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Distribution of chemical elements in soils and stream sediments in the area of abandoned Sb–As–Tl Allchar mine, Republic of Macedonia

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ABSTRACT

The aim of this study was to investigate the distribution of some toxic elements in topsoil and subsoil, focusing on the identification of natural and anthropogenic element sources in the small region of rare As–Sb–Tl mineralization outcrop and abandoned mine Allchar known for the highest natural concentration of Tl in soil worldwide. The samples of soil and sediments after total digestion were analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES). Factor analysis (FA) was used to identify and characterize element associations. Six associations of elements were determined by the method of multivariate statistics: Rb–Ta–K–Nb–Ga–Sn–Ba–Bi–Li–Be–(La–Eu)–Hf–Zr–Zn–In–Pd–Ag–Pt–Mg; Tl–As–Sb–Hg; Te–S–Ag–Pt–Al–Sc–(Gd–Lu)–Y; Fe–Cu–V–Ge–Co–In; Pd–Zr–Hf–W–Be and Ni–Mn–Co–Cr–Mg. The purpose of the assessment was to determine the nature and extent of potential contamination as well as to broadly assess possible impacts to human health and the environment. The results from the analysis of the collected samples in the vicinity of the mine revealed that As and Tl elements have the highest median values. Higher median values for Sb are obviously as a result of the past mining activities and as a result of area surface phenomena in the past.

1. Introduction

In many regions natural mineral deposits contain particularly large quantities of heavy metals, although the anthropogenic activities, such as mining and smelting of metal ores, have increased distribution of trace elements that appear to be a main reason for environmental pollution. Specifically, mine, opencast mining activities and mine tailings have a serious environmental impact on soils and water streams. In addition, these areas present severe erosion problems caused by wind and water run-off, where soil and mine spoil texture, landscape topography and regional and local meteorological conditions play an important role (Navarro et al., 2008).

The abandoned mines and mining areas are important issue because can be a major source of environmental pollution. In many areas worldwide, present and historical mining and smelting activities are causing a variety of environmental problems such as elevated metal concentrations in soils/sediments, dispersion of toxic elements in soil and water and ecological damage caused by extensive metal pollution (Alloway, 1995). Because ore is only a small fraction of the total volume of mined material, ore extraction, beneficiation processes and further processing of ores produce large amounts of waste that can contain metals (Siegel, 2002).

Although the contaminants have a long residence time in soils and waste materials at historical mining sites, research indicates that the mobility and bioavailability of metals in many of these environments is still high; the transfer of contaminants to the food chain and exposure of the local population still occur; significant quantities of contaminants are still being transported off the site (Alvarenga et al., 2004; Concas et al., 2004; Lee et al., 2001; Merrington and Alloway, 1994).

The objective of this investigation is to present the results from the soil survey in the As–Sb–Tl Allchar locality, Republic of Macedonia, abounded mine in the last 100 years (Boev and Jelenković, 2012; Volkov et al., 2006) and the river transport of sediments enriched with As, Sb, and Tl. These sediments are transported from Majdanska River to Crna River, and deposited in its alluvial sediment, on area of intensive agriculture activities. The content of Tl in the Allchar locality represents the highest established natural concentration in soil worldwide (Rieck, 1993). Special attention was given to the behavior of As, Sb and Tl and

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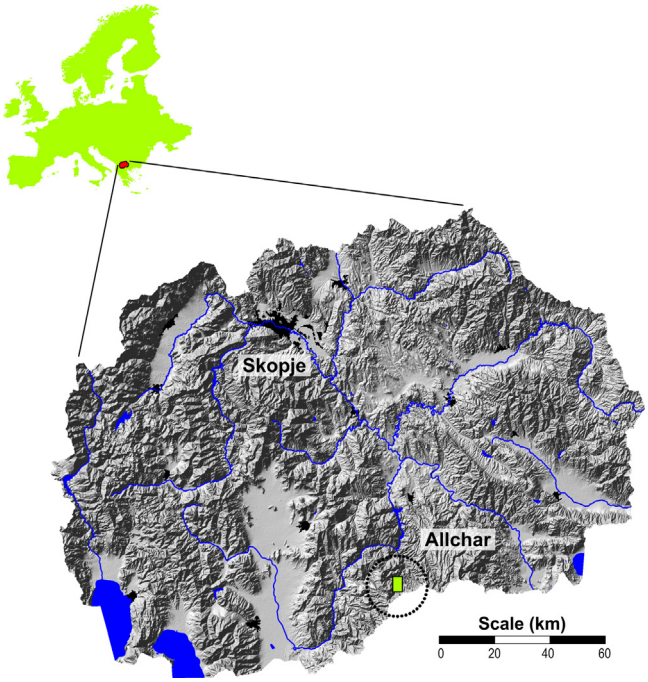

Fig. 1. The location of the study area in the Republic of Macedonia.

other trace elements following the main As–Sb–Tl mineralization. Therefore, the goals of this research were: (a) to investigate the distribution of various elements (Ag, Al, As, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Rh, S, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, V, W, Y, Yb, Zn and Zr) analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES), in topsoil, subsoil and the river sediments; (b) to define by statistical methods the main geochemical association and their spatial distribution in soil and river transport; (c) to identify the distribution of the elements in the survey area as either geogenic or anthropogenic.

