

Spatial distribution, ecological risk assessment, and source identification of metals in sediments of the Krka River estuary (Croatia)

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Table S1. Instrumental settings for HR ICP-MS

Parameter	Operating condition
Instrument	Thermo Finnigan Element 2
RF power	1200 W
Aux Ar flow	0.85-0.95 L/min (adjusted daily)
Sample Ar flow	0.90-1.10 L/min (adjusted daily)
Coolant Ar flow	15 L/min
Type of spray chamber	Twister, 50 ml, Cyclonic
Type of nebulizer	SeaSpray, 0.4 mL/min
Skimmer cone	Nickel, “H” mode
Sample cone	Nickel standard cone
Typical oxide level	<5% UO/U
Daily stability of signal	±3%
Autosampler	ESI SC-2 DX
Washing time	60 s
Take-up time	130 s

Table S2. Measured element mass fractions (mean \pm standard deviation) and obtained recoveries of certified reference material (PACS-2, National Research Council of Canada).

Element	Unit	Certified value	Measured value	Recovery rate
Al	g/100g	6.62 ± 0.32	3.74 ± 0.02	56%
Fe		4.09 ± 0.06	4.16 ± 0.03	102%
Ti		0.443 ± 0.032	0.296 ± 0.005	67%
P		0.096 ± 0.004	0.096 ± 0.002	100%
Li		32.2 ± 2	31.4 ± 0.24	97%
Cd	mg/kg	2.11 ± 0.15	2.61 ± 0.21	124%
Pb		183 ± 8	189 ± 9	103%
Cr		90.7 ± 4.6	74.3 ± 0.40	82%
Mn		440 ± 19	366 ± 4	83%
Co		11.5 ± 0.3	10.3 ± 0.10	89%
Ni		39.5 ± 2.3	46.4 ± 4.44	117%
Cu		310 ± 12	369 ± 5	119%
Zn		364 ± 23	390 ± 4	107%
As		26.2 ± 1.5	28.2 ± 0.47	108%

Table S3. Chemical and granulometric composition of the 40 surface sediment samples (0-5 cm) (K1-K40) from the Krka River estuary. Element concentrations are expressed in $\mu\text{g g}^{-1}$. Granulometric fractions ($< 63 \mu\text{m}$, $> 63 \mu\text{m}$) are expressed in percentages. Mean grain size (Mz) is expressed in μm .

