**Chemical and magnetic tracing of coal slag pollutants in karstic river sediments**

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**Abstract**

The Mrežnica River near Duga Resa (Croatia) serves as an ideal „natural laboratory” for studying downstream transport of material in river systems. This study expands the so far brief knowledge about magnetic and chemical properties of sediments along the lower course of this river, contaminated by discharge of coal slag and ash from a former textile factory, directly released into the river for 110 years (1884-1994).

Magnetic susceptibility of the river sediments is very high close to the pollution source and shows a decreasing trend downstream, still being above the level of unpolluted sediments just before the confluence with the Korana River app. 7 km away from the point source. Thermomagnetic curves reveal magnetite as the dominant magnetic mineral, and low frequency-dependent susceptibility indicates an anthropogenic origin. Most heavy metals and other elements in the sediments show a decreasing trend in the downstream direction, similar to the magnetic concentration signal. Correlation analysis between magnetic susceptibility and concentrations of 29 elements shows strongest correlations with Co (R=0.70), Fe (R=0.92), Sr (R=0.86), Al (R=0.74), U (R=0.78) and B (R=0.96). Cluster analysis distinguishes three clusters: Cluster 1 is under strong influence of contamination and contains four sampling sites; Cluster 2 has extreme values of Cd, Cr, Mo and Ni and contains seventeen sites; Cluster 3 reflects rather clean sites and contains nine sites. According to existing sediment quality criteria, Ni and Cr show the largest degree of contamination among six evaluated heavy metals.

Strong variability in the data and frequent extremes are to a large degree caused by heterogeneity in the spatial distribution of the coal-derived material. To account for this situation and to resolve the variability in more detail, statistical sampling of sediments in river cross-sections and estimation of the sediment volume are needed, being a target for further research.

**Keywords:**  Magnetic susceptibility, chemical composition, coal combustion products, river sediments, pollutant tracing

**Introduction**

Magnetic susceptibility is the degree of magnetization of materials as a response to an applied magnetic field. Determining volume-specific susceptibility is a fast and cost-efficient method, and it is possible to use it as an indicator of anthropogenic contamination of some metals in sediments. But, application of magnetic methods alone is not enough, as there is no uniform correlation between magnetic susceptibility and geochemical composition. Therefore, in addition to determination of magnetic properties at least some geochemical analysis should be also performed.

Applying magnetic measurements in different investigations in environmental research was initiated by Oldfield et al. (1985) and Thompson and Oldfield (1986). Following up this pioneering work the possible application of magnetic measurements as a replacement for, or in addition to expensive and complicated chemical analysis in contamination research was intensively investigated (e.g., Hay et al., 1997; Heller et al., 1998; Scholger, 1998; Plater et al., 1998; Kapička et al., 1999).

Investigations performed in industrial areas of Poland (Strzyszcz, 1993; Strzyszcz et al., 1996; Heller et al., 1998) have also shown that the distribution of magnetic susceptibility is closely connected with deposition of industrial dust and that determination of magnetic properties could be used as a method for the detection of the presence of heavy metals in soils and sediments. Many studies with similar work on atmospheric dust transport and deposition followed, as (e.g.) in the area of Leoben (Austria) by Hanesch and Scholger (2002). A detailed overview of magnetic monitoring methods in pollutant research was given by Petrovský and Ellwood (1999).

The results of the majority of those works comply with the conclusion that magnetometry is promising and useful for identification of polluted areas. Because this method is fast and cost-effective, it is possible to handle a dense network of sampling points and later determine the most important points from which chemical analysis should be performed (Cao et al., 2015) on the basis of obtained magnetic susceptibility maps. This cuts the costs of mapping heavy metals in the environment and contributes significantly to the quality of environmental research.

Rivers form an important system for distributing heavy metal contaminants in the environment, but in river systems the applicability of magnetic tracing is not well explored. Scholger (1998) reported strongly enhanced magnetic susceptibility values for sediments in the Mur River (Austria) in areas with known heavy metal contamination. Jordanova et al. (2004) identified an increase of magnetic susceptibility at industrial hotspots along the Danube River in Bulgaria with diminishing values further downstream. Zhang et al. (2011) found a good correlation between heavy metal concentrations and magnetic parameters in river sediments near an iron smelting plant in China. On the other hand, Knab et al. (2006), studying sediments on the Vltava River in the Czech Republic, demonstrated that the applicability of magnetic methods can be limited and lead to pitfalls when the geogenic background exhibits major magnetic anomalies.

The first measurements in Croatia using magnetic methods were performed by Frančišković-Bilinski (2008) on sediment samples from the Kupa River watershed, which was earlier investigated in detail with respect to geochemistry and mineralogy (Frančišković-Bilinski, 2007). The results of this investigation showed that the area with highest values of magnetic susceptibility in the whole Kupa River watershed is located in the lower reach of the Mrežnica River. It was found that this anomaly originates in un-careful disposal of coal burning products. The results of preliminary determinations have also revealed increased values of magnetic susceptibility in the upper part of the Dobra River (also belonging to the Kupa River watershed), whose source is of natural origin (Frančišković-Bilinski et al., 2014a). In the same year Frančišković-Bilinski et al. (2014b) studied magnetic, geochemical and mineralogical properties of sediments from karstic and flysch rivers in Croatia and Slovenia. They found that except in the highly polluted old metallurgic area of Celje in Slovenia, karstic and flysch rivers of Croatia and Slovenia could serve as a database for natural magnetic susceptibility background values of this region.

