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Geochemical anomalies of trace elements in unremediated soils of Mt. Karczówka, a historic lead mining area in the city of Kielce, Poland

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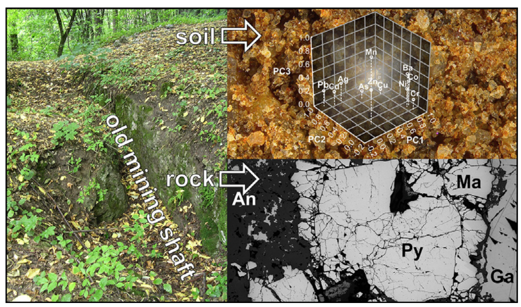
HIGHLIGHTS

- Impact of primitive lead ore mining on soil trace element geochemistry was studied.
- Trace elements were determined in soils by ICP-MS and in rocks by LA-ICP-MS and EMP.
- Soils show mostly Pb, Ni and Cu anomalies of lithogenic origin.
- Two-century period of natural attenuation has not removed impact of mining on soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Concentrations of selected trace elements (Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) and rare earth elements were determined in 61 samples of surface soils collected from Mt. Karczówka, a historic Pb ore mining area located in the city of Kielce, south-central Poland. Some of these samples were subjected to XRD analyses and Pb stable isotope measurements. The mineral and chemical composition of rock samples were also examined. Mining activity in the study area was conducted mostly during 15th–17th centuries using technologically primitive methods, and was finally ceased in the first half of the 19th century. More than three thousand old shafts, pits and adits occur in the study area and its vicinity. The soils of the study area have not been remediated since the end of the mining operations. The trace elements of the examined surface soils are heterogeneously distributed with lead concentrations in the range of 41–9114 mg/kg and Pb isotopic signatures similar to those of local galena. The results of trace element measurements allowed us to discriminate geochemical anomalies from background levels and to link mineralogy of the host rocks to the origin of anomalous element concentrations. This study shows that elevated levels of elements of geogenic origin have remained in surface soil for two centuries after cessation of mining operations.

1. Introduction

Historic metal ore mining and processing has influenced differently the quality of soils. Distribution of metals in dated profiles of ombrotrophic peat bogs in the Harz Mountains, Germany showed that atmospheric aerosols emitted from early mining and smelting caused a local pollution of surface environments (Kempter and Frenzel, 2000). Except for generation of metal-enriched mineral particles, their atmospheric transport and deposition, mining waste was responsible for soil contamination in historic metal ore mining areas. Abandoned mine waste spoil heaps may have lowered the quality of soil, air, groundwater and surface waters for a long time in the past, but their impact on the environment is persistent and can be detected after hundreds of years (Ciszewski et al., 2012; Bird, 2016; Sprague and Vermaire, 2018). Transport of water contaminated with metals and metalloids

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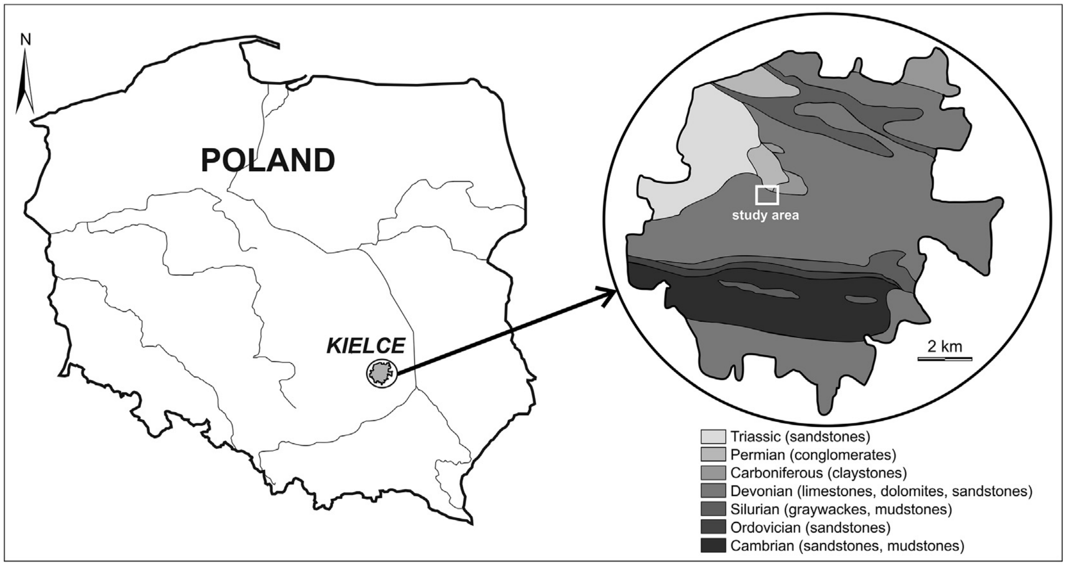

Fig. 1. Geologic map of the city of Kielce (after Czarnocki, 1938). Location of the study area is indicated by a white rectangle.

from mining activity caused their enrichment in river sediments (Macklin et al., 1997; Resongles et al., 2014; Gutiérrez et al., 2016b; Elbaz-Poulichet et al., 2017). This enrichment creates a risk of contamination of the catchments, especially during floods and may cause, among others, a poisoning of the livestock (Foulds et al., 2014), a decrease in fish populations and a loss of arable lands.

