Geospatial mapping, source identification and human health risk assessment of heavy metals in soils of Gyumri (Armenia)

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Abstract

Gyumri was destroyed by a devastating earthquake in 1988. Today the city is in the reconstruction stage, and noticeable traces of earthquake are a significant pollution source of the urban environment by heavy metals (HM). To assess HM pollution levels, to identify their possible sources and evaluate the potential impact to human health soils survey of Gyumri was done. Totally, 443 soil samples were collected, and the contents Fe, Ti, Mn, Co, Cu, As, Zn, Hg, Pb, Cd, Ag, Ba, and Mo have been determined by X-ray fluorescence spectrometry (Olympus Innov-X-5000 (USA)). Geospatial mapping and multivariate geostatistical analysis showed that there exist a significant spatial correlation between pollution sources and hot spots of studied elements. According to the Principal component analysis, four groups were generated explaining 73.4% of the total variance. PC1 including Cu, Zn, Ba, Pb and Mo, PC3: Ag and Cd, and PC4: Cu, Co and As were identified as an anthropogenic group. Risk assessment showed that observed contents of HM pose a non-carcinogenic risk to children health. The riskiest element was Pb which HI>1 in 1.6% of city territory. The results of this study highlight the need for further medico-ecological investigations and development of risk reduction measures.

Keywords: Heavy metals, urban soils, pollution, mapping, geostatistical analysis

1. Introduction

In urban areas, human activities change the soil environment and their properties (Johnson *et al.*, 2011). Acting as a geochemical sink for various hazardous contaminants urban soils can impact the health of the urban population (Filippelli *et al.*, 2012). Among soil contaminants, particular attention is given to heavy metals (HM) (Gu *et al.*, 2016; Peña-Fernández *et al.*, 2014; Wong *et al.*, 2006) which are known to cause different disorders when entering into the human organism (US EPA, 1989). For this reason human health risk assessment was done in different parts of the world (Gu *et al.*, 2016; Peña-Fernández *et al.*, 2014) and the results obtained (Lee *et al.*, 2006; Lu *et al.*, 2011; Rapant *et al.*, 2010) indicated that the model proposed by US EPA (Pepper *et al.*, 2011; US EPA, 1989) is applicable for the soils. Gyumri - Armenia's second biggest city, destroyed by the Spitak Earthquake in 1988. After that, during last 25 years the remnants of the disaster (collapsed buildings, debris and other garbage dumps, etc.) and post-earthquake industrial and social activities, as well as significantly mixed anthropogenic (asphalt, concrete, gravel layers, etc.) and natural horizons completely change the environmental status of the city. Therefore, Gyumri soils survey was done (2013) and the goal of this research was to assess HM pollution levels, to identify their possible sources and evaluate the potential impact to human health.

2. Methods and materials

2.1. Sampling and chemical analysis

Pedogeochemical survey of Gyumri was done on a scale 1:25000 (16 samples per/sq.km) in August 2013. Totally, 443 soil samples collected (Fig.1). To establish Gyumri soils HM local background (LB) 33 rural soils samples from the adjacent villages were collected. A bulk sample was generated by mixing of 3-5 randomly collected subsamples. In the laboratory, samples were air-dried, homogenized and sieved (2 mm), milled according to ISO-11464 (BSI Standards Limited., 2006). The total contents of 13 elements (Ti, Mn, Fe, Co, Cu, Zn, As, Mo, Ba, Hg, Pb, Ag, Cd) determined by XRF spectrometry (US EPA Method 6200, 2007). To ensure the quality assurance and quality control of the analysis, standard samples (NIST 2710a and NIST 2711a, USA), a blank (SiO_2) of NIST USA and 5.2% lab duplicate samples were analyzed. Precision for studied HM ranges 0.9-17.4%, and accuracy was < 20%. locations of industrial units in the city of Gyumri.

2.2. Statistical analysis and geospatial mapping

Descriptive statistics of datasets are summarized in Table 2. Principal Component Analysis (PCA) was performed to group studied HM and identifies their potential sources. Geospatial mapping was done to illustrate the spatial distribution of HM pollution levels, to juxtaposition them with the location of possible sources and to identify riskiest areas. Colour surface maps were created by IDW method (the power - 2, the number of neighboring samples - 8) using ArcGIS 10.1.

