

Initial magnetic susceptibility measurements in sediments of Croatian and Slovenian rivers

Stanislav Frančišković-Bilinski^{1*}, Halka Bilinski¹, Darko Tibljaš², Nenad Tomašić²,
Krešimir Maldini³ and Robert Scholger⁴

¹ Institute "Ruđer Bošković", Division for marine and environmental research, Zagreb, Croatia

² Univ. of Zagreb, Fac. Sci., Dep. of Geology, Institute of Mineralogy and Petrology, Croatia

³ Hrvatske Vode [Croatian Waters], Central Water Management Laboratory, Zagreb, Croatia

⁴ Montanuniversität Leoben, Department of applied geosciences and geophysics, Austria

*Corresponding author: francis@irb.hr

Abstract: Until recently, magnetic susceptibility (MS) measurements of stream sediments have not been used with the purpose of environmental quality assessment in Croatia. First such measurements in Croatia have been performed by Frančišković-Bilinski (2008) on samples from the Kupa River watershed (Figure 1). The area with the highest values of magnetic susceptibility in that watershed was found to be the lower flow of the Mrežnica River. Coal slag and ash, obtained from burning coal in a textile factory in Duga Resa was discharged directly into the Mrežnica River for 110 y (1884-1994), from where it entered the Korana River and further the Kupa River and pollution was traced up to ~50 km downstream. The geoaccumulation index (I_{geo}) for the anomalous elements and MS determined in the sediment fraction <2mm were: Hg (1.88), B (4.05), Na (1.44), Al (2.05), V (1.65), Cr (1.20), Fe (1.18), Ni (2.10), Cu (2.37), Zr (3.27), Mo (3.34), U (4.03) and MS (5.85). Correlation analysis showed good correlation of MS with: B (0.96), U (0.95), Zr (0.94), Sr (0.93), Na (0.92), Mo (0.92) and Ni (0.90). R-modality cluster analysis indicates linkage of MS with B, Mo, Na and U. Low correlation of MS with Fe (0.36) suggests that Fe is not present in a ferromagnetic form, especially as neither maghemite, nor magnetite phases were identified by XRD.

Increased MS values in the Kupa River watershed were also observed in stream sediments of the upper flow of the sinking karstic Dobra River, (Frančišković-Bilinski et al., 2014a), where any anthropogenic source for that contribution is absent. Thermomagnetic curves show a distinctive Curie-point of magnetite at 580°C. Additional transformation observed at 520-560°C comes from titanomagnetite. Significant correlation between MS and iron was not found. Magnetic particles from the Dobra River sediments contain pyroxene, plagioclase, hematite and quartz in addition to magnetite. White spherules within magnetic grains are also present. The major constituent of five separated magnetic spherules is Fe: minor constituents are Ca, Al, Si and Mg. There are numerous trace elements (Mn, K, Na, Ti, Ni, Cr, V, Ba). The ratio Ni/ Fe vs. Cr/Fe suggests that magnetic spherules are impactites, formed either by a shock event caused by meteorite impact or by volcanic processes, what presents a new and exciting finding and deserves further field and laboratory research.

Our work continued (Frančičković-Bilinski et al., 2014b) with the aim to perform for the first time low-field MS measurements on a decade earlier collected stream sediments in the frame of a Croatian-Slovenian bilateral project. Links between the MS and chemical and mineral composition of sediments have been investigated in order to determine possible anthropogenic influence. The investigated rivers are predominantly unpolluted rivers from Croatian and Slovenian karstic and flysch areas: the Dragonja, the Mirna, the Raša, the Rižana, the Reka, the Rak, the Cerknica, the Unec and the Ljubljanica rivers. For comparison, the Savinja, the Hudinja, the Voglajna rivers and Slivniško Lake from the Celje old metallurgic industrial area (Slovenia) were also investigated. Sediments of the clean karstic and flysch rivers showed extremely low MS values, with MS values ranging from $0.5 \cdot 10^{-7}$ to $5.11 \cdot 10^{-7}$ m³/kg, and IRM values ranging from 0.7 to 7.88 A/m. In the Celje industrial area, river sediments showed much higher MS values, ranging from $1.31 \cdot 10^{-7}$ to $38.3 \cdot 10^{-7}$ m³/kg and IRM values ranging from 0.91 to 100.42 A/m, with the highest MS value found in the Voglajna River at Teharje-Štore, the place which showed significant number of anomalies of toxic metals in our earlier research. Statistically significant correlations were obtained between MS and Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Ba in the Slovenian karstic region, and between MS and Cr, Fe, Co, Ni and Zn in flysch drainage basins.

Keywords: river sediments, Croatia, Slovenia, coal combustion, magnetic spherules



Figure 1: Regions in Croatia and Slovenia where river sediments were studied by magnetic susceptibility measurements: a – Celje area, b – karst rivers, c – flysch rivers, d - the Kupa River watershed

References :

Frančičković-Bilinski, S., 2008 : Detection of coal combustion products in stream sediments by chemical analysis and magnetic-susceptibility measurements. *Mineralogical Magazine*, 72, 43-48

Frančičković-Bilinski, S., Bilinski, H., Scholger, R., Tomašić, N., Maldini, K., 2014a : Magnetic spherules in sediments of the sinking karstic Dobra River (Croatia). *Journal of Soils and Sediments*, 14, 600-614

Frančičković-Bilinski, S., Scholger, R., Bilinski, H., Tibljaš, D., 2014b : Magnetic, geochemical and mineralogical properties of sediments from karstic and flysch rivers of Croatia and Slovenia. *Environmental Earth Sciences*, accepted.