

Geochemical Fractionation and Risk Assessment of Potentially Toxic Elements in Sediments from Kupa River, Croatia

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Figure Captions:

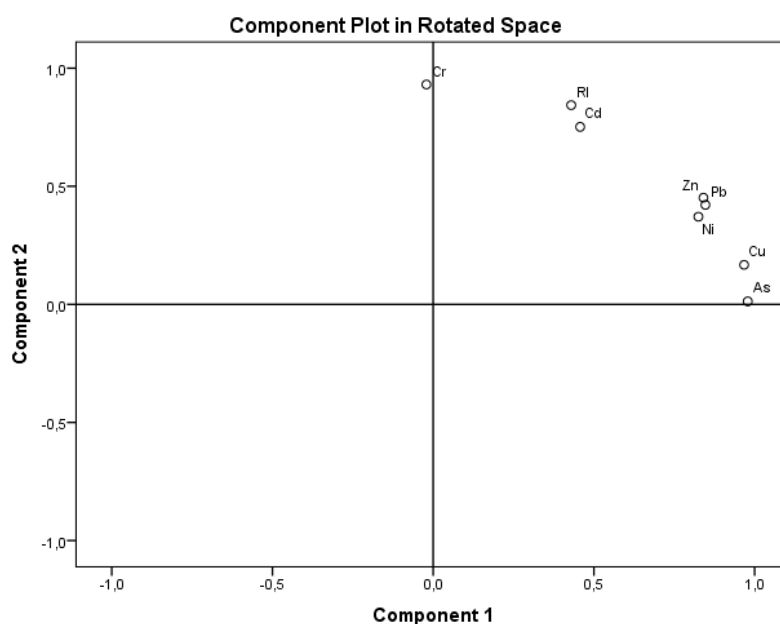


Figure S1. Loading plot of studied elements and RI.

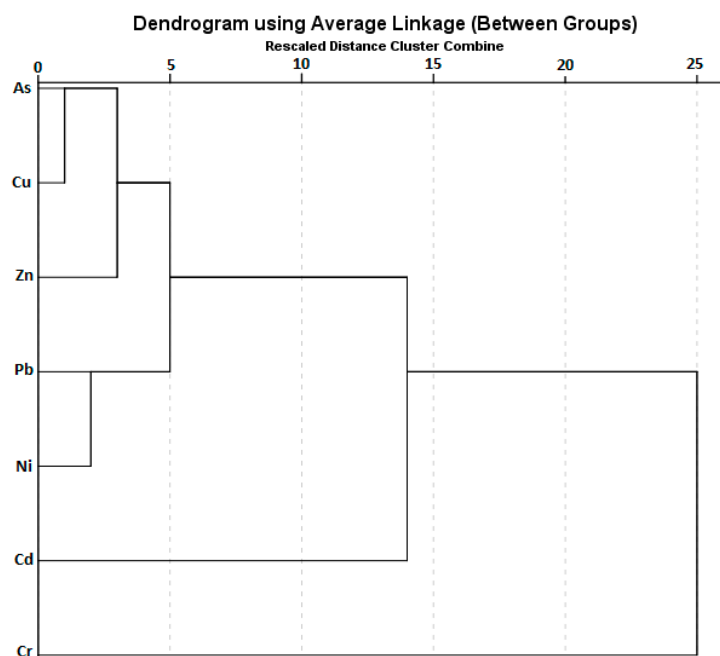


Figure S2. Dendrogram showing clusters of the elements.

