Chemical composition and heavy metal partition in mining-affected surface waters and stream sediments in Chiprovtsi area, NW Bulgaria

Химичен състав и разпределение на тежките метали в засегнатите от минната дейност повърхностни води и речни седименти в района на Чипровци, СЗ България

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The mines in Chiprovtsi region are known to be exploited from Roman times, through Middle Ages, but most intensively from 1950 to 1999, when the last mine ceased its activities. Three types of deposits containing minerals of *As, Pb, Zn* and *Cu* have been exploited here: *Pb-Zn-Ag* Chiprovtsi deposit with main minerals galena, chalcopyrite, tetrahedrite and arsenopyrite; *Fe-As-Au* Govezhda and Kopilovtsi deposits with main minerals arsenopyrite, galena, sphalerite, tennantite, proustite; *Fe-Mo* Martinovo deposit with main minerals arsenopyrite, löllingite, chalcopyrite, molybdenite. As a result numerous waste rock dumps and 3.5 million tones mill tailings stored in 3 tailings impoundments are available in the region.

This study reports the composition and the geochemical partition pattern of *As* and heavy metals (HM) in surface waters and in stream sediments in polluted section of Upper Ogosta River system in Chiprovtsi mining area as a consequence of past mining.

The sampling was performed during both wet (high water) (May 2007) and dry seasons (low water) (September 2007) along the Chiprovska Ogosta river and its tributaries downstream the mining sites, ore outcrop and tailings impoundments. Total of 18 sites are sampled in both seasons (Fig. 1).

Seasonal monitoring of the **surface waters** did not ascertain regular seasonal correlation of pH values. They vary from 7.12 (May 2007) up to 8.81 (September 2007), but remain almost equal to neutral-near neutral pH, due to the carbonate-buffering by the host rocks and gangue calcite and siderite. The measured in situ physico-chemical parameters of river waters at stream sediments sampling sites slightly differ during May 2007 and September 2007, but distinct increase of the total dissolved solids (TDS) and conductivity is observed during dry season for all sampled waters.

The concentrations of the dissolved heavy metals and *As* in general increase in September toward May 2007 although by several samples the reverse amounts are found especially when the concentrations are around the detection limit. The lower concentrations in May 2007 are due to the dilution by the snow thaw and by rainfalls.

Analysis of water samples yielded a range of *Pb* concentrations from <2 to 6 μg/l, of *Zn* – from <2 to 56 μg/l, of *Cu* – from <1 to 6 μg/l. These concentrations are much lower than the target values even for drinking waters. *As*-concentrations vary from under the detection limit to 437 μg/l, but at most sampling sites it exceed the guideline value for 2-nd surface waters category. It is apparent that the distribution of heavy metals and *As* reflect the interaction with ore dumps and tailings.

As trace elements in **stream sediments** have affinity for fine-grained particles chemical analyses were carried on the <63 μm fraction. According to hydrological conditions and mining activities at sampling sites, samples show large variation in their fine-grained particle content.

Since there are no agreed European standards for metal levels in river and floodplain sediment, we have used as reference the target values and soil remediation intervention values for selected metals in soils from the Dutch Ministry of Housing, Spatial Planning and Environment.

According to their geochemical behaviors the elements in stream sediments could be separate in 2 groups.

