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Detection of coal combustion products in stream sediments by chemical analysis and magnetic-susceptibility measurements

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ABSTRACT

Coal slag and ash, obtained from burning coal in a textile factory in Duga Resa (Croatia) was discharged directly into the Mrežnica River for 110 y (1884–1994), from where it travelled to the Korana River and further to the Kupa River at Karlovac, a total of ~50 km from its source. Of 54 elements determined by inductively coupled plasma mass spectrometry (ICP-MS) in the <2 mm sediment fraction, a number of anomalously high levels were recorded. The geoaccumulation index (I_{geo}) for the anomalous elements 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), Sr (0.97), Zr (3.27), Mo (3.34) and U (4.03). Low-field magnetic susceptibility (MS) was measured for each sample. The I_{geo} for MS in the anomalous region is 5.85. Correlation analysis showed good correlation (>0.90) 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). Cluster analysis of R-modality indicates that MS is linked to B, Mo, Na and U. Low correlation of MS with Fe (0.36) suggests that Fe in stream sediments is not in a ferromagnetic form. Neither maghemite, nor magnetite phases were identified by X-ray diffraction (XRD) in the sediments. Low-field magnetic susceptibility provides an indicator of contamination of river sediments by transported coal slag and ash, although it cannot be prescribed to a single element.

Keywords: coal combustion products; stream sediments; magnetic susceptibility; contamination; Kupa River drainage basin, Croatia.

Introduction

The aim of this preliminary study was to apply a rapid and inexpensive, low-field magnetic susceptibility method (MS) to stream sediments, as described by Scholger (1998) and Petrovsky *et al.* (2000), and to delineate polluted areas in the Kupa river basin. Geochemical characterization of the <63 μ sediment fraction has already been carried out (Frančišković-Bilinski, 2007). Increased MS was observed in two regions: (1) in the lower stretch of the Mrežnica and Korana rivers, where several elements (U, Sb, Sn, Zr, Nb, S, Na, Ni, Se, Sr, Y, Nb) showed anomalously high concentrations. This region is located on the Dinaric carbonate platform and the anomalies are of anthropogenic origin. (2) At the middle flow of Glina River, where several other elements showed anomalously high concentrations (Fe, Sc, V, Zr, Na, Cu, Ga, Y). The anomalies in this region are of natural origin, under the influence of the Supradinaric belt with ophiolites. The MS did not detect extreme Ba anomalies, described in the same drainage basin (Frančišković-Bilinski, 2006).

In the present work we concentrated our research on the MS anomaly observed in the lower parts of the Mrežnica and Korana rivers. The study area, including 22 sampling locations, is presented in Fig. 1. Sampling station details are listed in Table 1. The source of the pollution in the Mrežnica river was a large textile factory, 'Pamučna industrija Duga Resa', in Duga Resa (near Karlovac, Croatia), which burned coal for ~110 y, until 1994; all coal slag and ash were deposited directly into the Mrežnica river.

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FIG. 1. Study area with sampling locations represented by circles (left) and location map for Kupa River drainage basin within Croatia, Slovenia and Bosnia and Herzegovina.

Materials and methods

Stream sediments were collected during April 2007 and the <2 mm fraction was prepared for analysis by air drying and dry sieving, (2 mm sieve, Fritsch, Germany). Sieved samples were pulverized using a mortar grinder Pulverisette 2 (Fritsch, Germany).

TABLE 1. Detailed positions of each sampling station (sample number, locality name, river, flows to, geographical coordinates) and MS data for each sampling station ($\chi \times 10^{-8}$ m^3/kg)

