Early diagenetic processes in the sediments of the Krka River estuary

Nuša Cukrov [1], Neven Cukrov [1] and Dario Omanović [1,*]

[1] Division for Marine and Environmental Research, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia; cukrov@irb.hr (Nu.C.); ncukrov@irb.hr (Ne.C.)
* Correspondence: omanovic@irb.hr (D.O.)

Table S1. Information on cores sampled in the Krka River estuary: Core ID, sampling location, water column depth (m), core depth (cm) and sampling date.

Sediment core ID	Location	Water depth (m)	Core depth (cm)	Sampling date
K1	Head of the estuary	6.7	36	19 December 2017
K2	Prokljan Lake	16	36	24 July 2017
K3	Guduča River	7.3	26	4 December 2017
K4	The Fe-Mn factory	33	22	2 February 2017
K5	Šibenik Port	23.7	18	15 July 2017

Table S2. Indicators of long-term measurements (n = 68) of elemental concentration (μgL^{-1}) in the CASS-5 certified seawater reference material for trace metals (NRCC) using HR ICP-MS with indicated limits of detection (LOD) and quantification (LOQ) in seawater samples. For measurement purposes (HR ICP-MS), the sample is diluted 10× with ultra-pure water (Milli-Q).

Element	Certified value	AVG	STD (n=68)	Min	Max	LOD	LOQ
Mo	9.82	11.90	0.44	10.80	13.36	0.030	0.090
Pb	0.011	0.013	0.005	0.004	0.040	0.005	0.015
U	3.18	3.04	0.07	2.89	3.18	0.010	0.030
Mn	2.62	2.50	0.05	2.38	2.62	0.020	0.060
Fe	1.44	1.79	0.21	1.43	2.30	0.100	0.300
Co	0.095	0.091	0.008	0.067	0.112	0.003	0.010
Cu	0.380	0.403	0.045	0.270	0.505	0.015	0.045
Zn	0.719	0.757	0.100	0.525	0.992	0.020	0.060
As	1.24	1.35	0.14	1.09	1.67	0.100	0.300

Table S3. The analytical results and recovery rates of the certified reference material PACS-2 (National Research Council of Canada).

	Measured value ($\mu g\ g^{-1}$)	Certified value ($\mu g\ g^{-1}$)	Recovery (%)
Fe	33973 ± 351	40900 ± 600	83
Mn	305 ± 1.61	440 ± 19	69
Co	9.05 ± 0.137	11.5 ± 0.3	79
Cu	268 ± 5.69	310 ± 12	86
Zn	344 ± 9.07	364 ± 23	94
Pb	154 ± 0.509	183 ± 8	84
Mo	4.99 ± 0.087	5.43 ± 0.28	92
As	25.7 ± 0.767	26.2 ± 1.5	98
Li	28 ± 0.070	32.2 ± 2	88
P	957 ± 20.0	960 ± 40	100
S	12031 ± 391	12900 ± 1300	93