Multiple sources of natural origin (lithogenic factors) as well as historic and present anthropogenic activities contribute to very complex geochemistry of the local environment in historic metal ore mining areas (Osher et al., 2006; Gałuszka et al., 2015, 2016; Gutiérrez et al., 2016b). One of the most affected environmental compartments is soil, in which metals are accumulated through natural processes, including weathering of mineralized host rocks, wind erosion, complexation with humic acids and sorption on soil minerals, as well as a result of anthropogenic impact (mining and ore-processing activities) (Pérez-Sirvent et al., 2016). Many studies have reported contamination of soils of former metal ore mining areas (Navarro et al., 2008; Fernández-Caliani et al., 2009; Rieuwerts et al., 2009; García-Lorenzo et al., 2014; Bori et al., 2016). However, in-depth analysis of geochemical metal anomalies in unremediated soils of historical metal ore mining areas has rarely been made because the soil may have undergone self-restoration (natural attenuation) and soil/host rock interaction can be obscure (Alekseenko et al., 2017).

The aim of this study was to: (i) identify geochemical anomalies of lead and other trace elements of possible geogenic origin in surface soils of Mt. Karczówka in the city of Kielce, Poland, (ii) link chemical composition of the host rock and lead stable isotope ratios of galena with the soil geochemistry, and (iii) find associations of elements having the same sources in the examined soil. To complete these objectives a series of different mineralogical and geochemical methods was used and the results were interpreted with application of multivariate statistics. Our hypothesis is that despite intermittent six hundred-year primitive extraction of galena had been of historical relevance for a two-century period, it left a traceable geochemical signal in the composition of surface soil cover.

2. Materials and methods

2.1. Study area description

Mt. Karczówka with an elevation of 339 m a.s.l. (coordinates: 50°52′5.27″N; 20°35′11.51″E) is located in the western part of the city of Kielce, south-central Poland (Fig. 1). It is a forested mountain occupying an area of approximately 27 ha. Most of the study area lies within the Karczówka Landscape Reserve boundaries, which has been a popular place of recreation for the city inhabitants since the mid-twentieth century.

Mt. Karczówka is a part of the southern limb of the Kielce syncline and is mostly built of Upper Devonian (Frasnian) reef limestones whereas its northern slopes consist of Carboniferous dark claystones and Permian conglomerates (Fig. 1). The limestones are cut by numerous faults of north-south direction that were formed during Variscan and Alpine orogenies. The mineralization zone consists of galena-calcite-barite veins that are confined to the tectonic faults.

Lead was extracted in Mt. Karczówka probably from 13th century up to the 19th century, but the early history of mining activity in this area was not well documented. Primitive mining operations have left numerous shafts, pits and adits. Prospecting and mining activities were carried out along the fault zones (Fig. 2). There were two major mining fields in the study area – one located in the southern and the other, in the northwestern part of the mountain. At present, the area is overgrown by a mixed forest about 180 years old with Scots pine being a predominant tree species. Rendzic leptosols (brown, mixed and initial) are typical soils of the study area.

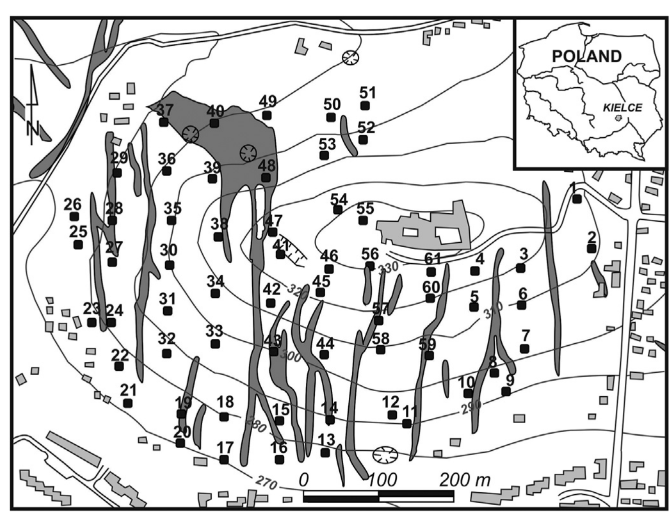

Fig. 2. Sketch map of the study area with location of sampling sites (1–61). Dark gray shapes represent historic mine workings located along the fault zones (after Czarnocki, 1956).