Data subset	Sample	Locality	River	Flows to	N(E)	E(E)	MS
BG	212	Belavići	Mrežnica	Korana	45.42036	15.48325	5.6
A	210	Mala Švarča	Mrežnica	Korana	46.46175	15.52789	539.2
	211	Donje Mrzlo Polje	Mrežnica	Korana	45.46394	15.50031	450.8
	221	Mala Švarča	Mrežnica	Korana	45.46331	15.54164	466.5
K	200	Iševnica	Kupica	Kupa	45.45053	14.85067	7.2
	201	Brod na Kupi	Kupica	Kupa	45.46361	14.85611	8.0
	202	Brod na Kupi	Kupa	Sava	45.46472	14.85611	5.7
	203	Golik	Kupa	Sava	45.47635	14.89837	6.6
	204	Zapeč, Blaževci	Kupa	Sava	45.47208	15.08508	5.2
	218	Ozalj, above PP	Kupa	Sava	45.61503	15.47328	11.5
	217	Levkušje-Zorkovac	Kupa	Sava	45.57800	15.52022	6.1
	209	Karlovac-Vodostaj	Kupa	Sava	45.50001	15.57669	10.8
DS-K	220	Turanj	Korana	Kupa	45.46742	15.57225	56.1
	219	Karlovac	Korana	Kupa	45.48856	15.56147	53.3
	216	Rečica	Kupa	Sava	45.48094	15.66719	14.3
	215	Zamršlje	Kupa	Sava	45.50844	15.69439	17.9
	214	Šišljavić	Kupa	Sava	45.51111	15.76661	26.4
	213	Lijevo Sredičko	Kupa	Sava	45.53144	15.88928	28.4
	208	Pokupsko	Kupa	Sava	45.48931	16.01806	15.6
	207	Letovanić	Kupa	Sava	45.50300	16.20000	2.7
	205	Sisak-Zibel	Kupa	Sava	45.47583	16.35972	3.5
	206	Sisak-Stari grad	Kupa	Sava	45.47087	16.38889	9.4

The MS was measured using magnetic susceptibility meter MS2 (Bartington Instruments, England) and sensor type MS2B. The sensor was calibrated for a sample mass of 10 g.

A Perkin Elmer SCIEX ELAN 6100 inductively coupled plasma-mass spectrometer (ACTLABS, Canada) was used to analyse for 54 elements with the program *Ultratrace 2*. Standard materials were obtained from the USGS: GXR-1, GXR-2, GXR-4 and GXR-6.

Analyses for C, TOC and S were performed using a LECO CS-300 (USA) instrument. Total combustion was at 1200ºC, adding wolfram granulate (HRT Labor Tecknik GmbH). The standard used was LOT number R1201-1, LECO Corporation, USA.

Results

Increased values of low-field magnetic susceptibility (MS, $\chi \times 10^{-8}$ m^3/kg) were observed in Mrežnica River, downstream of the pollution source in Duga Resa; in the Korana River, downstream of Mrežnica River inflow; and in Kupa River, downstream of Korana River inflow; and in Pokupsko, ~50 km downstream of the pollution source. Magnetic susceptibility data are presented in Table 1.

The ICP-MS and MS data were divided into four subsets for statistical evaluation, in order to find the elements which are enriched in the anomalous area. The subset BG consists of only one sampling station (212) and represents the background values for Mrežnica River above the pollution source. Subset A consists of three sampling stations (210, 211, 221) in Mrežnica River, downstream of the pollution source. The subset K consists of eight sampling stations (200, 201, 202, 203, 204, 218, 217, 209) in Kupica River and in Kupa River above the Korana River inflow. Subset DS-K consists of 10 sampling stations (220, 219, 216, 215, 214, 213, 208, 207, 205, 206) in the Korana and Kupa Rivers, downstream of Korana River inflow.

In Table 2, statistical parameters for MS and selected elements, which are enriched in the anomalous area (A) are presented. Data are presented for all four subsets. The geoaccumulation index, I_{geo} (=log2(C_n/1.5B_n) where C_n = measured elemental concentration and B_n = background concentration; Müller, 1979) was calculated for subset A. I_{geo} describes the intensity of contamination of sediments, with respect to metal pollutants (Förstner *et al.*, 1993). The largest I_{geo} values were observed for B, U, Mo and Zr.

Cluster analysis of R-modality was performed on the total dataset to find the relationship between the 54 elements and MS (Fig. 2). MS clustered with B, Mo, Na and U. Significant correlations (>0.90) existed between MS and the following elements: B (0.96); U (0.95); Zr (0.94); Sr (0.93); Na (0.92); Mo (0.92); Ni (0.90).

Discussion

According to the I_{geo} classification of Förstner *et al.* (1993), in the anomalous region of the present study, sediments are strongly contaminated with U, B, Mo and Zr, moderately to strongly contaminated with Al, Ni and Cu, moderately contaminated with Hg, Na, V, Cr and Fe, and uncontaminated to moderately contaminated with Sr.