	K1	K2	K3	K4	K5	K6	K7	K8	K9	K10	K11	K12	K13	K14	K15	K16	K17	K18	K19	K20
Li	27.6	25.9	32.4	27.3	41.0	51.4	60.7	38.0	58.5	64.0	25.8	63.2	37.2	69.0	56.3	41.4	46.1	60.5	71.3	50.9
Cd	0.468	0.471	0.530	0.434	0.444	0.426	0.433	0.532	0.426	0.369	0.203	0.383	0.255	0.382	0.383	0.280	0.441	0.384	0.452	0.960
Pb	18.0	18.0	23.6	21.7	29.8	35.0	38.5	19.9	30.4	47.2	24.5	52.1	38.4	82.3	78.3	45.8	64.3	83.3	117	665
U	2.47	2.40	2.19	2.19	2.05	2.09	2.23	2.66	2.55	1.67	1.83	2.65	1.94	2.22	2.42	2.62	3.50	2.45	2.49	3.69
Al	21666	21025	27130	18939	27948	33003	40700	36247	49234	43109	16948	41421	25733	49204	50933	33211	38883	44543	52861	38615
Ti	806	708	1002	696	856	1058	1207	1282	1814	1263	525	1352	872	1610	1911	1340	1555	1499	1733	1322
Cr	43.0	43.7	56.9	38.3	49.7	56.5	69.2	72.8	92.5	72.6	30.1	69.0	44.7	83.8	94.8	59.6	70.4	77.2	91.6	88.1
Mn	128	147	195	184	336	329	478	166	467	752	501	686	584	1014	329	261	454	1130	1689	32038
Fe	11211	11239	14938	10016	15090	17185	21074	21080	27382	22569	10074	21613	14080	26533	30140	19620	25300	24037	28405	27603
Co	3.51	3.56	5.03	3.62	4.91	5.28	7.21	6.01	8.70	7.56	3.53	7.67	5.42	9.65	9.04	6.71	8.26	8.90	11.0	16.1
Ni	25.4	26.4	35.5	22.2	30.3	34.0	46.3	44.1	57.0	47.5	19.5	45.4	30.2	57.0	58.3	37.5	44.8	52.0	63.4	63.2
Cu	16.6	20.6	30.8	12.0	15.8	15.1	17.3	27.2	24.0	20.3	9.27	20.6	14.6	30.6	88.3	24.5	73.0	30.1	39.8	89.8
Zn	76.0	70.2	99.7	66.0	86.6	82.0	96.8	70.0	101	108	52.0	106	74.9	151	133	75.8	125	146	191	495
As	5.43	6.26	7.72	7.49	7.73	8.49	9.93	9.16	13.6	10.0	6.87	11.5	7.51	10.2	18.0	12.0	16.9	10.6	11.8	19.9
C	10.1	9.65	8.76	10.2	9.27	8.79	7.76	8.66	7.09	7.55	9.65	7.95	8.95	7.27	6.46	7.72	8.85	7.94	7.28	9.88
P	0.0	0.04	0.05	0.0	0.04	0.04	0.05	0.06	0.06	0.06	0.05	0.06	0.05	0.08	0.08	0.05	0.08	0.08	0.09	0.16
$< 63 \mu\text{m}$	70.6	70.2	78.4	73.5	76.3	77.4	69.9	57.0	65.7	80.1	52.0	65.7	56.2	70.5	83.7	68.2	58.9	70.5	73.2	68.8
$> 63 \mu\text{m}$	29.4	29.8	21.6	26.5	23.6	22.5	30.1	42.9	34.3	19.9	48	34.2	43.8	29.4	16.3	31.9	41.2	29.4	26.8	31.3
Mz	53.9	83.6	44.3	70.5	41.9	41.2	56.0	80.2	120	45.4	96.9	75.5	93.3	47.3	53.6	85.4	113	57.3	45.8	72.0

Table S3. (continued)

	K21	K22	K23	K24	K25	K26	K27	K28	K29	K30	K31	K32	K33	K34	K35	K36	K37	K38	K39	K40
Li	53.1	52.4	49.8	11.4	22.6	15.6	12.1	25.6	32.8	36.4	42.0	50.3	44.5	42.5	15.9	28.3	45.1	47.6	52.9	43.2
Cd	0.473	0.458	0.542	0.582	0.141	0.159	0.112	0.321	0.241	0.739	0.953	0.906	2.70	1.36	3.84	11.2	1.32	0.648	0.574	0.413
Pb	123	108	132	93.2	21.5	19.0	21.1	45.0	57.1	130	152	231	144	159	78.5	192	165	149	117	85.4
U	2.40	2.23	3.31	5.01	2.81	2.25	2.43	3.18	2.68	3.44	4.00	4.30	5.61	3.98	8.22	25.02	3.12	2.97	2.99	2.31
Al	40501	39254	39000	8432	18257	9778	5453	17264	22999	28517	33175	35222	41191	38117	19992	32450	34064	35469	37143	30076
Ti	1295	1375	1364	434	856	397	174	603	799	905	1096	1276	1337	1272	470	875	1224	1329	1326	1059
Cr	80.5	79.7	82.6	31.3	45.0	26.3	20.7	46.0	51.9	64.2	75.5	80.6	90.2	88.6	49.1	129	85.5	80.5	83.0	65.5
Mn	3643	2161	1723	309	226	215	216	610	897	895	850	623	746	603	350	866	1027	1263	1365	1454
Fe	23977	23357	24050	6474	11075	8124	11865	14735	17624	18637	22141	25063	24642	26342	12438	19025	22542	22752	23241	18751
Co	10.2	9.51	10.2	2.52	3.90	3.23	4.03	6.28	7.23	7.39	8.26	7.64	8.03	8.41	3.68	6.18	8.33	9.11	9.78	8.11
Ni	55.9	52.7	55.2	16.1	29.7	16.5	11.3	27.6	36.4	38.9	41.7	43.9	51.8	58.2	20.0	38.2	49.9	51.8	55.1	44.5
Cu	46.3	44.0	62.0	133	12.4	8.17	5.25	19.3	25.9	54.2	65.7	90.9	76.7	92.5	32.7	112	92.0	74.0	55.8	36.0
Zn	198	187	243	474	40.7	37.6	47.8	98.2	123	241	300	341	497	389	280	1201	367	281	224	143
As	12.4	12.1	14.7	9.78	8.90	8.14	9.75	8.47	8.92	18.6	23.4	39.6	16.9	17.2	22.1	22.4	20.2	15.4	14.4	10.4
C	8.82	8.66	8.92	10.6	9.69	10.4	12.0	10.5	9.62	9.59	9.15	9.09	8.51	8.22	9.75	7.39	9.16	9.02	8.81	8.86
P	0.112	0.115	0.191	0.287	0.023	0.023	0.028	0.059	0.072	0.186	0.271	0.159	0.677	0.280	1.35	4.28	0.235	0.151	0.130	0.099
< 63 μm	62.2	79.3	66.4	51.5	56.5			30.7	58.2	57.0	58.2	56.3	71.7	81.6	54.7	51.3	52.9	66.9	68.0	74.7
> 63 μm	37.8	20.7	33.6	48.5	43.4			69.3	41.8	43	41.9	43.7	28.3	18.4	45.4	48.8	47.1	33.1	32	25.3
Mz	59.7	41.3	53.6	130	91.0			157	94.4	121	78.5	101	48.9	45.5	95.3	102	71.1	62.8	99.4	82.2