The aim of this study is to expand the scarce knowledge of magnetic and chemical properties of sediments along the lower course of the Mrežnica River, contaminated with coal slag and ash. Concentrations of potentially toxic metals will be compared to the existing sediment quality and FOREGS data. Which toxic elements remain bound to the sediment during transport process and which present an environmental threat due to extraction with river water will be suggested for selected elements, based on limited water analyses and earlier model adsorption experiments. Meaningful sampling of river sediments is a difficult task, and thus our findings will also be discussed in terms of improving the necessary sampling strategy for obtaining the most reliable results for modeling downstream transport of pollution in rivers.

**Study area**

The study area, including all 30 sampling sites, is shown in Figure 1. A description of the sampling localities, including geographical coordinates is given in Table 1. The Mrežnica is a river in Karlovac County, Croatia. It is 63 km long and its basin covers an area of 64 km2. The Mrežnica is considered special due to its large number of waterfalls, totalling 93. It rises in Kordun, west of Slunj, and flows northwards, in parallel to the Dobra and the Korana, through Generalski Stol and Duga Resa, when it finally flows into the Korana in the south of Karlovac (at Mostanje/Turanj) (URL 1). The Mrežnica is a tufa-forming river and its waterfalls consist of tufa. It was investigated for the first time by Frančišković-Bilinski et al. (2004).

The nearest meteorological station is at Karlovac, which is in an air-line distance of 2-6 km from the studied part of the river. According to the Köppen-Geiger climate classificationKarlovac is located in the temperate oceanic climate zone, Cfb, with mean annual temperature of 11.6 °C and mean annual rainfall of 1097 mm (data taken from: <https://en.climate-data.org/location/33794/> ). The Mrežnica River near its confluence with the Korana River has an average annual discharge of 27 m3s-1 (Frančišković-Bilinski et al., 2012). The geology of the area is composed by Upper Cretaceous limestones and dolomites (~40% of the area), Upper Triassic limestones, dolomites and conglomerates (~20%), Pliocene clastic sediments and limestones (~15%), Quaternary sediments (~10%), while the rest are mostly Jurassic rocks, predominantly limestones, dolomites and clastic sediments (Frančišković-Bilinski, 2005). According to FAO UNESCO soil map of Croatia (<http://esdac.jrc.ec.europa.eu/images/Eudasm/HR/cro1.jpg>), chromic cambisols prevail in the studied region, and humic acrisols and eutric dystric cambisols are also present in some parts. The studied part of the Mrežnica River valley is rather densely populated. Duga Resa town, the uppermost part of the study area where the pollution point source is located, is an urban settlement, while other parts are rural areas with mixed farming. Hills above the river valley are forested. In the lower part of the studied area rather close to the river is the industrial zone of Mala Švarča.

The study area covers the whole polluted stretch of the Mrežnica River, starting from the pollution source unto the confluence with the Korana River with a total length of 7.7 km. The source of pollution in the Mrežnica River was a large textile factory, ’Pamučna industrija Duga Resa’, in Duga Resa town (near Karlovac, Croatia), which burned coal for ~110 years, until it stopped in 1994. There is no information about all the types of coal used in that long period, but it is known that in the several last decades it was Raša coal from the Istrian peninsula (Croatia) rich in organic sulphur. The properties of that coal are described in detail by Medunić et al (2016). Other coal mines containing brown coal and lignite from Bosnia and Herzegovina may also have been utilized. All these coals are a source of elevated uranium concentrations and its natural radionuclides. Coal slag and ash material was deposited directly into the Mrežnica River. Therefore, this river presents today a unique natural laboratory for studying the transport of pollutants in rivers originating in a known point source.

**Materials and methods**

**Sampling and sample preparation**

Altogether 30 samples were collected from the river using a plastic spoon. About 100 g of material was obtained from each sampling site. The sampling sites are distributed along the whole 7.7 km long stretch of the Mrežnica River downstream of the pollution source, which is being investigated within the current research. Two of the samples (DR7, DR8) were collected from a river channel close to the factory where no coal and ash was dumped. Another two of the samples (DR29, DR30) were collected from the Korana River, in the last ~100 m upstream from the confluence point of the Korana and Mrežnica rivers, for comparison. All details about the sampling points are given in Table 1. This part of the river is full of branched channels and river islands, so that different types of river environments were covered and selected, mostly sediments, but in some places samples of mixed material with soil and roots could not be avoided.

After sampling the sediments were dried in air at room temperature and then sieved through a 2 mm sieve (Fritsch, Germany) to get rid of impurities and relatively coarse gravel. Sieved samples were pulverized using a mortar grinder Pulverisette 2 (Fritsch, Idar-Oberstein, Germany) and stored for further analysis.

For the purpose of determining magnetic parameters, some sieved sample material was wrapped with plastic tape and put into cylindrical plastic boxes with a 2.5 cm diameter. The boxes were weighed both before and after putting samples in, to determine the mass of the samples for further mass- specific calculations.