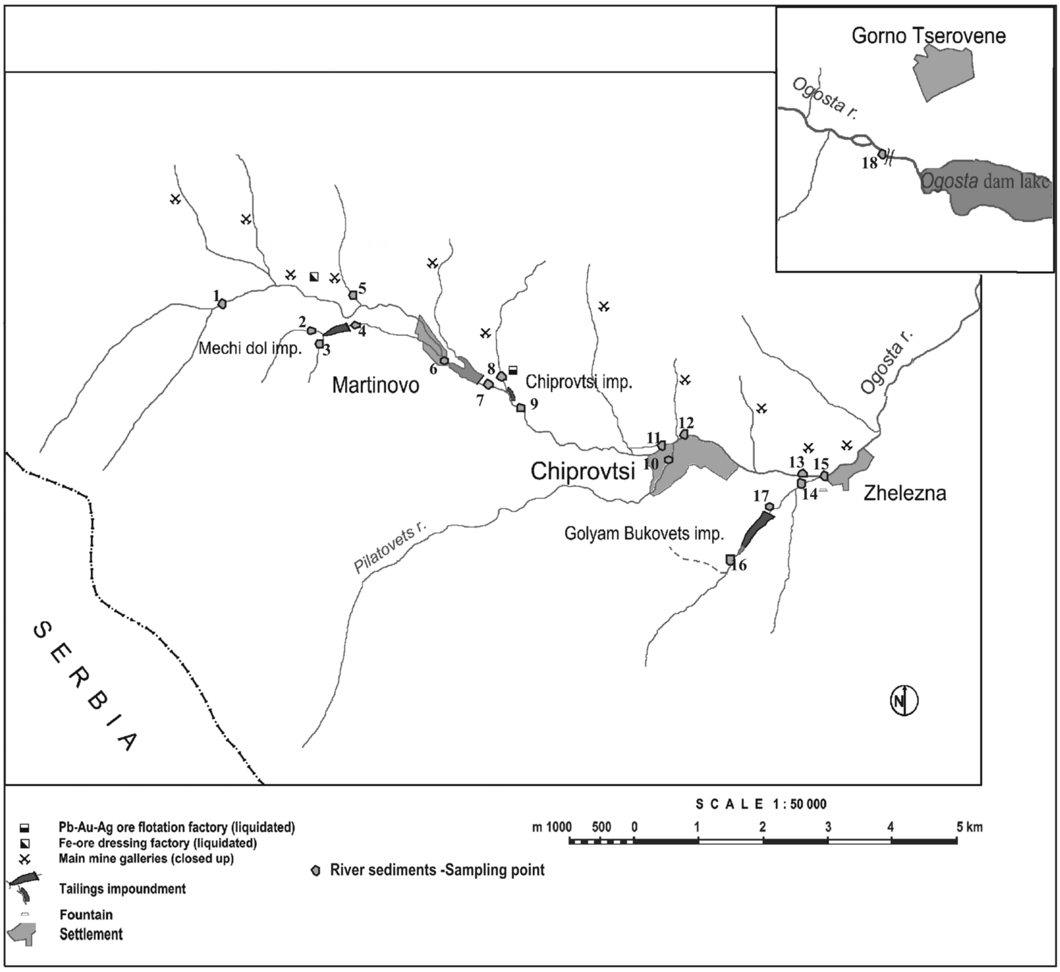

Fig. 1. Chiprovtsi mining area with sampling sites

The first group includes the elements *Al, K, Na* and *Mg* bonded in the rock-forming minerals in the region.

The second group includes the elements from the various mined and treated ores in Chiprovtsi area. To this group belong *Cu, Pb, Fe, Zn, As, Ag, Au, Mn, Sb, Cd, Bi, Ni, Co.*

Despite *Mg* and *Fe* are assigned to the first and to the second group respectively they have much widely distributions as in the host rocks as well as in the ores. This applies to *Ca* distribution too.

The first group of elements (*Al, K, Na, Mg*) do not show noticeable variation in their concentration.

In the second group of elements distinct correlations between elements could be seen which reflect the genetical association between their host minerals. The well expressed correlations are *As-Au, Zn-Cd, Pb-Ag-Sb, Bi-Fe, Ni-Co*. The correlative distribution pattern in stream sediments of genetically connected elements in ores suggest that the stream sediments contain preserved sulfide grains from the different type of deposits. The site with highest contents of HM and *As* is after Mechi dol tailings impoundment. The extremely high values of almost all elements reflect a direct supply with tailings from the above situated impoundment.

The oxidation of sulfide minerals results in the release of H^+ into the water. Gangue mineral can neutralize the H^+. Minerals that can contribute to acid-neutralizing reactions are calcite, dolomite and alumo-silicate minerals. Their dissolution typically leads to a distinct sequence of pH-buffering plateaus.

The surface waters have neutral to near neutral pH what contribute to maintain high As-concentrations in water and do not favour the adsorption of *As*(V)-species. This also prevents acid mine drainage (AMD) generation discharge from the mines and retains the sulphides dissolution ability low.

The preservation of ore minerals in stream sediments is due to the abundant presence mainly of calcite in host rocks as well as in ore bodies.

Despite that many waste dumps and all tailings impoundment are remediated, presently the remobilization of contaminants is due to the rain falls, to the mining wastes abandoned nearby the river course and to the mine dumps without specific cover.

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