The study area is a model area to study the behaviour of coal slag and coal ash deposited in a clean karstic tufa-forming river. The MS data illustrate clearly that coal combustion products have been transported far downstream from their source. The poor correlation of MS with Fe (0.36) indicates that Fe in this river is in neither paramagnetic nor ferromagnetic form. This result suggests that just as in soils (Kapička *et al.*, 2001) the properties of the coal-combustion products have altered following exposure to the river water. Neither ourselves or Kapička *et al.* (2001) detected magnetite or maghemite by XRD, yet these minerals are characteristically present in coal combustion products. The significant correlation of MS with B, Na and Ni is most likely due to formation of sodium borate glass during the combustion process; Ni is known to partition into sodium borate glass (Kashif *et al.*, 1991). Similarly Mo and U can be incorporated in

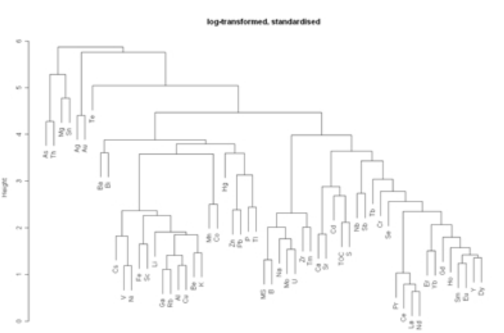

FIG. 2. Dendogram obtained by cluster analysis of R-modality for 55 variables.

TABLE 2. Statistical parameters for MS and selected elements in all subsets; I_{geo} for subset A. Data for Hg are in ppb; Na, Al, Fe in %; all other elements are in ppm.

Subset	Mean	Geom. Mean	Median	Min	Max	Variance	Std. Dev.	I_{geo}
MS-BG	5.6000	5.6000	5.6000	5.6000	5.6000			
MS-A	485.5000	484.0183	466.5000	450.8000	539.2000	2224.39	47.1634	5.85
MS-K	7.6375	7.3521	6.9000	5.2000	11.5000	5.48	2.3415	
MS-DS-K	22.7600	15.4899	16.7500	2.7000	56.1000	354.18	18.8196	
Hg-BG	30.0000	30.0000	30.0000	30.0000	30.0000			
Hg-A	165.0000	126.2319	87.0000	68.0000	340.0000	23059.00	151.8519	1.88
Hg-K	81.6250	80.5300	80.5000	61.0000	100.0000	200.27	14.1516	
Hg-DS-K	97.4000	78.1565	114.5000	24.0000	161.0000	3186.49	56.4490	
B-BG	3.0000	3.0000	3.0000	3.0000	3.0000			
B-A	74.6667	70.7660	69.0000	48.0000	107.0000	894.33	29.9054	4.05
B-K	4.8750	4.6431	5.0000	3.0000	8.0000	2.70	1.6421	
B-DS-K	6.5000	5.9955	6.5000	3.0000	12.0000	7.17	2.6771	
Na-BG	0.0340	0.0340	0.0340	0.0340	0.0340			
Na-A	0.1383	0.1333	0.1240	0.1000	0.1910	0.00	0.0472	1.44
Na-K	0.0420	0.0411	0.0450	0.0280	0.0500	0.00	0.0087	
Na-DS-K	0.0399	0.0390	0.0420	0.0250	0.0500	0.00	0.0082	
Al-BG	0.3700	0.3700	0.3700	0.3700	0.3700			
Al-A	2.2933	2.1903	1.8400	1.7200	3.3200	0.79	0.8911	2.05
Al-K	0.9238	0.8785	0.9300	0.5300	1.4000	0.10	0.3089	
Al-DS-K	1.0510	0.8911	1.1900	0.2700	1.8100	0.30	0.5439	
V-BG	13.0000	13.0000	13.0000	13.0000	13.0000			
V-A	61.0000	59.0265	57.0000	44.0000	82.0000	373.00	19.3132	1.65
V-K	20.0000	19.0603	20.0000	12.0000	33.0000	46.00	6.7823	
V-DS-K	24.6000	22.2448	27.0000	8.0000	37.0000	101.60	10.0797	
Cr-BG	14.6000	14.6000	14.6000	14.6000	14.6000			
Cr-A	48.8000	47.6596	41.1000	40.9000	64.4000	182.53	13.5104	1.20
Cr-K	18.5875	17.3056	15.9000	11.3000	32.7000	62.24	7.8893	
Cr-DS-K	35.1100	29.9695	30.2500	13.2000	96.1000	554.10	23.5394	
Fe-BG	0.8400	0.8400	0.8400	0.8400	0.8400			
Fe-A	2.8133	2.7590	2.6500	2.2200	3.5700	0.48	0.6897	1.16
Fe-K	2.2963	2.1678	2.1350	1.2400	3.5900	0.70	0.8363	
Fe-DS-K	1.7730	1.6543	1.6650	0.8900	2.6400	0.44	0.6626	
Ni-BG	9.7000	9.7000	9.7000	9.7000	9.7000			
Ni-A	62.6333	61.5038	58.4000	50.3000	79.2000	222.24	14.9078	2.10
Ni-K	18.5375	17.7655	18.3500	11.0000	26.7000	32.14	5.6695	
Ni-DS-K	22.6700	21.1623	24.9000	10.4000	32.5000	64.38	8.0234	
Cu-BG	3.3400	3.3400	3.3400	3.3400	3.3400			
Cu-A	25.9000	25.8444	25.4000	24.1000	28.2000	4.39	2.0952	2.37
Cu-K	12.9638	12.1953	12.1000	7.3000	20.5000	23.39	4.8368	
Cu-DS-K	13.6110	10.9435	14.7000	2.7300	25.0000	60.79	7.7965	
Sr-BG	68.3000	68.3000	68.3000	68.3000	68.3000			
Sr-A	200.0000	193.1699	186.0000	143.0000	271.0000	4243.00	65.1383	0.97
Sr-K	33.3250	31.9755	29.8500	24.3000	60.4000	135.40	11.6361	
Sr-DS-K	36.3200	30.4111	40.4500	9.5000	67.8000	362.07	19.0280	
Zr-BG	0.7000	0.7000	0.7000	0.7000	0.7000			
Zr-A	10.1000	9.4890	8.9000	6.4000	15.0000	19.57	4.4238	3.27
Zr-K	0.6625	0.6280	0.6500	0.4000	1.0000	0.05	0.2264	
Zr -DS-K	1.0100	0.9233	0.8500	0.5000	1.9000	0.21	0.4630	