**Determination of magnetic parameters**

Mass-specific susceptibility is calculated when the sample volume is difficult to determine, such as for soil and sediment samples. An MFK1 Kappabridge (Agico, Brno, Czech Rep.) was used to measure magnetic susceptibility at two different frequencies of 976 Hz and 15616 Hz. Mass-specific susceptibility (χ) was determined based on the sample mass and expressed in units of m3kg-1. The low frequency susceptibility (χlf) and high frequency susceptibility (χhf) were taken to determine the percentage frequency dependence χfd% by 100\*(χlf- χhf)/χlf. Values of χ (χlf) are considered as a measure of magnetic concentration for further analysis. The frequency dependence χfd% is particularly useful for detecting the presence of very small, superparamagnetic particles (SP). Larger values (ca. >4%) indicate the presence of a significant amount of SP grains.

The temperature dependence of magnetic susceptibility (χ−T) is widely used to determine the Curie temperatures (Tc) and magnetic phase transformations, and to further characterize magnetic mineralogy through changes during heating (Liu, 2005). Based on Tc one can identify different magnetic minerals, such as magnetite, hematite, goethite, pyrrhotite and greigite. The presence of maghemite can be seen by its destruction at between about 300-400 °C. The MFK1 Kappabridge with an attached heating unit was used to delineate the thermomagnetic χ−T curves.

The S-ratio is a simple measure of relative soft magnetic (as magnetite) and hard magnetic (hematite, goethite) fractions. This ratio is determined from isothermal remanent magnetizations (IRM) in opposite directions. A saturation IRM (SIRM) was imparted in a 1.0 T pulse magnetic field using an MMPM9 pulse magnetizer (Magnetic Measurements LTD, Lancashire, UK), and afterwards a reverse field of 0.3 T was applied producing an IRM-0.3T. The resulting remanence values were determined with a Minispin magnetometer (Molspin LTD, UK; company withdrawn). The S-ratio results from IRM-0.3T /SIRM.

**ICP-MS analysis of elements**

Aliquots of approximately 0.1 g of the powder sediment samples were digested with 2.5 mL of Suprapur® nitric acid and 7.5 mL of Puriss® hydrochloric acid and heated for half an hour at 1000 W in an Anton Paar Multiwave 3000 oven (Graz, Austria), followed by ISO 11466 processing (soil quality-extraction of trace elements soluble in aqua regia). The digested samples were quantitatively transferred to volumetric flasks and diluted to 50 mL with deionized water. All laboratory glassware was submerged for 24 h in a 1% HNO3 solution and rinsed three times with deionized water prior to use. Elements in sediments were detected by Inductively Coupled Plasma Mass Spectrometry employing an ICP MS Elan 9000 (Perkin Elmer, Shelton, USA). Quality control was performed by the analysis of the standard reference materials (RTC, Trace elements on fresh water sediment, catalog number: CNS392-050), which were analyzed at the beginning and after analyzing each series of samples. A generally good agreement within 15% was observed between our data and the certified values.

**Determination of mineralogical composition using XRD**

The mineral composition of the samples was determined by X-ray powder diffraction (XRD). A Philips X’Pert PRO powder diffractometer (Philips, Almelo, The Netherlands) was employed operating at 40 kV and 40 mA. Mineral phases in the samples were identified using a Powder Diffraction File (PDF) database (2004). Semi-quantitative mineralogical analysis was performed using the method described by Boldrin et al. (1992).

**Statistical evaluation**

Anomalies (extremes and outliers) for elements in sediments were determined using the software STATISTICA 7.0 (Statsoft, 2001), using the boxplot method. Box-plots are constructed on the basis of the empirical cumulative distribution plots. The box length was the interquartile range, where outlier values were defined as 1.5 and 3 box lengths from the upper or lower edge of the box. Extremes were values more than 3 box lengths from the edge of the box (Tukey, 1977).

Multivariate cluster analysis in Q-mode was performed to find groups which contain similar samples. In the Q-mode cluster analysis clusters of samples are sought, while in the R-mode clusters of variables (in our case, elements) are desired.

Although the investigated dataset (*n* = 30) is rather small, it could be assumed that results of the obtained boxplot and Q-mode cluster analysis in the current research are reliable. Generally, according to Hogg and Tanis (1988), if *n* is greater than 25 or 30, statistical evaluation of the data will be meaningful. However, in the case that the underlying distribution is symmetric, unimodal, and of the continuous type, a value of *n* even as small as 4 or 5 can yield a very adequate approximation (Hogg and Tanis, 1988).

**Results and discussion**

**Composition of the river sediments**

Semi-quantitative mineralogical XRD analysis of four selected samples (DR1, DR5, DR8, DR19) revealed calcite (+++) in DR1, DR5, DR19; calcite (++) in DR8; quartz (++) in DR1, DR5; quartz (+++) in DR8; quartz (+) in DR19; dolomite (++) in DR5; dolomite (+) in DR8 as the main mineral constituents of the river sediments (with traces of muscovite (+) in DR8 and of sodium calcium tecto alumosilicate (+) in DR19). Magnetite and other magnetic minerals therefore occur in concentrations below the detection limit (~5%) of the XRD method. The same conclusion was obtained in the preliminary paper of Frančišković-Bilinski (2008). However, magnetite was clearly detected in the thermomagnetic χ−T curves (Figure 2A; DR1) by its Curie temperature of around 580 °C. The gradual decrease beyond about 500℃ indicates substituted magnetite-like phases, or a grain size effect of magnetite particles. The non-polluted sample DR8 (Figure 2B) also shows the occurrence of magnetite; strong formation of new magnetite during heating (revealed by the higher χ values in the cooling curve) points out a dominating natural origin of the sample material as in soil such new formation is frequently observed due to clay mineral transformation (e.g., Zhang et al., 2012). Magnetite or magnetite-near phases dominate in all samples as S-ratios (Figure 3) are, with two exceptions, generally high (0.97-1.0) and non-discriminative.

