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Heavy metal pollution of soils and sediments at the historical smelting site of the Rudawy Janowickie Mountains (Lower Silesia, Poland).

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Multidisciplinary studies of historical slags are mostly focused on exploring how metallurgy evolved through human history. Another purpose for studying historical slags are potentially harmful interactions between slags, surrounding soils, sediments and waters. Metallurgical slags generally concentrate potentially toxic elements (PTE) such as arsenic, copper and lead. These elements may be mobilized and transferred into immediate surroundings. The main aim of our work is to identify factors controlling migration of metals at the historical smelting site of the Rudawy Janowickie Mountains. This study involves detailed analyzes of historical slags (older than 300 years) containing PTE, as well as surrounding soils and sediments.

The Rudawy Janowickie Mountains represented an important centre of copper mining and smelting in Poland until 1925 with metallurgical activities being documented as early as in the XIV century. The exploitation of Cu ores has left large amounts of mine tailings and slags extending over ca. 35ha. The slags were deposited on ground and no barriers between the slags and environment were set. Therefore, they were continuously affected by variable factors, for example, changing weather conditions.

Soils located in the study area are derived from granitic rocks. They are shallow ($<$ 1 meter depth) and skeletic (containing $>$ 50 wt. % of coarse fragments). Their pHw is acidic and varies from 3.4 to 4.5 from the topsoil to the deeper horizons in which slags are widespread. Mineral composition of soils and sediments is dominated by quartz, alkali feldspar, plagioclase and biotite. However, some samples may contain additionally numerous slag fragments.

At present, the slags occur within three types of environments: (1) at the surface, (2) in soils and (3) in sediments from two streams: Janówka and Smelter Stream.

Studied slags were sampled in the vicinity of both streams from (1) surface, (2) soil profiles and (3) streambeds. Furthermore, samples of soils and stream sediments were collected at the same time in order to observe weathering features of slags in different environments and to verify the influence of those wastes on properties of soils and sediments.

Studied slags are isometric and well rounded (pebble-like), with size ranging from few to dozens of centimetres. The average chemical composition of slags is 47 wt. % Fe_2O_3, 40 wt. % SiO_2, 8 wt. % Al_2O_3. Slags show elevated concentrations of Cu (up to 13400 ppm), Zn (up to 3640 ppm), Pb (up to 270 ppm) and As (up to 130 ppm).

Dominant type of slag occurring in all environments is black and has massive texture. It consists of silicate glass, fayalite, hercynite, bornite, pyrhotite, intermetallic compounds of Fe and As, metallic Pb and Cu. Sulfides and metallic phases are the most important PTE carriers. Second type of slag was found only on surface. It is highly porous and often encloses small fragments of granitic rocks. Despite weathered appearance, it has similar phase composition to the dominant type of slag. The weathering products occur as aureoles and interstitial replacements within the sulfides. Secondary phases in the aureoles are: brochantite, malachite and Fe oxy-hydroxides.

PTE initially concentrated in primary phases such as sulfides can be mobilized by weathering and be subsequently bounded in secondary phases (brochantite, malachite). The stability of these phases depends on the surrounding conditions ($e.g.$ here, secondary phases are stable only in slags from surface). Presence of slags at the studied site is clearly documented by geochemical analysis of stream sediments. The Cu concentration in sediments from the

area where no slags have been found is 8 ppm, while it exceeds 130 ppm in the site where slags are widespread.

Our observations thus show that the studied slags release some potentially toxic elements (especially Cu) during weathering and the slag texture appears to be an important factor controlling metal migration.

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