2.3. Pollution levels and human health risk assessment

To study city soils poly-elemental pollution levels the summary pollution index (Zc) (Johnson *et al*., 2011; Perelman and Kasimov, 1999) calculated using the following formulae:

$$K_c = C_i / C_b, \text{ (1)},$$

$$Z_c = \sum_{i=1}^{n} K_c - (n-1), \text{ (2)},$$

where *Kc* is anomaly coefficient, C_i is the concentration of studied HM in the sample, C_b is the LB values, *n* is the number of elements with *Kc>1*. Zc was classified as low level (*Zc<16*), mean i.e**.** moderately hazardous level (16<Zc<32), high i.e. hazardous level (*32<Zc<128*), and very high i.e. extremely hazardous level (*Zc>128*) (Perelman and Kasimov, 1999).

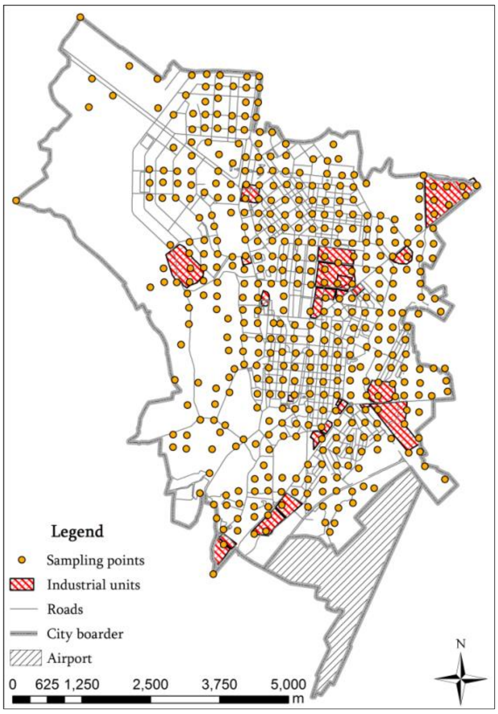

Figure 1. Spatial distribution of soil sampling points and

Non-carcinogenic risk assessment was done, and as a preferential exposure pathway of HM for humans, soil ingestion was chosen. In this study non-carcinogenic risk was assessed for Ag, As, Ba, Cd, Co, Cu, Fe, Hg, Mn, Mo, Pb and Zn due to the lack of quantitative information concerning elements toxicity level and impact to the human health. Non-carcinogenic risk (RAIS, 2017) calculated by the following formula:

$$CDI_{childre,adult} = \frac{C * EF * ED * IRS * CF}{AT \times BW}, \text{ (3)}$$

where: C is the element concentration in soil (mg/kg), IRS is ingestion rate: in the case of children 200 mg/day, for adults 100 mg/day; ED is exposure duration: for children 6 years and for adults 26 years; EF is exposure frequency: 350 days/year (RAIS, 2017), BW is average body weight: 15 kg for children and 70 kg for adults (US EPA, 1989).

Non-carcinogenic hazard quotient per element was calculated by the formula (3).

$$HQ = \frac{CDI}{RfD}, \text{ (4)}$$

where: RfD is a reference dose for a corresponding element (Table 1). The sum of HQ values represents a Hazard Index $HI=\Sigma HQ_i$. HI<1 indicates the absence of significant non-carcinogenic health risk, whereas HI>1 denotes a possibility of adverse health effects (RAIS, 2017; US EPA, 1989).

Table 1. Defined oral reference doses (RfD, $mg/kg^{-1}\ day^{-1}$) for evaluated risk elements

Heavy metals	RfD	Data source
As	0.0003	(RAIS, 2017)
Cr	0.003	
Hg	0.00016	
Pb	0.0035	(WHO, 2008)
Cu	0.04	(RAIS, 2017)
Zn	0.3	
Mo	0.005	
Ni	0.02	
Co	0.0003	
Mn	0.024	
Ba	0.2	
V	0.00504	

3. Results and discussion

3.1. Heavy metals contents

Descriptive statistics of the contents of HM (Ti, Mn, Fe, Co, Cu, Zn, As, Mo, Ba, Hg, Pb, Ag, and Cd) in Gyumri soils, LB values and Predicted Empirical Global Soil (PEGS2) reference values (De Caritat *et al*., 2012) are given in Table 2. For all HM (Table 2) skewness is different from 0, indicating nonnormality of the data distribution. Moreover, the comparison of mean and 5% trimmed mean showing the presence of outliers and extreme values in the case of Cu, Zn, Pb, Ag, and Cd. Besides Cu, all these elements showed a significant value of CV: 119.1%, 180.4%, 222.1% and 119.8% for Zn, Pb, Ag and Cd, respectively. Excesses of mean contents vs. PEGS2 and vs. LB observed for Cu, Zn, Pb, Ag and Cd 4.1, 4.4, 4.8, 5.4 և 6.1 times, and 1.4, 2.1, 3.5, 1.9 and 6.0 time, correspondingly. The latter inferred the anthropogenic origin of these HM. The mean values of Ti, Mn, Fe, Co, As, Hg and Ba vs. LB ranges 0.8-1.1, suggesting that the differences in comparison with PEGS2 values of Mn, Fe, Co, As, Hg, Ba, and Mo can be the outcome of local peculiarities of origin and spatial distribution of these elements.

