Long-term migration of heavy metals in the small catchment affected by historical lead and zinc mining

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Introduction: Discharge of mine waters from metal mines causes pollution of adjacent floodplain soils and aquatic sediments with heavy metals. After cessation of mining, metals stored within a catchment are mobilized and transported downstream with the rate depending on their chemical associations and physical factors like rainfalls intensity and hydrological regime [1, 2, 3]. In some cases reconstruction of this rate since closure of the mine is possible from dated sediment record or monitoring [4, 5]. However, usually dynamics of post-depositional heavy metal redistribution is deduced rather from single than from repeated investigations or accretionary sediments [6, 7].

The aim of the studies is to estimate the rate of metal migration in the small catchment historically polluted by discharge of mine waters from lead and zinc mine in southern Poland and to formulate strategy of pollution mitigation in the investigated area.

Materials and Methods: The lead and zinc mine "Matylda" exploited mainly galena and sphalerite between 1850 and 1972 discharging up to 1 m^3/sec of mine waters to the small stream channel with capacity not exceeding several tens of liters per second. This initially caused inundation of some valley sections. In 20^{th} century the stream channel was converted into the straight, lined channel with dykes closing local depressions and ponds, which became permanent or periodical water reservoirs.

Samples of soils and sediments were collected in the upper and in the middle reach of the Matylda valley. In every reach five cores up to about 0.5 m long was sampled. Cores were split in 1-6 cm increments and silt-clay fraction (0.063 mm) was wet-separated. Moreover, active and near-bank channel bed sediments were sampled at four locations over the distance about 4 kilometers. In fine fraction of the all collected sediments, concentrations of Cu, Cd, Pb, Zn, Mn and Fe were determined using flame AAS after digestion in Teflon bombs with nitric acid. In selected samples speciation of heavy metals was determined using standard BCR procedure, whereas mineralogical analyses (XRD) are in process. Moreover, concentration of the same elements soluble in waters, sampled 12 times at four locations from the stream, was determined by ICP-MS.

Results: Concentrations of heavy metals in the investigated profiles are extremely variable. Generally, peaks of Zn, Cd and Pb vary between 4 and 5.5%, 300 and 600 ppm and 3-5%, respectively. Peaks occur at depth 40 cm in the channel sediments, at 10-15 cm in alluvial valley bottom and at more variable depths in ponds. In most profiles concentrations of Zn, Cd and Pb in surface organic sediments are 3-5 times lower whereas Cu peaks in these sediments frequently exceed 100 ppm. In most of samples analyzed for metal speciation about 50% of Zn and Cd is associated with highly mobile fractions (exchangeable and carbonates) and less than 20% of Zn and Cd is bound to sulphidic-organic fraction. In contrary, Pb and Cu are present almost exclusively in the least mobile forms. Moreover, heavy metal concentrations in Matylda stream waters changes with distance downstream. Soluble zinc content decreases from average 1.3 to 0.7 ppm whereas Pb and Cd contents increase 2 and 4 times, respectively.

Discussion: Observed changes in metal concentrations and sediment stratigraphy in profiles suggest rapid decrease of metals load migrating downstream after the mine closure in 1972. Transport with mine waters and accumulation of extremely polluted clay sediments in the inundated valley bottom was followed by relatively short period of reworking of mine sediments in the stream channel. Since 1980s stream waters polluted with municipal sewages with discharge of few liters/sec are able to transport mainly products of biological degradation with higher Cu content and relatively lower Zn, Cd and Pb concentrations not exceeding 10 000, 100 and 5 000 ppm, respectively. Potentially high ability of Cd and Zn to migration is also reflected in high proportion of these metals in mobile fractions. It seems that despite extreme metal concentrations actual migration rate of the metals stored within the catchment is much lower than potential one with little importance for downstream river catchment pollution.

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