**Results of magnetic measurements**

Figure 3 shows the data for mass-specific susceptibility, frequency-dependent susceptibility and S-ratio downstream from the pollution source (data listed in the Appendix 1 in Supplementary Material).

The samples DR1-4, which were collected at less than a 100 m distance from the pollution source and DR5 about another 100 m downstream show predominantly high χ values; however, with strong variability. Compared to these clearly contaminated samples, the two samples (DR7 and DR8), which were collected from another (left) channel of the river close to the factory show very low χ values. Polluted material was thrown into the right channel of the river from the textile factory only, which is located on the island between the two river channels. After those two channels of the river merge, χ values are still higher than in the non-polluted channel, but clearly lower than for the first samples close to the pollution source. In the further course downstream, until the confluence with the Korana River, there is a decreasing trend of χ with strong variability, reaching values at the end of the Mrežnica River course which are still higher than in the Korana River close to the confluence.

Frequency-dependent magnetic susceptibility (χfd%) values are low along the polluted channel of the Mrežnica River, mostly between ~2-4% with an increasing trend downstream, reaching the highest values, around 6%, shortly before the confluence. The χfd% values in the non-polluted river channel (~6-9%) and in the Korana River (~13%) are clearly higher implying a larger content of soil-derived fine particles.

The behavior of χ and χfd% values gives insight into downstream distribution and transport of magnetic pollutant particles, whose quantity decreases downstream. The variability is likely caused by deposition of those particles at some places in “pockets”, where accumulated particles are trapped and stay for a relatively long time. Comparison with the properties of the non-polluted samples DR7-8 and DR29-30 indicates that near the confluence the river sediments are still significantly contaminated with coal and ash material.

**Elemental composition of sediments**

The elemental composition data for the sediments, including 29 chemical elements determined is listed in Appendix 2 of Supplementary Material. Concentrations of eight selected elements (Fe, U, Pb, Cu, Bi, Cd, Ca, K) in the Mrežnica River sediments in downstream direction are presented in Figure 4. The elements studied show several patterns. The first and largest group of elements consists of Al, B, Ba, Be, Co, Fe, Li, Mg, Mn, Na, Sb, Sn, Sr, Ti, Tl, U and V. All behave very similarly regarding their downstream distribution. As can be seen in Figure 4, the highest concentrations of Fe and U occur at the sites close to the pollution source and show a decreasing trend further downstream to the confluence with the Korana River, with strong fluctuations. The decreasing trend is most clearly seen in the U data. The elements Pb, Cu and Zn behave similarly to the first group, but there are very large extremes at certain sites: These extremes occur at DR10 with concentrations exceeding 500 µgg-1for Pb, and at DR3, with concentrations exceeding 500 µgg-1 for Cu and 600 µgg-1 for Zn. A second group of elements with a similar pattern consists of Cd, Cr, Mo and Ni. Concentrations of these elements are approximately the same, rather low, throughout the whole stretch of the river investigated, except at locations DR18, DR19 and DR20, where strong extremes occur. Bi is an example with a very different pattern to the elements mentioned above. Its concentration is rather low near the pollution source and in the furthest downstream part, but with the highest concentrations, including some extremes, in the middle part of the investigated river section. The K and W concentration pattern is also unusual. The concentration of K is rather uniform in the upper and middle part of the stretch of the river investigated, but it increases significantly in its furthest downstream part. The behavior of W is very unusual. At site DR1 near the pollution source its concentration reaches the extreme of almost 80 µgg-1. There is also a much lower secondary maximum at station DR19. At all other sites its concentration is low. Values of Ca show an inversely proportional pattern to the heavy metals and the majority of other elements. Its minimal concentrations are observed at sites near the pollution source and secondary maximum values occur at sites where the concentrations of Cd, Cr, Mo and Ni are highest. This could be due to the fact that the Mrežnica River is a carbonate rich tufa-forming river. Therefore at clean locations Ca concentrations in sediments are relatively high, while in places where the sediment is mixed with a lot of slag material the Ca concentration is lower.

**Statistical evaluation of element concentrations**

To get a better insight into the statistical significance of elevated concentrations of different elements, a box-plot determination of anomalies (extremes and outliers) was carried out and the results are presented in Table 2. As can be seen from this table, locations with the largest number of anomalies are those close to the pollution source, especially sites DR1, DR3 and DR5. At those contaminated sites Fe and Al concentrations, and also magnetic susceptibility are extreme. Elements which are known to be bound to coal (Ba, Na, Sr, B and U) appear as extremes or outliers at the same sites.