2. Materials and methods

2.1. Study area

The Allchar locality is rare antimony–arsenic–thallium mineralization outcrop, located on the northwestern part of Kožuf Mt., Republic of Macedonia (Fig. 1). The locality of Allchar is unique in its mineral composition, and excluding very intriguing mineral lorandite ($TlAsS_2$), there are 45 other minerals, some of them very rare minerals. It is worldwide known locality as the richest deposit with thallium minerals and the largest number (12) different thallium minerals, four of them nowadays known as type-locality species: jankovicite ($Tl_5Sb_9(AsSb)_4S_{22}$), picotpaulite ($TlFe_2S_3$), rebulite ($Tl_5Sb_5As_8S_{22}$), simonite ($TlHgAs_3S_6$), (Boev et al.,

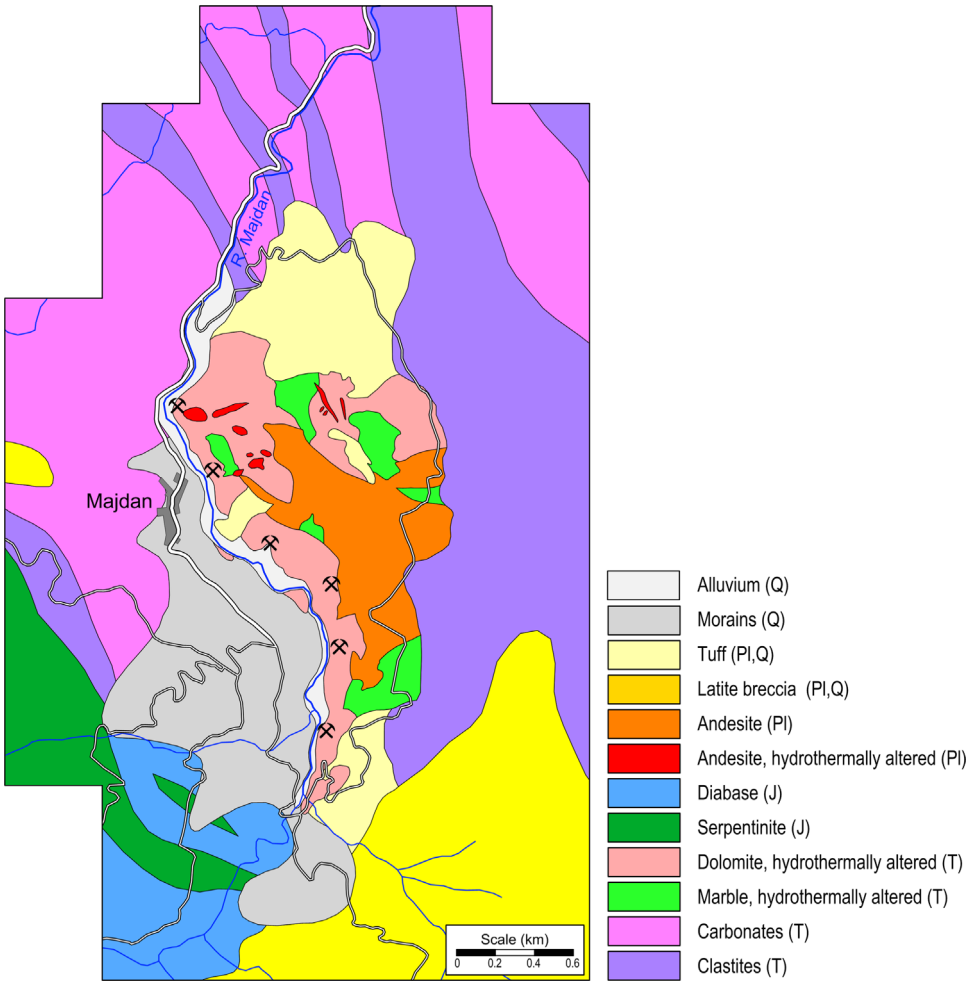

Fig. 2. Geological map of the studied area after Boev and Jelenković (2012).