3.2. Principal component analysis of heavy metals in Gyumri soils

According to the PCA results first four principal components (PC) showed >1 eigenvalues (PC1-3.4; PC2-3.3; PC3-1.7 and PC4-1.1) and explained 73.4 % of the total variance.PC1 (26.5% of the total variance) showed strong (>0.7) positive loading for Zn, Pb, Ba, moderate (>0.5) positive loading for Cu, Mo. Negative moderate loading of Hg in PC1 inferred other sources of origin that .

Table 2. Descriptive statistics, local background (LB) and Predicted Empirical Global Soil (PEGS2) reference values of studied heavy metals (mg/kg)

Elements	Parameters									
	Mean	5% Trimmed Mean	Median	SD	Min	Max	Skew	CV, %	PEGS2	LB
Ti	3011.8	2983.1	2957.0	511.6	1352.0	9117.0	4.2	17.0	-	3381
Mn	640.8	635.6	626.0	101.6	335.0	1068.0	0.8	15.9	370.0	805.5
Fe	31439.1	31353.8	30916.0	3956.6	13118.0	45881.0	0.3	12.6	17066.0	32379
Co	5.1	5.1	5.03	0.73	1.6	8.3	0.6	14.3	9.0	5
Cu	53.7	50.1	47.9	26.8	25.1	289.0	4.7	49.9	13.0	39
Zn	207.7	180.0	162.4	247.3	42.8	4071.0	9.9	119.1	47.0	100
As	0.75	0.74	0.75	0.20	0.2	3.5	7.8	27.2	5.0	0.68
Ba	519.6	505.1	505.0	170.5	214.0	3077.0	11.1	32.8	353.0	526.5
Pb	80.9	60.2	50.8	145.9	5.4	1714.0	7.9	180.4	17.0	23.2
Ag	0.14	0.10	0.10	0.30	0.0002	3.3	8.4	222.1	0.025	0.07
Cd	0.67	0.57	0.41	0.80	0.002	7.0	3.1	119.8	0.11	0.11
Mo	0.47	0.45	0.47	0.27	0.08	3.2	4.7	58.1	0.31	2
Hg	0.07	0.07	0.07	0.04	0.01	0.38	2.1	52.3	-	0.07

those in the case of Zn, Pb, Ba, Cu and Mo. The visualization of PC scores (Fig. 2) showed that high values (>0.5) of PC1 are spatially allocated near industrial units and in densely populated part of the city suggesting that PC1 is an anthropogenic group. The latter is also confirmed by high values CV of some elements included in PC1. For Pb, Zn and Cu, similar results were observed in the case of Yerevan (Tepanosyan *et al*., 2016) and other studies worldwide (Chabukdhara and Nema, 2013; Guo *et al*., 2012; Sun *et al*., 2010; Yuan *et al*., 2014).PC2 (25.1% of total variance) showed strong positive loadings for Fe, Ti, Mn, and Co indicating they may have a natural origin, which is also confirmed by low values of CV. However, Co with Cu (moderate positive loading) and As (strong positive loading) formed also PC4 (8.5% of total variance). The latter can be explained by the presence of Gyumri bicycle plant which operated before the earthquake. This plant is known by its workshops of metal plating and paint-and-lacquer coating, assemblage and woodworking, pressing which were potential sources of Co, Cu and As. Thus, although the contents of Co in city soils have mainly natural origin, there still exist some local sites where the fingerprint of historical pollution observed. PC3 (13.3% of total variance) showed strong positive loadings for Ag and Cd. The detailed inspection of the PC3 map (Fig. 2) revealed that significant areas of high scores are spatially associated with industrial units located in the eastern and south parts of the city. Th latter suggests that PC3 is an anthropogenic group which confirmed by the high values of CV of Ag and Cd.