Correlation analysis between concentrations of the 29 elements and low-field magnetic susceptibility was performed to get an insight into the relationship between χ and particular elements. A strong positive correlation (correlation factors) was obtained for χ with Co (0.70), Fe (0.92), Sr (0.86), Al (0.74), U (0.78) and B (0.96). A moderate positive correlation for χ was obtained with Cu (0.42), Ba (0.66), Mg (0.66), Na (0.68), Be (0.52), Li (0.52), Sb (0.41) and Ti (0.42).

A Q-mode cluster analysis was performed to distinguish groups of similar samples according to their chemical composition. Three clusters were obtained (see their spatial distribution in Figure 1): Clusters 1, 2 and 3 contain 4, 17 and 9 sampling sites, respectively. Members of each cluster and cluster means for all 29 elements are presented in Table 3.

Cluster 1 consists of sites closest to the point source. This cluster is under a strong influence of the contamination from the factory. In comparison with the other two clusters, its concentrations of Al, B, Ba, Be, Co, Fe, Li, Mg, Mn, Na, Sb, Sn, Sr, Ti, Tl, U, V, Pb, Cu and Zn are elevated. The highest values for all these elements occur near the point source.

Cluster 2 is the largest cluster. Its members are widespread in all parts of the section of the Mrežnica River flow investigated. Among other sites, this cluster contains sites where concentrations of Cd, Cr, Mo and Ni are much elevated and therefore mean values of those elements are the highest among all clusters. Mean values for other elements are much lower than in Cluster 1, but at the same time higher than in Cluster 3.

Cluster 3 members are predominantly located in the middle part of the section of the Mrežnica River investigated. This cluster is least influenced by the contamination. Concentrations of almost all elements are the lowest among all clusters. At the same time the concentration of Ca is the highest among all clusters, as carbonate influence is prevalent in these samples.

**Geoaccumulation index (Igeo)**

The Igeo, originally introduced by Müller (1979), was used as a measure of metal contamination in the river sediments. This index is based on comparing the present metal concentrations with pre-industrial concentrations. Igeo is calculated using the following equation:

Cn is the concentration determined for the metal n examined in a sample, and Bn is the geochemical background value for this metal. In our case, background value data from Frančišković-Bilinski (2008) was taken to represent natural elemental concentrations in the Mrežnica River before reaching the point source of contamination. The factor 1.5 is used as a background matrix correction due to lithological discrepancies. The Igeo results were evaluated according to the Müller (1981) scale, which consists of seven grades ranging from class 0 (unpolluted, Igeo ≤ 0) to class 6 (extremely polluted, Igeo > 5).

Igeo values were calculated for the 20 elements, for which background data is available. Figure 5 presents Igeo values in downstream direction for selected elements (for values of all 30 sampling stations see Appendix 3 in Supplementary Material). From the results we can conclude that for 3 elements only (Mn, Co and Sr) all sites can be considered unpolluted to moderately polluted.. All other elements show a much higher degree of pollution, at least at some sites. The majority of the elements have elevated Igeo values at the sites close to the point source of pollution, and the values gradually decrease downstream with a high variability and extremes as seen in the element concentration and magnetic data presented above. The Igeo values of Cd, Cr, Mo and Ni are highest further downstream, around sampling locations DR18, DR19 and DR20. Some of them, like Cd, have very low Igeo values at all other sites, and only their values at these three sites reach levels of moderately to strongly or even extremely polluted sediments. Among all elements, Na has the highest Igeo values. Although Na is not a pollutant, the highly elevated Igeo concentrations are certainly derived from coal and thus indicate coal-related pollution in the sediments.

**Assessment of sediment quality**

Unfortunately, sediment quality criteria for Croatia as well as at the level of the European Union do not exist. Therefore sediments will be evaluated in this chapter according to the criteria of the University of Waterloo, Canada, which collected and systematized existing legislative regulations worldwide (SMSP and FALCONBRIDGE NC SAS, 2005). Currently the Croatian water authorities are working on limit values for sediments, which will be valid in Croatia and will cover the 8 most hazardous elements (As, Cd, Cr, Cu, Pb, Hg, Ni and Zn). Of those elements, As and Hg were not investigated in our study. Therefore we will assess the sediment quality with respect to the 6 remaining metals Cd, Cr, Cu, Pb, Ni and Zn. We also compare their concentrations with available data for aqua regia dissolved sediments (available at <http://weppi.gtk.fi/publ/foregsatlas/>). In Table 4 the existing sediment quality criteria according to the literature mentioned (SMSP and FALCONBRIDGE NC SAS, 2005) are summarized.

According to USA federal criteria, the Cd concentrations correspond to heavily contaminated sediments at one location only (DR19). At all other locations, Cd concentrations are rather low at the lowest toxic level according to the legislative regulation of St. Lawrence River, Canada. For Cd there is no FOREGS data available.

The situation with Cr in the sediments of the stretch of the Mrežnica River investigated is not satisfactory. At several locations near the pollution source, but also in the lower part of the section of the river studied, Cr concentrations significantly exceed the limit for significantly toxic effects according to the legislative regulation of British Columbia, Canada. The worst situation with Cr contamination is found around location DR19, where the concentration determined dramatically exceeds the limit about 45 times. The average concentrations of Cr according to the FOREGS data are16-27 mg/kg.

