Element geochemistry as a tool for determining the suspended particulate matter (SPM) pollution sources in the Sava River headwaters

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Introduction: Suspended particulate matter (SPM) plays a major role in transport of many natural and anthropogenic substances [1]. Hence, determining the SPM sources is important task in contaminated sediment management [2]. Increasing human activities, such as growing industry, regulations of the river course, construction of dams, reservoirs and uncontrolled exploitation of gravel, are especially evidenced in the upper reaches of the Sava River.

Recently, geochemistry is increasingly used in determining of sediment sources. Three main processes could be singled out as a potential influence on the sediment composition; (I) chemical physical sorting weathering, (II) and (III) anthropogenic perturbation. To circumvent this effects, author's [3] developed theoretical scattergrams for assessing sediment sources using immobile elements ratios.

Beside above mentioned method, enrichment factor (EF) analysis is often widely used method in determining geochemical nature of elements in river sediments. [4, 5]

 $EF(X) = (X/Al)_{sample} / (X/Al)_{ucc}$

EF(X) = enrichment factor of selected element; X/Al = selected element concentration normalized to Al concentration

Before statistical analysis compositional data were treated using the log-ratio transformation considering their composite nature [6]

Methods: A time-integrated mass flux sampler (TIMS) was used for collecting the SPM at four different locations along the Sava River headwaters and its main tributaries Ljubljanica, Savinja and Krapina during four periods. Sediment ($<63\mu$ m) and soil samples were also collected in the surrounding area.

The analyses consisted of the particle size determination (laser diffractometry), mineral composition (x-ray diffraction) and trace elements concentration (ICP-MS). The hydrological data were obtained from the National Meteorological and Hydrological Service.

Results: Silt fraction dominated in all analyzed SPM samples. The X-ray diffraction revealed presence of quartz, calcite, dolomite and feldspars. Illite/muscovite was most abundant in the clay fraction, followed by smectite, chlorite, kaolinite and

vermiculite. In all sampling campaigns high flow conditions were observed except in the summer. The highest SPM concentration was found in the spring sampling period.

Discussion: Ce, Nb, Ti and Th were established as the most conservative of the immobile elements, and the best indicators of the SPM sources. Using element ratios Nb/Ce and Th/∑LREE (Light Rare Earth Elements) compared to Nb/Ti, fluvisol was revealed as the most probable source of the SPM of the Sava River upper catchment, especially during high river discharges. Only the Krapina SPM samples showed deviation and different source region.

The EFs indicated depletion of Na in samples, due to its soluble character, while vast majority of lithogenous elements followed UCC-similar abundances. Higher values of Ca and Mg were the result of geological background –carbonate-rich rocks and soils. The highest EF values (between 3 and 22) were obtained for potentially toxic elements: As, Bi, Cd, Cr, Cu, Ni, Mo, Pb, Sb, Sn, Zn, P and S. Among analysed rivers, the Krapina displayed the most significant anthropogenic pressure with regard to P, S, As, Pb, Sb, Sn, while Savinja and Ljubljanica with regard to Cd and Zn, respectively.

Spatial distribution of anthropogenic elements in soils and sediments pointed out three main areas under the anthropogenic pressure; the first area includes the Moste dam and Acroni Jesenice steel factory, which is characterized by element association of Cr-Cu-Ni, the second area is related to the zinc production in Celje and the element association of Cd-Mo, and the third area is related to agricultural activities and sewage discharges in the surrounding of Zaprešić area which is characterized by Pb-Sn-Zn element association.

References:

[1] Horowitz and Stephens (2008) Sci Total Environ 400:290–314; [2] Owens et al. (2005) River Res Applic 21:693–717; [3] Fralick and Kronberg (1997) Sediment Geol 113:111-124; [4] Chen et al. (2014) Geochem Geophys Geosyst 15:4526–4546; [5] Gaillardet et al. (1999) Geochim Cosmochim Acta 63:4037–4051; [6] Aitchison (2003) The Statistical Analysis of Compositional Data. Black Press, USA