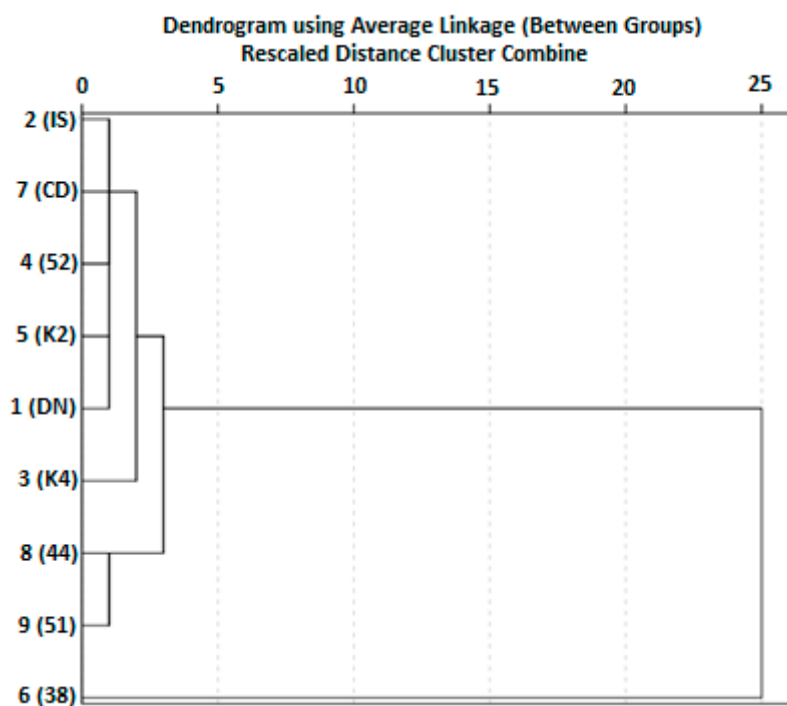


Figure S3. Dendrogram showing clusters of the studied sites.

Table Captions:

Table S1. Certified values, analytical values, and recovery of the BCR Reference Material (BCR 701).

		Cd	Cr	Cu	Ni	Pb	Zn
F1*	Analytical value (mg/kg)	7.61 ± 0.23	2.59 ± 0.11	48.5 ± 0.87	13.4 ± 0.36	2.98 ± 0.13	188.7 ± 5.4
		7.34 ± 0.35	2.26 ± 0.16	49.3 ± 1.7	15.4 ± 0.9	3.18 ± 0.21	205 ± 6.0
	Certified value (mg/kg)						
	Recovery (%)	103.6	114.5	98.4	86.9	93.7	92.0

F2**	Analytical value (mg/kg)	3.96 ± 0.22	45.4 ± 1.6	122.8 ± 3.8	24.9 ± 2.1	120.0 ± 4.3	105.6 ± 6.1
	Certified value (mg/kg)	3.77 ± 0.28	45.7 ± 2.0	124 ± 3.0	26.6 ± 1.3	126 ± 3.0	114 ± 5.0
	Recovery (%)	105.1	99.5	99.0	93.8	95.2	92.6
F3***	Analytical value (mg/kg)	0.25 ± 0.01	130 ± 7.6	45.3 ± 1.8	13.4 ± 1.1	10.6 ± 1.8	42.7 ± 3.1
	Certified value (mg/kg)	0.27 ± 0.06	143 ± 7.0	55.2 ± 4.0	15.3 ± 0.9	9.3 ± 2.0	45.7 ± 4.0
	Recovery (%)	91.1	90.9	82.1	87.8	114.1	93.4

*F1 – Exchangeable fraction; **F2 – Reducible fraction; ***F3 – Oxidizable fraction;

Table S2. Category of risk assessment code.

Class	RAC	Category
1	$RAC \leq 1$	No risk
2	$1 < RAC \leq 10$	Light risk
3	$10 < RAC \leq 30$	Medium risk
4	$30 < RAC \leq 50$	High risk
5	$50 < RAC$	Very high risk

Table S3. Values of I_{geo} and the pollution level.

I_{geo} rank	I_{geo}	Pollution Level
0	<0	Uncontaminated
1	0–1	Uncontaminated to moderately contaminated
2	1–2	Moderately contaminated
3	2–3	Moderately to strongly contaminated
4	3–4	Strongly contaminated
5	4–5	Strongly to extremely strongly contaminated
6	>5	Extremely contaminated

Table S4. Values of EF and pollution level.

