River-to-floodplain pollutants transfer in the hyporheic zone affected by Zn-Pb mining

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Introduction: The interface of groundwater and surface water, called the hyporheic zone, along the river channel is characterized by large gradients of nutrients and trace metal concentrations, and contrasting environmental conditions. The presented work couples groundwater and sediment chemistry in the metal mining-polluted Biała Przemsza River valley in southern Poland in order to reveal regularities in pollutant distribution and to relate them to sedimentary processes and surface water/ groundwater exchange.

Methods: Studies of sediment and groundwater pollution were carried out on the floodplain in the middle reach of the Biała Przemsza River near Sławków town (Upper Silesia Upland, southern Poland).
Water: Five piezometers were installed in 25 m-long transects across near-bank zone of the river channel. Values of pH and PEW of groundwater from the piezometers as well as river water were established in situ. Concentrations of Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-} and Ca^{2+}, Mg^{2+}, Na^+, K^+ ions were determined within 48 hours using Ion Chromatography (DIONEX 1000). Content of Zn, Cd, Pb, Cu, Fe and Mn were measured using ICP-MS method.
Sediment: Values of pH were measured on-site while other parameters (density, water content, concentration of carbonates and organic matter) were analyzed right after transport to the laboratory. The content of the silt-clay fraction of sediments (<0.063 mm) was determined after wet-sieving. This fine fraction samples were digested wet in closed system in a mixture of 10 cm^3 of 65% HNO_3 and 2 cm^3 of 30% H_2O_2. The contents of studied heavy metals in the prepared solution were determined using F-AAS method.

Results:
Water: River waters supplied with mine waters from the Zn-Pb mine, situated 15 km upstream, were characterized by the high conductance and content of ions: SO_4^{2-} (200-220 mg/L), Ca^{2+} (120-130 mg/L), Mg^{2+} (36-40 mg/L) and CO_3^{2-} (280-320 mg/L) strongly influenced by the mine. Conductance was lower albeit constant over 5 meters from the channel and decreased rapidly further over the next 20 meters. Generally, the same distribution pattern was observed for SO_4^{2-} and Ca^{2+} which drop to about 20 mg/L and 80 mg/L, respectively. Ions Ca^{2+} and CO_3^{2-} with increase of their content from the channel appeared the opposite distribution pattern.

Sediments
Sediments were generally weakly acidic to alkaline (pH 5.7-7.1). They contained very low amounts of organic matter and carbonates (below 1%). Concentrations of mine-originated heavy metals varied within broad range: Zn (350-36,990 mg/kg), Pb (52-18,100 mg/kg) and Cd (2-167 mg/kg). Content of these metals was the highest in the top stratum and decreased progressively down the core up to the depth of 4 m. Metal concentration was the highest in cores drilled in the channel bottom and decreased away from the channel.

Discussion:
The Biała Przemsza River in the investigated reach, formed narrow valley incised into the dolomite cuesta rocks with narrow, sandy alluvial floodplain underlayed with gravels. The river water infiltrate into sandy sediments over the width controlled by hydraulic gradient. Moreover, river waters escape to the Triassic aquifer, and deposits beneath the river channel constitute the hyporheic zone which may extend far below the investigated 3.5 m under the channel. The infiltration of the river water favour transfer of contaminants from the channel to sediments. It explains high content of Zn and Cd at the depth of 3 m (over 1 wt. % and 50 mg/kg, respectively) and content of many chemical constituents in the groundwater as high as in the river water. Higher content of calcium and carbonates in sediments at larger distances from the channel are probably related to longer infiltration time and drainage of carbonaceous rocks in the slopes of this valley section. Decrease of chlorides content at the distance about 15 m from the channel also indicates here the width of the zone influenced by the river water.

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