TABLE 2 (*contd.*).

Subset	Mean	Geom. mean	Median	Min	Max	Variance	Std. Dev.	I_{geo}
Mo-BG	0.1900	0.1900	0.1900	0.1900	0.1900			
Mo-A	2.8933	2.6879	2.6200	1.7000	4.3600	1.82	1.3509	3.34
Mo-K	0.3975	0.3802	0.3700	0.2300	0.6000	0.02	0.1278	
Mo-DS-K	0.3810	0.3451	0.4350	0.1400	0.5800	0.02	0.1567	
U-BG	0.3000	0.3000	0.3000	0.3000	0.3000			
U-A	7.3333	6.9485	8.3000	4.3000	9.4000	7.20	2.6839	4.03
U-K	0.7000	0.6866	0.7000	0.5000	0.9000	0.02	0.1414	
U-DS-K	0.5800	0.5050	0.6000	0.2000	1.1000	0.08	0.2898	

sodium borate glasses. Several Mo and U compounds have positive (uranium (VI) oxide and molybdenum (VI) oxide) and high positive (Mo IV, V compounds and U IV, III compounds) MS (Fermi, 2008) which again could explain the clustering of MS with Mo and U. At present we do not have information on redox conditions in the studied sediments, which could influence the oxidation state of Mo and U.

Concentrations of TOC and S are increased in the anomalous region, but are not significantly correlated with MS. These two parameters cluster together (Fig. 2) and are strongly correlated (0.96). Their concentrations are measured independently of multi-element analyses and can serve as complementary indicators of coal slag and ash transport.

Conclusions

A quick and inexpensive, low-field magnetic susceptibility method (MS) provided an indicator of contamination of stream sediments by coal combustion products. Low correlation of MS with Fe (0.36) and the absence of magnetite and maghemite in sediments suggest that elements other than Fe contribute to magnetic properties. Cluster analysis of R-modality performed on the total dataset shows that MS data are related to B, Mo, U and Na. A detailed future study of chemical reactions and redox conditions in stream sediments contaminated with coal combustion products is anticipated.

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