3.3. Pollution levels and human health risk

A low level (Zc<16) of summary pollution index (Fig. 3) was observed in 75.2% of the city (33.4sq.km, 317 soil samples). Mean pollution level covers 22.3% (9.9sq.km, 102 soil samples) of the area and is spatially distributed in the central part of the city. High level of pollution have a local character, point-like shape and are surrounded by mean pollution level. High level occupies only 2.5% (1.1.sq.km. 24 soil samples) of the city area. Extremely high pollution level has not been found. It should be mentioned that mean and high levels poly-element pollution are found mainly near industrial units and densely populated parts of Gyumri. Human health risk assessment showed that in the case of adults HI<1. However, children's health non-carcinogenic risk (Fig. 3) observed in the whole area of the city indicating adverse health effect for children. Mean HQ values of studied HM decrease in the order of Fe>Mn>Pb>Co>Cu>Ba>As>Cd>Hg>Mo>Ag>Zn. The HQ>1 observed only for Cu (1 sampling site) and Pb (17 sampling site).

4. Conclusions

The study revealed that the excesses of mean vs. LB and vs. PEGS2 observed for Cu, Zn, Pb, Ag and Cd ranges1.4-6.0, and 4.1-6.1, respectively, indicating that the concentrations of these HM influenced by anthropogenic and industrial activities. Also, based on the PCA results, three groups of HM identified as having an anthropogenic origin. According to the Zc values, low level of pollution observed in 75.2% of Gyumri area. The areas of medium and high pollution levels lie near industrial units and in densely populated parts of the city. Human health risk assessment revealed that in whole city HM in soils serves as risk factors for children's health. The riskiest element was Pb. Therefore, more detailed investigations and risk reduction measures needed.