Concentrations of Cu exceed the limit value of the USA federal criteria for heavily contaminated sediments at 3 locations (DR1, DR3 and DR10), mostly rather close to the point source of pollution. If we apply the less strict legislative regulation of Ontario, Canada, only two locations (DR1 and DR3) display Cu concentrations above the limit value that might cause significant toxic effects. The average concentrations of Cu according to the FOREGS data are 14-19mg/kg.

Only at one location (DR10) concentrations of Pb exceed the limit concentration for significant toxic effects according to the legislation of British Columbia, Canada. At several other locations the observed concentrations are at the lowest toxic level, while at all other locations the Pb concentrations of the sediments are rather low. The average concentrations of Pb according to the FOREGS data are 14-19 mg /kg.

The situation for Ni in the sediments of the section of the Mrežnica River investigated is the worst among all elements studied. At many locations in all parts of the river section studied Ni concentrations significantly exceed the limit value that might cause significant toxic effects according to the legislative regulations of British Columbia, Canada, especially at site DR19, where the Ni concentration determined exceeds the limit value for significantly toxic effects almost 200 times. The average concentrations of Ni according to the FOREGS data are 16-23 mg/kg.

Concentrations of Zn exceed the limit value of the USA federal criteria for heavily contaminated sediments at two locations (DR3 and DR7). At the majority of the other locations the sediments are clean with respect to Zn. Only at a few locations are Zn concentrations in the range for moderately contaminated sediments according to the same criteria. The average concentrations of Zn according to the FOREGS data are 45-60 mg/kg.

**Aspects of sampling strategies**

The magnetic and chemical results presented and discussed above reveal a trend of the downstream fate of metals with very high concentrations occurring very close to the pollution source in most cases. Namely, magnetite (which was detected by thermomagnetic curves) is known as an adsorbent for many hazardous species from aqueous solution (Petrova et al., 2011). The data therefore approximately reflects the signature of coal slag and ash contamination in the river. A potential advanced goal is to use such results for developing general models of sediment transport in a river system. However, a number of difficulties exist as additional processes are at present unknown. Leaching of some minor and major elements during slag and ash transport in water should be studied to improve the quality of the data, similar to those performed on model systems by Popović et al. (2001). At present, two sampling stations on the Mrežnica River can be used to obtain comparative results for water, regularly surveyed by Croatian Waters (Croatian Waters Annual Report, 2015). One station (Mostanje) is at the confluence of the Mrežnica to the Korana River, close to DR28. The other station (Juzbašići) is far upstream from the pollution source. Concentrations of Cu, Zn, Cr, Mg and Na determined in river water are compared in Figure 6. Concentrations of dissolved Cu and Zn are not significantly higher in the lower stretch of the Mrežnica, suggesting that they do not cause an environmental threat by slag and ash transport downstream. This is supported by the results of model adsorption measurements (Bilinski et al., 1991; Kozar et al., 1992). On the contrary, the dissolved Cr concentration is higher in the lower stretch of the river and can induce an environmental threat. Similarly, Popović et al. (2001) concluded that Cr is the most abundant pollutant involved in coal ash transport. The concentration of dissolved Mg does not change as a result of slag and ash transport, while the concentration of dissolved Na is significantly higher downstream. Although dissolved Na is not considered to be a pollutant it can serve as a complementary indicator of coal slag and ash dissolution during transport.

Because of the complex hydrodynamic conditions in the river, the downstream patterns of slag and ash related magnetic and chemical parameters in the river sediments are likely resolved with limited accuracy by the sediment samples studied. The distribution of contaminants in the river sediments along the course of the river depends on their concentrations in the sediment and the volume of river sediment at the positions sampled. In a future project we therefore intend to perform more detailed statistical sampling of sediments in river cross-sections plus an estimation of the sediment volume. This is a work-demanding task, but the results could provide a clue as to how sampling of river sediments can be optimized in order to obtain the most significant distribution pattern of pollutants.

**Conclusions**

From our research presented in the current paper, the following conclusions can be drawn:

* Magnetic susceptibility in the Mrežnica River sediments is very high close to the pollution source and decreases downstream, still being above the level of unpolluted sediments just before the confluence with the Korana River app. 7 km away from the point source. Thermomagnetic curves reveal magnetite as the dominant magnetic mineral, and frequency-dependent susceptibility along the course of the river indicates an anthropogenic origin.
* XRD results showed that the main mineralogical constituents are calcite, quartz and dolomite, with traces of muscovite in some samples.
* The results of ICP-MS analysis show that concentrations of most heavy metals and other elements in the sediments show a decreasing trend in the downstream direction of the pollution source, similar to the magnetic signal. The highest values for most of them have and statistical anomalies determined by the boxplot method are found at locations close to the pollution source, but concentrations of some elements like Cd, Ni, Cr, Mo increase further downstream.
* Correlation analysis between magnetic susceptibility and concentrations of 29 elements shows that a strong correlation exists with Co (R=0.70), Fe (R=0.92), Sr (R=0.86), Al (R=0.74), U (R=0.78) and B (R=0.96), and moderate correlation exists with Cu, Ba, Mg, Na, Be, Li, Sb and Ti.
* Q-mode cluster analysis distinguishes three groups of similar samples according to their chemical composition: Cluster 1 (under strong influence of contamination) containing 4 sampling sites, Cluster 2 (with extreme values of Cd, Cr, Mo and Ni) containing 17 sampling sites and Cluster 3 (rather clean carbonate cluster) containing 9 sampling stations.
* According to the geoaccumulation index (Igeo), most heavy metal concentrations in the samples studied are classified from moderately to extremely polluted. The highest Igeo values for the majority of the elements occur just after the point source of pollution, while the highest Igeo values for Cd, Cr, Mo and Ni occur further downstream. Na is the element with the highest Igeo values.
* According to existing sediment quality criteria, , Ni and Cr show the largest degree of contamination of the 6 heavy metals evaluated and their concentrations in many parts of the river course part studied might cause significant toxic effects. All the elements in coal can be found in a variety of forms (Ruppert et al., 1995).
* The quality of the results obtained is not yet sufficient to analyze mechanisms of sediment transport, here in particular of the coal combustion products. Strong variability in the data and frequent extremes are to a large degree caused by heterogeneity in the spatial distribution of coal-derived material. To account for this situation, statistical sampling of sediments in river cross-sections and estimation of the sediment volume are needed as a target of further research.

