Mineralogy of the heavy metal and metalloid pollution of the Ogosta river floodplains, NW Bulgaria

Минералогия на замърсяването с тежки метали и металоиди в заливни тераси на река Огоста, СЗ България

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Chiprovtsi area is contaminated with As and heavy metals as a result of the long-lived intensive operation (1950–1999) of the three major mines in NW Bulgaria – Chiprovtsi Ag-Pb, Martinovo Fe and Govezhda Au (arsenopyrite) and the ore processing carried out in the two ore-dressing plants near the town of Chiprovtsi. The mining waste was discharged mostly in the Ogosta River channel by 1979 because the existing two tailings ponds (Mechi Dol and Chiprovtsi) were too small to take the produced waste. As a result, this waste became the main source of pollution for the alluvial soils in the floodplains many kilometers far from the mining area. In 1979 the Golyam Bukovets tailings pond was constructed and the waste was deposited there.

At present, 30 years after the construction of the Golyam Bukovets tailings pond and almost 10 years after the mine closures, pollution of the Ogosta River downstream can still be detected.

The vertical distribution of the pollutants in soil profiles of the Ogosta River floodplains was studied at three points: 1) in a meadow located near the Ogosta River bank in the vicinity of Gavril Genovo village; 2) in agricultural land near the Gorno Tserovene village; 3) in a meadow located right before the influx of the Ogosta River in the Ogosta Dam Lake. The 3 points are located 30, 35 and 36 km downstream from the Chiprovtsi mining area, respectively. Profiles 1 and 2 are situated 20–30 m away from the river bank, while profile 3 is situated at the river bank. The soil profiles 1 and 2 were most thoroughly studied. The sampling has been carried out in 2005th and some of the geochemical data has been already published (Kotsev et al., 2006).

Geochemistry

Distribution of heavy metals at depth. The concentrations of Mn, As, Cd, Cu, Pb, Sb, Zn and Fe in two soil fractions (<2 mm and <63 μm) from all sampling points were determined by ICP-AES. The measured pH values of the soil in the studied profiles are between 7.63 and 8.03 probably because of the calcite in the tailing material drifted by the river and deposited in the floodplains. As and Pb are the main pollutants, as the determined concentrations exceed the MPL (Maximum permissible levels) up to 600 and 17 times, respectively. Unlike the concentrations of Zn and Cu, which barely exceed the MPL, the concentrations of Cd reach values 4 times above MPL. Two patterns of contaminant distribution in depth of the floodplain sediments are distinguished: 1) associated with the low-lying floodplain sections to 1 m above the river level, supposed to be formed mostly during the mine operation period (profiles 1 and 3). The pollutant concentrations tend to increase in depth which reveal the more intensive river pollution in the beginning of the mining activities and the reduced metal load after 1979; and 2) associated with the older and higher floodplain sections that are 1–2.5 m above the river level (profile 2). The sediments contaminated with tailing material were de-

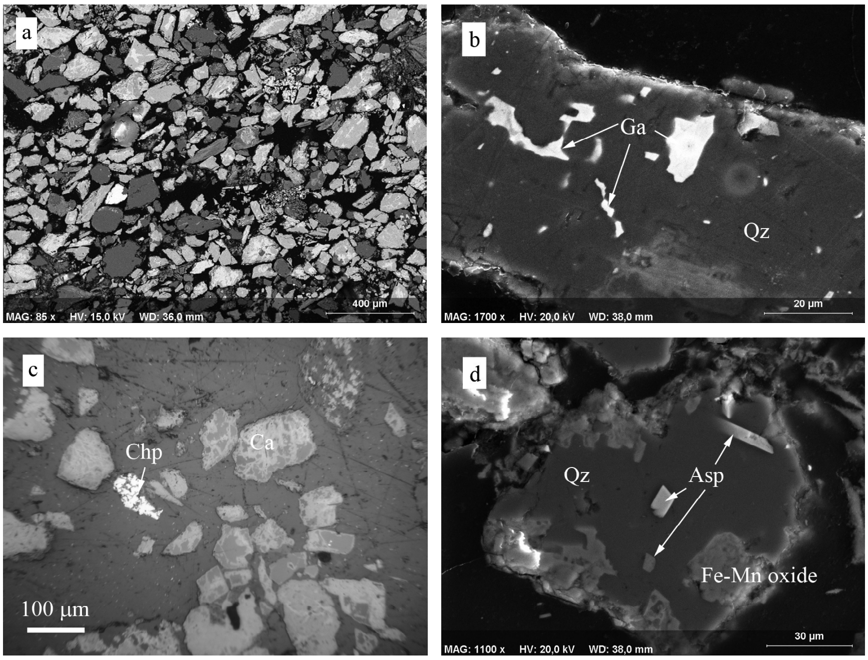

Fig. 1. Microphotographs showing the size and distribution of the mineral grains in the dense brownish soils constituents: a) general view of the particles; b) galena in quartz; c) chalcopyrite, calcite and Fe-oxides; d) euhedral arsenopyrite crystals and calcite included in quartz

Abbreviations: Asp – Arsenopyrite, Chp – chalcopyrite, Ga – galena, Qz – quartz, Ca – calcite

posited only in the upper part of the profile. However, certain migration of the pollutants in depth is also recorded by their elevated concentrations.

The ore mineral weathering in the higher floodplains is carried out primarily under oxidizing conditions, while the most contaminated deeper sediments in the low-lying sections are often under reducing conditions, because of elevated groundwater table. The alternation of iron reduction and oxidation is supposed to be one of the major factors that control the arsenic mobility in the contaminated floodplains (Kotsev et al., 2006).

Mineralogy

In the three profiles only pyrite crystals and Fe (III) oxides and oxy-hydroxides are visually observed. Brownish dense spherical soil constituents are observed at profile 1 (depth from 40 to 50 cm) and profile 2 (depth from 20 to 40 cm). The pyrite crystals that are found on the layer surface on the river bank at profile 3 were exposed to oxidation during the lowest river flow. Arsenopyrite, galena, sphalerite, chalcopyrite, Pb-Sb-S sulphide (boulangerite?) and Fe (III) oxides are also identified by optical microscopy and microprobe analysis in the tailing waste particles (Fig. 1, a–d). The gangue minerals are calcite and quartz. The mineral grains in the tailing waste particles have angular shape and size up to 200 µm (Fig. 1a). The sulphides are embraced by carbonates (mainly calcite) or quartz which explains their preservation in soil for decades. The most common sulphide mineral is pyrite. The observed calcite grains have distinct zonation with various colored zones. Those probably suggest different chemical composition. The analyses confirmed the presence of zones enriched in As due to absorption. This process is very favorable for the environment because calcite fix the As preventing its dissemination in the soils.

Conclusions

The presence of the described ore minerals in the floodplain sediments 30 km away from the mining region is a result of the tilling and flooding of the Ogosta River. Most of the sulphide minerals in the contaminated soils seem to have undergone weathering, except those included in quartz. The mobilized heavy metals were absorbed by soil constituents at some extent. Calcite grains have adsorbed arsenic in their peripheral zones thus retaining arsenic in themselves. Calcite in the tailing material deposited in the floodplains decreases the risk of soil acidification. More detailed study of the Ogosta River valley between the mining area and its influx in the Danube River is necessary to determine the chemical composition and spatial distribution of the pollutants in the alluvial soils and their impact over the riverine landscape.

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