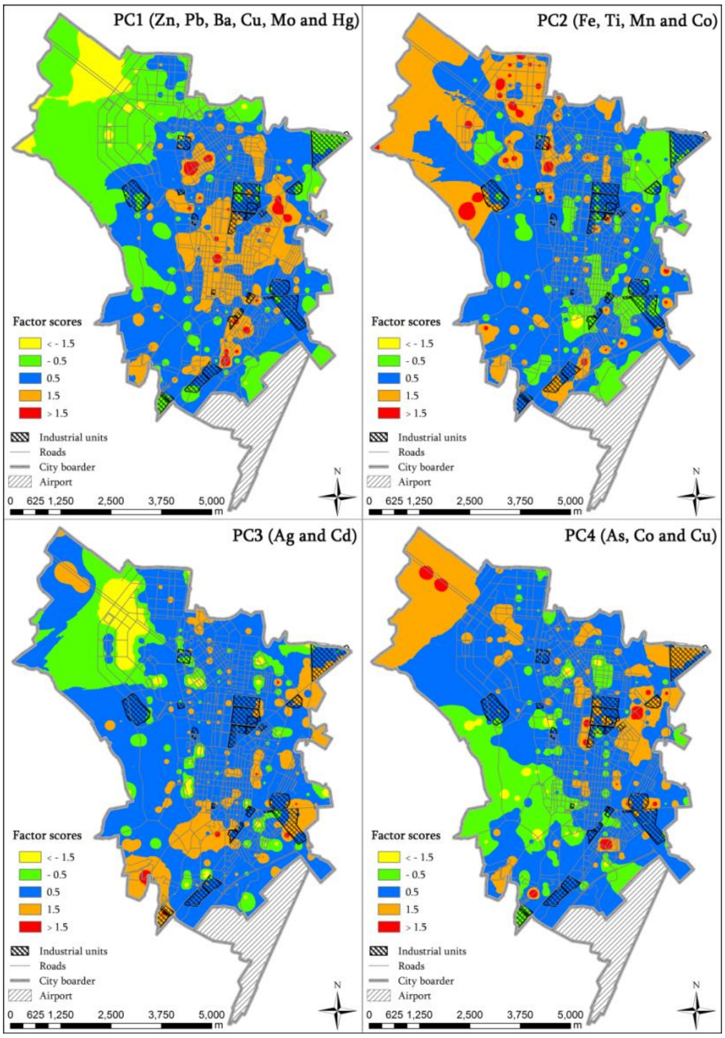

Figure 2. Spatial distribution of PC scores in the city of Gyumri

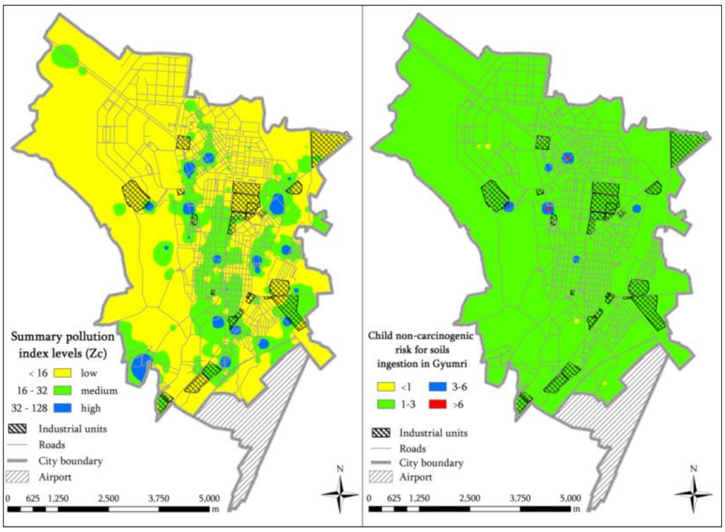

Figure 3. Spatial distribution of soils HM pollution and health risk levels in the city of Gyumri

References

BSI Standards Limited., 2006. BS ISO 11464:2006 Soil quality. Pretreatment of samples for physio-chemical analysis.

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. doi:10.1016/j.ecoenv.2012.08.032

De Caritat, P., Reimann, C., Bastrakov, E., NGSA Project Team and GEMAS Project Team, 2012.. Comparing results from two continental geochemical surveys to world soil composition and deriving Predicted Empirical Global Soil (PEGS2) reference values. Earth Planet. Sci. Lett. 319–320, 269–276. doi:10.1016/j.epsl.2011.12.033

Filippelli, G.M., Morrison, D., Cicchella, D., 2012. Urban Geochemistry and Human Health. Elements 8, 439–444. doi:10.2113/gselements.8.6.439

Gu, Y.-G., Gao, Y.-P., Lin, Q., 2016. Contamination, bioaccessibility and human health risk of heavy metals in exposed-lawn soils from 28 urban parks in southern China's largest city, Guangzhou. Appl. Geochemistry 67, 52–58. doi:10.1016/j.apgeochem.2016.02.004

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. doi:10.1016/S1001-0742(11)60762-6

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

Lee, S.-W., Lee, B.-T., Kim, J.-Y., Kim, K.-W., Lee, J.-S., 2006. Human risk assessment for heavy metals and as contamination in the abandoned metal mine areas, Korea. Environ. Monit. Assess. 119, 233–44. doi:10.1007/s10661-005-9024-5

Lu, Y., Yin, W., Huang, L., Zhang, G., Zhao, Y., 2011. Assessment of bioaccessibility and exposure risk of arsenic and lead in urban soils of Guangzhou City, China. Environ. Geochem. Health 33, 93–102. doi:10.1007/s10653-010-9324-8

Peña-Fernández, a., González-Muñoz, M.J., Lobo-Bedmar, M.C., 2014. Establishing the importance of human health risk assessment for metals and metalloids in urban environments. Environ. Int. 72, 176–185. doi:10.1016/j.envint.2014.04.007

Pepper, I.L., Gerba, C.P., Brusseau, M.L., 2011. Environmental and Pollution Science. Academic Press.

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

RAIS, 2017. Risk Exposure Models for Chemicals User's Guide [WWW Document]. Risk Assess. Inf. Syst. URL https://rais.ornl.gov/tools/rais_chemical_risk_guide.html (accessed 1.1.17).

Rapant, S., Fajčíková, K., Khun, M., Cvečková, V., 2010. Application of health risk assessment method for geological environment at national and regional scales. Environ. Earth Sci. 64, 513–521. doi:10.1007/s12665-010-0875-x

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. doi:10.1016/j.jhazmat.2009.09.074

Tepanosyan, G., Sahakyan, L., Belyaeva, O., Saghatelyan, A., 2016. Origin identification and potential ecological risk assessment of potentially toxic inorganic elements in the topsoil of the city of Yerevan, Armenia. J. Geochemical Explor. 167, 1–11. doi:10.1016/j.gexplo.2016.04.006

US EPA, 1989. Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (HHEM). Part A. Baseline risk assessment. EPA/540/1-89/002.

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/attachment 1.pdf#_ga=1.260838029.1899728909.1418825614

WHO, 2008. Guidelines for drinking-water quality - Volume 1: Recommendations. Third Ed. Inc. first Second addenda 668.

Wong, C.S.C., Li, X., Thornton, I., 2006. Urban environmental geochemistry of trace metals. Environ. Pollut. 142, 1–16. doi: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. Geochemical Explor. 136, 40–47. doi:10.1016/j.gexplo.2013.10.002