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Continuous impact of mining activities on soil heavy metals levels and human health

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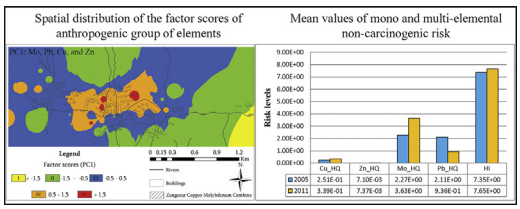
HIGHLIGHTS

- Anthropogenically predominant groups of elements include Mo, Cu, Zn and Pb.
- Superposition of natural and anthropogenic factors formed highly polluted areas.
- Multi-elemental non-carcinogenic risk to children health detected.

GRAPHICAL ABSTRACT



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ABSTRACT

Soils samples collected during different geochemical surveys of the city of Kajaran located near the biggest Cu-Mo mining area in Armenia were subjected to the multivariate geostatistical analysis and geochemical mapping in order to reveal soil heavy metals spatial distribution pattern and assess human health risk level under continuous impact of mining activities. In addition, human health risk assessment was done for the contents of Pb, Cu, Zn, Co, Mo, Mn, Ti, and Fe.

The results of Principal Component Analysis and Cluster Analysis verify each other and were also complemented by the spatial distribution features of studied heavy metals indicating that two groups of elements have been generated. The first anthropogenically predominated group includes the main industrial elements Mo and Cu, and their accessories Pb and Zn while Ti, Mn, Fe and Co with the naturally predominant contents were observed in the second group. Moreover, the study reveals that the superposition of geogenic and anthropogenic components lead to the alteration of the shapes of areas with the high natural contents of heavy metals and formation of polluted areas with the intensive anomalies of elements.

Health risk assessment showed that Mo was the only studied element which poses a non-carcinogenic risk to adult and children's health in some sampling sites during the whole period of investigations. Moreover, in all studied locations multi-elemental non-carcinogenic risk to children health from all studied heavy metals were detected. Special attention was given to the soils of kindergarten territories, and the results indicated that Hazard Index in kindergartens was >1 indicating an adverse health effect to children. The results obtained can serve as a basis for the development and implementation of risks reduction measures and systematic monitoring program planning.

1. Introduction

Mining industry is both a leading factor of economic development in a country and a significant source of environmental pollution by heavy metals (Anju and Banerjee, 2012; Carkovic et al., 2016; Chakraborty et al., 2017; Ding et al., 2017; Li et al., 2014; Martínez López et al., 2008). In this respect, the anthropogenic contents of heavy metals

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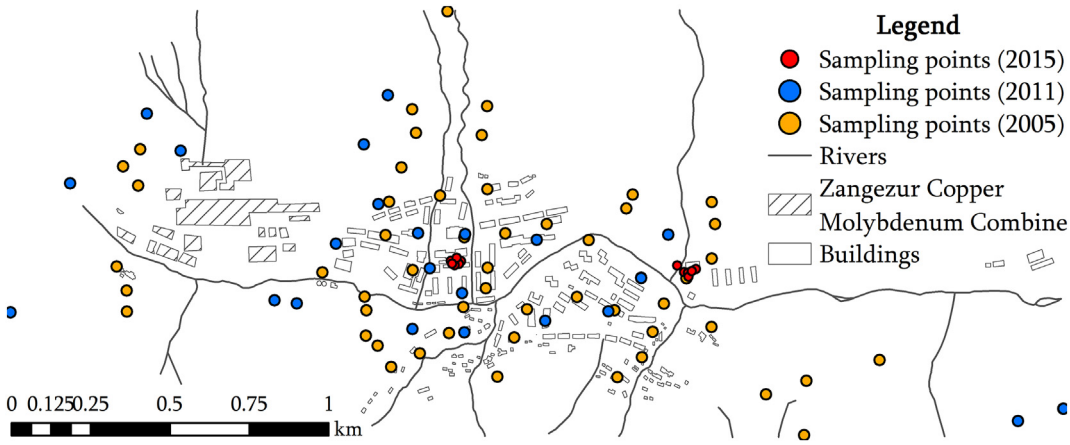

Fig. 1. Soils sampling points in 2005, 2011 and 2015 of the city of Kajaran.

may become a human health risk factor. It has been repeatedly demonstrated through the investigations of cities (Gabari and Fernández-Caliani, 2017; Kamunda et al., 2016; Lee et al., 2006; Martínez López et al., 2008; Saghatelyan et al., 2010; Wu et al., 2010) located near mining complexes. To describe the integrated fingerprint of long-term pollution, soils of such cities should be studied first, as they accumulate both pollutions through the diffusion and emission from the point sources (Chakraborty et al., 2017; Johnson et al., 2011; Protano and Nannoni, 2018). Moreover, peculiarities of heavy metal migration in the environment of cities, as well as final shapes of polluted areas and conditions of their formation highly depend on the accumulative and barrier features of the soils (Golovin et al., 2004).

