchronous use of different methods. J. Atmos. Pollut. 2, 12–16. http://dx.doi.org/10.12691/jap-2-1-3.

Sahakyan, L.V., 2006. The assessment of heavy metal stream in the air basin of Yerevan. Chin. J. Geochem. 25, 95–96. http://dx.doi.org/10.1007/BF02839921.

Sahakyan, L.V., 2008. Peculiarities of the Dynamics of Yerevan Soil Pollution With Heavy Metals (Ag, Pb, Cu, Zn, Ni, Co, Cr, Mo).

Steinnes, E., 2013. Lead. Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability, pp. 395–409 http://dx.doi.org/10.1007/978-94-007-4470-7.

Sun, Y., Zhou, Q., Xie, X., Liu, R., 2010. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. J. Hazard. Mater. 174, 455–462. http://dx.doi.org/10.1016/j.jhazmat.2009.09.074.

US EPA, 2007. Field portable x-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment. Method 6200.

US EPA Method 6200, 2007. Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment [WWW Document]. URL http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/3dc283e6c5d6056f88257426007417a2/e599199dc919b049882576a300616943/$file/attachment1.pdf#_ga=1.260838029.1899728909.1418825614

Vardanyan, M., 2006. National Atlas of Armenia. Tigran Mets, Yerevan.

Wang, X.S., Qin, Y., 2005. Correlation between magnetic susceptibility and heavy metals in urban topsoil: a case study from the city of Xuzhou, China. Environ. Geol. 49, 10–18. http://dx.doi.org/10.1007/s00254-005-0015-1.

Winther, M.S.E., 2010. Heavy Metal Emissions for Danish Road Transport.

Wong, C.S.C., Li, X., Thornton, I., 2006. Urban environmental geochemistry of trace metals. Environ. Pollut. 142, 1–16. http://dx.doi.org/10.1016/j.envpol.2005.09.004.

Yuan, G.-L., Sun, T.-H., Han, P., Li, J., Lang, X.-X., 2014. Source identification and ecological risk assessment of heavy metals in topsoil using environmental geochemical mapping: Typical urban renewal area in Beijing, China. J. Geochem. Explor. 136, 40–47. http://dx.doi.org/10.1016/j.gexplo.2013.10.002.

Zglobicki, W., Lata, L., Plak, A., Reszka, M., Zgłobicki, W., 2011. Geochemical and statistical approach to evaluate background concentrations of Cd, Cu, Pb and Zn (case study: Eastern Poland). Environ. Earth Sci. 62, 347–355. http://dx.doi.org/10.1007/s12665-010-0529-z.

Zhang, C., Qiao, Q., Piper, J.D.A., Huang, B., 2011. Assessment of heavy metal pollution from a Fe-smelting plant in urban river sediments using environmental magnetic and geochemical methods. Environ. Pollut. 159, 3057–3070. http://dx.doi.org/10.1016/j.envpol.2011.04.006.

Zhao, W., Ding, L., Gu, X., Luo, J., Liu, Y., Guo, L., Shi, Y., Huang, T., Cheng, S., 2015. Levels and ecological risk assessment of metals in soils from a typical e-waste recycling region in southeast China. Ecotoxicology 24, 1947–1960. http://dx.doi.org/10.1007/s10646-015-1532-7.

Zhou, F., Guo, H., Liu, L., 2007. Quantitative identification and source apportionment of anthropogenic heavy metals in marine sediment of Hong Kong. Environ. Geol. 53, 295–305. http://dx.doi.org/10.1007/s00254-007-0644-7.