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**References**

Bilinski H, Kozar S, Plavšić M, Kwokal Ž, Branica M (1991) Trace metal adsorption on inorganic solid phases under estuarine conditions. Marine Chemistry 32:225-233.

Boldrin A, Juračić M, Menagazzo V, Rabitti S, Rampazzo G (1992) Sedimentation of riverborne material in a shallow shelf sea: Adige River, Adriatic Sea. Marine Geology 103:473-485.

Cao LW, Appel E, Rösler W, Magiera T (2015) Efficiency of stepwise magnetic-chemical site assessment for fly ash derived heavy metal pollution. Geophysical Journal International 203:767–775.

Croatian Waters (2015) Annual Report on state of waters in the Karlovac county.

Frančišković-Bilinski S (2005) Geochemistry of stream sediments in Kupa River drainage basin [In Croatian] / Doctoral thesis. University of Zagreb, Faculty of Science, 197 pp.

Frančišković-Bilinski S (2007) An assessment of multielemental composition in stream sediments of Kupa River drainage basin, Croatia for evaluating sediment quality guidelines. Fresenius Environmental Bulletin 16(5):561-575.

Frančišković-Bilinski S (2008) Detection of coal combustion products in stream sediments by chemical analysis and magnetic-susceptibility measurements. Mineralogical Magazine 72(1):43-48.

Frančišković-Bilinski S, Barišić D, Vertačnik A, Bilinski H, Prohić E (2004) Characterization of tufa from the dinaric karst of Croatia: mineralogy, geochemistry and discussion of climate conditions. Facies 50(2):183-193.

Frančišković-Bilinski S, Bhattacharya AK, Bilinski H, Bhattacharya BD, Mitra A, Sarkar SK (2012) Fluvial geomorphology of the Kupa River drainage basin, Croatia: A perspective of its application in river management and pollution studies. Zeitschrift für Geomorphologie. 56(1):93-119.

Frančišković-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(3):600-614.

Frančišković-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 72(10):3939-3953.

Hanesch M, Scholger R (2002) Monitoring of heavy metal loadings in soils by means of magnetic susceptibility measurements. Environmental Geology 42:857–870.

Hay KL, Dearing JA, Baban SMJ, Loveland P (1997) A preliminary attempt to identify atmospherically derived pollution particles in English topsoils from magnetic susceptibility measurements. Physics and Chemistry of the Earth 22(1-2):207-210.

Heller F, Strzyszcz Z, Magiera T (1998) Magnetic record of industrial pollution in forest soils of Upper Silesia, Poland. Journal of Geophysical Research 103(B8):17767-17774.

Hogg RV, Tanis EA (1988) Probability and Statistical Inference, 3rd Ed. New York: McMillan.

Jordanova D, Hoffmann V, Fehr KT (2004) Mineral magnetic characterization of anthropogenic magnetic phases in the Danube river sediments (Bulgarian part). Earth and Planetary Science Letters 221(1): 71-89.

Kapička A, Petrovský E, Ustjak S, Macháčková K (1999) Proxy mapping of fly ash pollution of soils around a coal-burning power plant. Journal of Geochemical Exploration 66:291-297.

Knab M, Hoffmann V, Petrovský E, Kapička A, Jordanova N, Appel E (2006) Surveying the anthropogenic impact of the Moldau river sediments and nearby soils using magnetic susceptibility. Environmental Geology 49(4): 527-535.

Kozar S, Bilinski H, Branica M (1992) Adsorption of lead and cadmium ions on calcite in the Krka estuary. Marine Chemistry 40:215-230.

Medunić G, Ahel M, Božičević Mihalić I, Gaurina Srček V, Kopjar N, Fiket Ž, Bituh T, Mikac I (2016) Toxic airborne S, PAH, and trace element legacy of the superhigh-organic-sulphur Raša coal combustion: Cytotoxicity and genotoxicity assessment of soil and ash. Science of the Total Environment 566-567:306-319.

Müller G (1979) Schwermetalle in den sedimenten des Rheins–Veranderungen seitt 1971. Umschan 79:778-783.

Müller G (1981) Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. Chemical Zeitung 105:157-164.

Oldfield F, Hunt A, Jones MDH, Chester R, Dearing JA, Olsson, Prospero JM (1985) Magnetic differentiation of atmospheric dusts. Nature 317:516-518.