The city of Kajaran is the biggest mining industrial center of the Republic of Armenia and accommodates the Zangezur Copper Molybdenum Combine (ZCMC). In the city, systematic multipurpose geochemical studies were performed since 2005 by The Center for Ecological-Noosphere Studies (CENS) (Saghatelyan et al., 2010). The results of the studies indicated that Kajaran soils are polluted by heavy metals (Ghazaryan et al., 2017; Saghatelyan et al., 2008, 2010). Moreover, the Artsvanic tailing repository of the ZCMC is located 42 km away northwest from Kajaran. The so-called "clean" water of the tailing repository is discharging into the main river Voghchi through its effluents, thus polluting the agroecosystems irrigated by the water of the river and its affluents (Saghatelyan et al., 2008, 2010).

The impact of the mining activities of ZCMC was also traced in Yerevan, the capital and industrial center of Armenia. Particularly, the "Plant of Pure Iron" and "Armenian Molybdenum Production" located in the southern industrial district of Yerevan is operating on the base of molybdenum concentrate (containing 50% of molybdenum) received from Kajaran. The products of the "Plant of Pure Iron" include ferromolybdenum, molybdenum powder, metal molybdenum briskets and alloys, as well as rhenium salts (Zangezur Copper Molybdenum Combine, 2017). Therefore, Mo mining and processing activities impact both Kajaran and Yerevan population.

Although the city of Kajaran is located within the natural biogeochemical province (Saghatelyan et al., 2010) which implies the high contents of Mo and Cu in soils, the results of previous studies have shown that main industrial elements are of primary environmental concern. Moreover, besides Cu and Mo, within the soil pollutants the accessory elements such as Pb and Zn have also been found (Saghatelyan et al., 2008, 2010). However, studies targeting the assessment of risk arising from heavy metal contents of soils are insufficient. Therefore, the goal of this study was: 1) to investigate the spatial distribution peculiarities of heavy metals in the Kajaran city soil and identify possible sources, 2) to assess the human health risk the heavy metals pose, using the databases of the multipurpose geochemical studies of 2005 (Saghatelyan et al., 2008), 2011 (Asmaryan et al., 2014) and 2015.

2. Materials and methods

2.1. Study area and local geology

The city of Kajaran (N 39°9′ and E 46°9′) is the biggest mining center of the Republic of Armenia and is situated in the south of the country, in the province of Syunik. The establishment of the city of Kajaran is linked to the exploitation of the mine and creation of "Zangezur Copper Molybdenum Combine (ZCMC)." Today, ZCMC produces 18.5 mln. tons of ore per year which constitutes >60% of the mining industry of Armenia (Worldbank, 2016). The city covers an area of 2.74 km^2 (7061 inhabitants) (NSS RA, 2016), has a rugged relief and is situated at the height of 1750–1800 m. The city is located in the temperate mountainous climatic zone (maximum in summer: +35 °C; minimum in winter: −30 °C). The amount of precipitation is approximately 650 mm and is distributed round the year unevenly with most quantities during May and June. Northwestern and western winds are dominant in the city (The atlas of conditions and resources of Armenian SSR. Climate, 1975).

In the territory of Kajaran, two types of erosion landforms are distinguished: U-shaped river valleys in the middle and lower course of the river and V-shaped river valleys in the riverheads.

Due to the heavy spring floods in the southern and partly in the western slopes, the soil layer is missing. Up to the height of 1800 m, the soils are brown, while from 1800 to 2400 m chestnut soils predominate. The northern slope is covered with gray mountain-forest skeletal soils (Klopotovski, 1947).

The geological base includes volcanogenic sedimentary and intrusive rocks of the Tertiary period, particularly monzonites and porphyry granites. The Kajaran sulfide copper molybdenum deposit is timed to the monzonites, which were significantly altered by the hydrothermal processes, and two types of metallizing is observed: stringer-disseminated (the main type) and vein (subordinate type). The main ore minerals are molybdenite (MoS_2) and chalcopyrite ($CuFeS_2$), and the accessory minerals pyrite (FeS_2), magnetite ($FeO \cdot Fe_2O_3$), hematite

Table 1
Levels of single- and poly-element pollution (RA Government, 2005).

Element	Contents corresponding to pollution level, mg/kg				
	Level 1 Allowable	Level 2 Low	Level 3 Medium	Level 4 High	Level 5 Extremely high
Pb	<65	65–130	130–250	250–600	>600
Zn	<220	220–450	450–900	900–1800	>1800
Cu	<132	132–200	200–300	300–500	>500
Mo	<132	132–200	200–300	300–500	>500
Mn	<1500	1500–2000	2000–3000	3000–4000	>4000
SCI	<8	8–16	16–32	32–128	>128