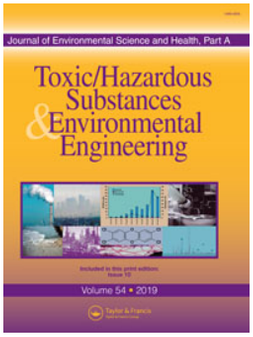

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Enchasing anthropogenic element trackers for evidence of long-term atmospheric depositions in mine environs

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ABSTRACT

In this work attic dust was examined as historical archive of anthropogenic emissions, with the aim of elucidating the pathways of enrichments associated with exploitation of Cu, Pb, and Zn minerals in the Bregalnica river basin region. Attic dust samples were collected from 84 settlements. At each location for attic dust sampling, topsoil samples from the house yards were also collected. Mass spectrometry with inductively coupled plasma (ICP-MS) was applied as analytical technique for determination of Ag, Bi, Cd, Cu, In, Mn, Pb, Sb, Te, W, and Zn. The Universal Kriging method with linear variogram interpolation was applied for the construction of spatial distribution maps. These elements are normally associated with air pollution (Cd-Pb-Zn), and usually are not influenced by lithological background. This investigation fortifies an extended anthropogenic association (Ag, Bi, In, and Mn) that implement some other anthropogenic activities such as agricultural activities (use of urban sludge, manure and fertilizers) or their occurrence can be a secondary affection from mine poly-metallic pollution. Spatial patterns showed intensive deposition in the areas of Pb-Zn mining activities ("Sasa" and "Zletovo" mines) and copper mine "Bučim". Long-distance distributions of higher contents of these elements from the mines were not detected.

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Air pollution; attic dust; Kriging modeling; ICP-MS

Introduction

Atmospheric pollution represents solutions or suspensions of minute amounts of harmful compounds in the air. Taking into account that their contents in the environment is variable, it is important to identify the regions with anomalous contents, differing from the natural distribution of the elements in air.[1,2] The most bio-affective distribution occurs through the dry deposition pathways of introducing the particles in the lower segments of the atmosphere. Dry deposition is characterized by direct transfer of gas phase and particulates from air to ground, vegetation, water bodies and other Earth surfaces.[3] This transfer can occur by sedimentation and diffusion to surfaces.[4,5] In the absence of precipitation, dry deposition plays major role in removing pollutants from atmosphere.[6] Atmospheric particles originate both from natural (e.g., erosion, dust storm, volcanoes) and anthropogenic sources. The anthropogenic activities for exploitation of natural resources and their processing through adequate technological processes and management of the waste produced by the same, represent a global problem of pollution of the environment. The territory of Macedonia does not diverge from this global framework of air-pollution. The studies implemented so far shows that certain areas on the territory of the Republic of Macedonia are stricken by the anthropogenic introduction of different chemical elements in high contents in the air and soil.[7–17]

Long-term airborne emissions from mining, have left a legacy of widespread contamination around industrial areas. The Eastern part (Bregalnica River basin) of the country is significantly affected due to the major emissions from the two lead and zinc mines (Sasa and Zletovo mines), Bučim copper mine and former Damjan iron mine.[16,17] Considering these long time emissions (more than 50 years), an alternative approach is to use exposed attic dust, because over long periods of time atmospheric particles can accumulate, providing a record of historical local deposition.[18] The determination of historical emissions is based on the data of heavy metals concentration in the attic dust from different measuring sites of the weight of total monthly air deposit.[2,19,20] Undisturbed attic dust is potential archive for atmospherically deposited particles and have been shown to be effective across urban areas and in the vicinity of smelters, mines and other potentially emission sources.[18,21–24]

The region of the Bregalnica river basin presents a unique area with dominance of lithogenic enrichments of Pb-Zn-Cu-Cd group of elements. However, despite the lithogenic enrichments causes, there are still presence of the anthropogenic pathways that interrupt the natural distribution of the elements in the air distributed dust, leading to anomalous deposition of concerning elements content. The exposure of mining and flotation tailings, as well as the exposure of the open ore pit to the air streams, leads to

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