Value	Pollution Category
$EF < 1$	No enrichment
$1 < EF \leq 3$	Minor
$3 < EF \leq 5$	Moderate
$5 < EF \leq 10$	Moderately severe
$10 < EF \leq 25$	Severe
$25 < EF \leq 50$	Very severe
> 50	Extremely severe

Table S5. Category of Ecological risk factor (Er^i) and Ecological risk index (RI).

Ecological risk factor (Er^i)	RI	Category
$Er^i \leq 40$	$RI \leq 150$	Low ecological risk
$40 < Er^i \leq 80$	$150 < RI \leq 300$	Moderate ecological risk
$80 < Er^i \leq 160$	$300 < RI \leq 600$	Considerable ecological risk
$160 < Er^i \leq 320$	$600 < RI$	High ecological risk
$320 < Er^i$		Very high ecological risk

Table S6. Magnetic susceptibility measurements (10^{-3} SI units).

Sample	MS-1	MS-2	MS-3	MS-Avg
DN-2	0.02	0.019	0.017	0.019
IŠ-2018	0.011	0.011	0.01	0.011
K-4-2018	0.012	0.011	0.011	0.011

52-2018	0.007	0.007	0.007	0.007
K-2-2018	0.017	0.019	0.015	0.017
38-2018	0.038	0.041	0.034	0.038
ČD-2018	0.016	0.011	0.016	0.014
44-2018	0.015	0.015	0.015	0.015
51-2018	0.017	0.017	0.019	0.018

Table S7. Rotated Component Matrix.

	Component 1	Component 2
Cd		0.752
Cr		0.931
Cu	0.967	
Pb	0.847	
Zn	0.841	
RI		0.844
Ni	0.825	
As	0.979	

Details of BCR sequential extraction procedure:

Sediment samples were analysed by the optimized BCR three step sequential extraction procedure [1–3]. A description of this procedure is given below and is as follows:

Step 1 (fraction soluble in acid—metals exchangeable or associated with carbonates): Each 1 g of sample was added to 40 mL of a 0.11 mol L⁻¹ acetic acid solution, with agitation for 16 h at 22 °C. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min and the supernatant was stored for later analysis.

Step 2 (reducible fraction—metals associated with oxides of Fe and Mn): Residue from Stage 1 was added to 40 mL of a 0.5 mol L⁻¹ acid hydroxyl ammonium chloride solution (pH 1.5). The suspension was then agitated for 16 h at 22 °C. The extract was separated from the solid phase by centrifugation, as described for Stage 1.

Step 3 (oxidizable fraction—metals associated with organic matter and sulfides): Residue from Stage 2 was added to 10 mL of 8.8 mol L⁻¹ H₂O₂ solution (pH 2–3) and the mixture was left at room temperature for 1 h. It was then heated to 85 °C for 1 h in a water bath. Another 10 mL portion of 8.8 mol L⁻¹ H₂O₂ solution was added and the mixture was heated to dryness at 85 °C. After cooling, 50 mL of a 1.0 mol L⁻¹ solution of ammonium acetate (pH 2) was added to the residue, followed by agitation for 16 h at 22 °C. The extract was separated from the solid phase by centrifugation, as above.

After the first three extraction steps, the extract was separated from solid residue by centrifugation at 3000 × g for 10 min, supernatant was decanted, diluted to 50 mL with 1M HNO₃, and stored in a polyethylene bottle at 4 °C until metal analysis. The residue was washed with 20 mL deionized water and shaken for 15 min, followed by centrifugation for 10 min at 3000×g. The supernatant was decanted and discarded, acting cautiously to avoid discarding any solid residues. In this way, the residue was prepared for the next BCR step.

Step 4 (residual fraction—metals strongly associated with the crystalline structure of minerals): The Stage 3 residue was digested using a mixture of the acids (8 mL aqua regia, 3:1, v/v, HCl to HNO₃) on water bath at 85 °C, until the volume was reduced to 2–3 mL. Another 8 mL portion of aqua regia was added and the mixture was heated to dryness at 85 °C for 1 h. The final residue was dissolved in 1 M HNO₃ and diluted to 50 mL and stored in a polyethylene bottle at 4 °C until metal analysis. Digestion of the residual material is not specified in the BCR protocol.

References

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