Table S4. Metal concentrations in the slag (^athis study, ^b[48]) and soil (^b[48]) from the former TEF factory. Values are expressed in $\mu\text{g g}^{-1}$, except for Mn, Al and Fe which are in %

Element	Slag ^a	Slag ^b	Soil ^b
Al	6.62	-	-
Fe	1.02	63.6	4.4
Mn	12.4	1.0	13.0
Co	45.6	-	-
Ni	37.8	-	-
Cu	63.2	410	172
Zn	70.3	1 480	612
As	22.9	-	-
Cr	30.9	700	152
Pb	16.8	250	198
Cd	0.52	-	-

Table S5. Ranges of metal concentrations in the Krka River estuary and in the costal and estuarine environments in Croatia and other European countries. Values are expressed as $\mu\text{g g}^{-1}$.

Location	Mn	Co	Ni	Cu	Zn	As	Cr	Pb	Cd	Reference
Neretva River delta	107-1 318	0.36-17.9	3.63-87.9	5.14-108	10.6-162	-	-	4.36-48.8	0.10-2.01	[35]
Bakar Bay	-	11.5-14.3	56.3-80.7	30.7-89.3	85.5-156	10.3-19	52.8-69.8	41.2-71.5	0.17-0.4	[17]
Rijeka Harbour	-	9.00-16.4	54.8-143	30.6-429	69.8-1 260	9.50-37.7	42.7-117	23.6-637	0.14-4.66	[18]
Makirina Bay	200-300	7.05-10.8	26.5-37.9	27.6-34.1	47.7-50.6	14.5-17.4	82.1-120	23.7-27.4	0.25-0.33	[36]
Toulon Bay	-	-	8.8-37.6	5.8-846	24.3-1 340	6.7-61	8.5-121	14.9-469	0.05-2.90	[65]
Loire estuary	-	-	0.88-68.6	<LOD-84.0	3.87-349	0.53-47.7	2.02-315	1.49-104	0.01-3.33	[14]
Gulf of Trieste	-	-	88.0-97.0	28.0-35.0	155-175	10.9-15.7	150-171	64.0-76.0	0.16-0.23	[1]
Tiber estuary	-	-	6.22-494	16.0-528	6.18-413	2.65-45.3	8.52-190	3.07-187	0.08-2.22	[45]
Nerbioi-Ibaizabal estuary	66-935	0.3-16	3.4-120	15-571	41-1 260	0.6-220	5.0-134	21-445	0.01-17	[25]
Krka River estuary	128-32 038	2.52-16.1	11.3-63.4	5.25-63.4	37.6-1 201	5.43-39.6	20.7-129	18.0-665	0.11-11.2	This study

Table S6. Percentage of variance, cumulative variance, loadings and component scores (after Varimax rotation) of the principal components obtained in the analysis.