Petrova TM, Fachikov L, Hristov J (2011) The magnetite as adsorbent for some hazardous species from aqueous solutions: A review. International Review of Chemical Engineering 3:134-152.

Petrovský E, Ellwood BB (1999) Magnetic monitoring of air-, land-, and water-pollution. In: Quaternary Climates, Environments and Magnetism (Editors: Maher BA, Thompson R). Cambridge University press, Cambridge, pp. 279-322.

Plater AJ, Ridgeway J, Appleby PG, Berry A, Wright MR (1998) Historical contaminant fluxes in the Tees estuary, UK. Marine Pollution Bulletin 37:343-360.

Popović A, Djordjević D, Polić P (2001) Trace and major element pollution originating from coal ash suspension and transport processes. Environment International 28:251-255.

Powder Diffraction File (2004) Database Sets 1-54, International Centre for Diffraction Data (ICDD). Newtown Square, Pennsylvania.

Ruppert LF, Hower JC, Eble CF (1995) Significance of the modes of occurrence of arsenic in coal. Proc. of 12th Annu. Int. Pittsburgh Coal Conf., pp. 1152-1156.

Scholger R (1998) Heavy metal pollution monitoring by magnetic susceptibility measurements applied to sediments of the river Mur (Styria, Austria). European Journal of Environmental and Engineering Geophysics 3:25-37.

SMSP and FALCONBRIDGE NC SAS (2005) Koniambo project, Environmental and Social Impact Assessment, Chapter 4 Mine, 4.2-7 Quality criteria for freshwater sediment.

Stat Soft, Inc. Statistica., 2001. (data analysis software system), ver. 7. <http://www.statsoft.com>

Strzyszcz Z (1993) Magnetic susceptibility of soils in the areas influenced by industrial emissions. Soil Monitoring (Editor: R.Schulin). Monte Verita, Birkhäuser Verlag, Basel, pp. 255-269.

Strzyszcz Z, Magiera T, Heller F (1996) The influence of industrial emissions on the magnetic susceptibility of soils in Upper Silesia. Studia geophisica et geodetica 40:276-286.

Thompson R, Oldfield F (1986) Environmental Magnetism. Allen & Unwin, London.

Tukey JW (1977) Exploratory data analysis. Addison-Wesley, ISBN 0-201-07616-0. OCLC 3058187.

URL 1 <https://en.wikipedia.org/wiki/Mre%C5%BEnica> Accessed 27th January 2017.

Zhang CX, Qiao Q, Piper JD, Huang BC (2011) Assessment of heavy metal pollution from a Fe-smelting plant in urban river sediments using environmental magnetic and geochemical methods. Environmental Pollution 159(10): 3057-3070.

Zhang CX, Paterson GA, Liu QS (2012) A new magnetic enhancement mechanism of hematite during heating: the role of clay minerals. Studia Geophysica et Geodaetica 56(3): 845–860.

**Figure captions**

**Figure 1:** Study area on Google Maps with sampling locations (DR with numbers) along the Mrežnica River; the downstream direction is from left/West to right/East. The map at the bottom shows the sites near the factory in detail. Cluster memberships of multivariate geochemical analysis are indicated by stars on top of the sites symbols (red: Cluster-1, yellow: Cluster-2, blue: Cluster-3). The small sketch-map shows the Kupa River drainage basin, to which the Mrežnica River belongs.

**Figure 2:** Temperature dependence of magnetic susceptibility (normalized to the starting value at room temperature) of samples from a polluted site (left; DR1) and from an unpolluted site (right; DR8). The arrow marks the heating curve.

**Figure 3:** Downstream behavior of mass-specific magnetic susceptibility (diamonds), frequency-dependent susceptibility (squares) and S-ratio (crosses) in the Mrežnica River sediments in downstream direction (sites shown by bold symbols between the dashed lines). Scaling on the x-axis is in subsequent downstream order of the sites (for distances see Figure 1). The two leftmost (DR7, DR8) and two rightmost sampling sites (DR29, DR30) are located in a parallel non-polluted branch of the Mrežnica River close to the factory, and in the non-polluted Korana River close to the confluence with the Mrežnica River.

**Figure 4:** Concentrations of eight selected elements (Fe, U, Pb, Cu, Bi, Cd, Ca, K) in the Mrežnica River sediments in downstream direction. Scaling on the x-axis is in subsequent downstream order of the sites (for distances see Figure 1). The two leftmost (DR7, DR8) and two rightmost sampling sites (DR29, DR30) are located in a parallel non-polluted branch of the Mrežnica River close to the factory, and in the non-polluted Korana River close to the confluence with the Mrežnica River.

**Figure 5:** Values of Igeo for five selected elements in the Mrežnica River sediments in downstream direction. Scaling on the x-axis is in subsequent downstream order of the sites (for distances see Figure 1). The two leftmost (DR7, DR8) and two rightmost sampling sites (DR29, DR30) are located in a parallel non-polluted branch of the Mrežnica River close to the factory, and in the non-polluted Korana River close to the confluence with the Mrežnica River.

**Figure 6:** Concentrations in water of Cu, Zn and Cr dissolved and of Mg and Na on 8 dates during the year 2015 at two locations on Mrežnica River – Mostanje (blue crosses; below the point source) and Juzbašići (red stars; above the point source).