		PC1	PC2	PC3
Variability (%)		41.5	29.2	18.8
Cumulative %		41.5	70.7	89.5
Factor loadings	Li	0.935	-0.175	0.083
	Cd	-0.021	0.976	-0.023
	Pb	0.175	0.243	0.942
	U	-0.068	0.981	-0.001
	Al	0.987	0.032	0.083
	Ti	0.968	-0.064	0.105
	Cr	0.812	0.513	0.228
	Mn	0.045	-0.050	0.893
	Fe	0.922	0.061	0.311
	Co	0.735	-0.031	0.624
	Ni	0.921	0.016	0.333
	Cu	0.208	0.576	0.507
	Zn	0.072	0.910	0.347
	As	0.263	0.494	0.454
	C	-0.893	-0.201	0.250
	P	-0.047	0.973	-0.054
	Li	0.935	-0.175	0.083
Component scores	Cd	-0.021	0.976	-0.023
	Pb	0.175	0.243	0.942
	U	-0.068	0.981	-0.001
	Al	0.987	0.032	0.083
	Ti	0.968	-0.064	0.105
	Cr	0.812	0.513	0.228
	Mn	0.045	-0.050	0.893
	Fe	0.922	0.061	0.311
	Co	0.735	-0.031	0.624
	Ni	0.921	0.016	0.333
	Cu	0.208	0.576	0.507
	Zn	0.072	0.910	0.347
	As	0.263	0.494	0.454
	C	-0.893	-0.201	0.250
	P	-0.047	0.973	-0.054

Table S7. Pearson correlation matrix for parameters measured in the surface sediment from the Krka River estuary

	Li	Cd	Pb	U	Al	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	C	P	<63 µm
Li	1.00																
Cd	-0.18	1.00															
Pb	0.22	0.23	1.00														
U	-0.22	0.98	0.24	1.00													
Al	0.94	0.02	0.27	-0.03	1.00												
Ti	0.89	-0.10	0.24	-0.13	0.96	1.00											
Cr	0.67	0.48	0.48	0.45	0.83	0.78	1.00										
Mn	0.15	0.01	0.88	0.01	0.15	0.14	0.21	1.00									
Fe	0.85	0.03	0.45	-0.01	0.93	0.92	0.85	0.27	1.00								
Co	0.75	-0.04	0.70	-0.06	0.77	0.75	0.73	0.61	0.88	1.00							
Ni	0.87	-0.01	0.47	-0.05	0.93	0.92	0.85	0.33	0.95	0.91	1.00						
Cu	0.07	0.43	0.60	0.47	0.24	0.27	0.57	0.25	0.39	0.38	0.38	1.00					
Zn	-0.05	0.86	0.56	0.88	0.13	0.04	0.61	0.25	0.21	0.24	0.21	0.77	1.00				
As	0.18	0.39	0.56	0.40	0.30	0.28	0.55	0.19	0.48	0.39	0.34	0.66	0.56	1.00			
C	-0.78	-0.19	0.00	-0.15	-0.87	-0.83	-0.75	0.11	-0.72	-0.47	-0.72	-0.16	-0.16	-0.17	1.00		
P	-0.20	0.99	0.20	0.99	-0.01	-0.13	0.45	-0.02	-0.01	-0.06	-0.05	0.41	0.85	0.36	-0.18	1.00	
< 63 µm	0.50	-0.23	-0.02	-0.31	0.49	0.48	0.22	0.06	0.35	0.24	0.42	-0.11	-0.21	-0.18	-0.47	-0.25	1.00

p=0.01, r critical = 0.40264; p=0.001, r critical = 0.50070