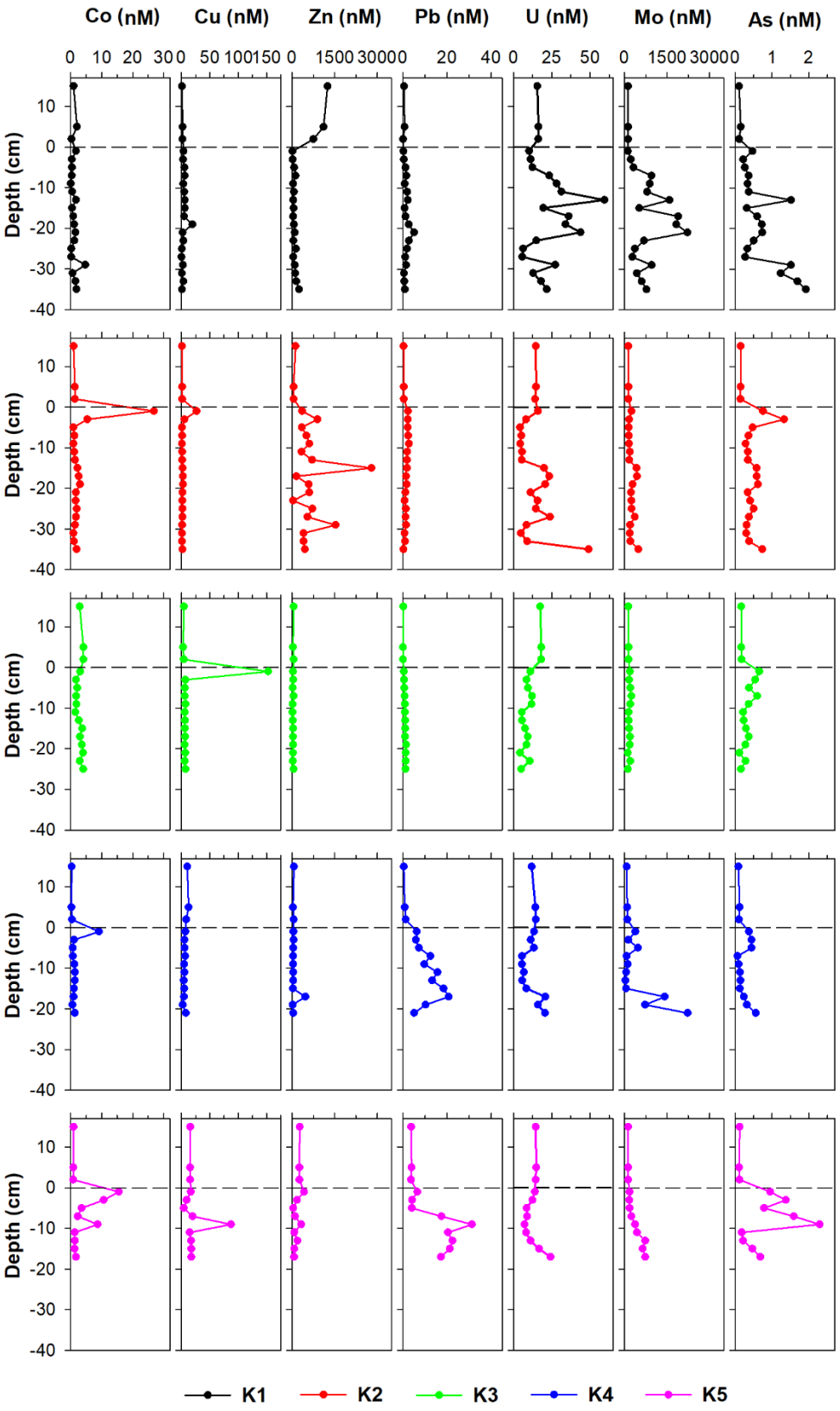

Figure S1. The vertical distribution of metals (Co, Cu, Zn, Pb, U, Mo, V, As and Cr) in the overlying water and pore water of sediment cores K1-K5. The dashed line marks the sediment-water interface (SWI).

Table S4. Chemical composition of the overlying water and pore water samples from the K1 sampling location (ow – overlying water, pw – pore water, numbers in the sample name indicate distance from the bottom for the overlying water or sediment layer from which pore water was extracted). Values are expressed in μg L^{-1}.

	Mo	Pb	U	Mn	Fe	Co	Cu	Zn	As
ow 15 cm	12.4	0.113	3.68	43.9	0.656	0.057	0.069	81.8	1.39
ow 5 cm	12.8	0.164	3.88	210	2.09	0.120	0.127	72.3	1.99
ow 2 cm	12.5	0.024	3.86	6.61	1.39	0.016	0.115	48.9	1.41
pw 0-2 cm	11.6	0.046	2.39	1385	135	0.104	0.247	0.751	6.29
pw 2-4 cm	21.4	0.077	2.66	119	56.3	0.023	0.194	1.14	2.88
pw 4-6 cm	30.8	0.248	2.95	117	49.6	0.025	0.333	4.79	3.45
pw 6-8 cm	91.3	0.324	5.55	41.4	43.7	0.023	0.368	7.82	4.87
pw 8-0 cm	85.6	0.169	6.70	17.0	16.4	0.004	0.198	2.52	4.44
pw 10-12 cm	76.8	0.400	7.45	56.1	24.6	0.030	0.315	4.23	4.95
pw 12-14 cm	153	0.457	14.1	56.2	33.0	0.102	0.369	2.92	20.3
pw 14-16 cm	50.3	0.163	4.63	30.7	15.9	0.027	0.361	3.42	4.14
pw 16-18 cm	182	0.254	8.57	69.7	14.2	0.050	0.294	2.55	7.96
pw 18-20 cm	175	0.548	8.08	67.2	24.7	0.064	1.24	4.34	9.63
pw 20-22 cm	213	1.05	10.4	83.5	16.7	0.093	0.137	6.23	9.83
pw 22-24 cm	65.9	0.568	3.55	112	43.5	0.073	0.224	3.11	6.66
pw 24-26 cm	35.6	0.391	1.46	127	27.1	0.015	0.044	9.21	4.42
pw 26-28 cm	26.8	0.221	1.32	147	6.58	0.013	0.008	2.83	3.61
pw 28-30 cm	92.3	0.291	6.51	125	3.54	0.280	0.175	6.10	20.2
pw 30-32 cm	42.3	0.097	3.03	199	3.17	0.039	0.044	7.27	16.5
pw 32-34 cm	58.5	0.128	4.26	179	5.49	0.092	0.228	9.82	22.6
pw 34-36 cm	74.7	0.193	5.16	206	5.84	0.110	0.067	16.1	25.6

Table S5. Chemical composition of the overlying water and pore water samples from the K2 sampling location (ow – overlying water, pw – pore water, numbers in the sample name indicate distance from the bottom for the overlying water or sediment layer from which pore water was extracted). Values are expressed in μg L^{-1}.

	Mo	Pb	U	Mn	Fe	Co	Cu	Zn	As
ow 15 cm	13.2	0.072	3.47	15.8	1.09	0.06	0.76	7.80	1.96
ow 5 cm	13.8	0.079	3.49	16.1	1.19	0.08	0.61	3.55	1.95
ow 2 cm	13.3	0.079	3.35	18.3	2.62	0.08	0.56	3.35	1.87
pw 0-2 cm	24.2	0.468	3.80	4268	944	1.58	0.21	23.2	10.1
pw 2-4 cm	16.3	0.455	1.91	1508	2775	0.32	0.16	58.2	17.7
pw 4-6 cm	14.3	0.450	0.98	1184	987	0.05	0.08	22.5	6.36
pw 6-8 cm	15.2	0.497	1.19	1115	462	0.07	0.20	33.3	4.83
pw 8-0 cm	15.2	0.569	1.02	1189	207	0.05	0.17	39.6	3.73
pw 10-12 cm	18.6	0.395	1.30	1200	108	0.07	0.08	21.5	4.58
pw 12-14 cm	16.8	0.390	1.23	1164	74.3	0.08	0.12	46.2	4.60
pw 14-16 cm	41.0	0.387	4.75	902	26.9	0.13	0.24	183	7.80
pw 16-18 cm	42.6	0.289	5.57	950	14.2	0.15	0.08	9.92	7.78
pw 18-20 cm	27.6	0.362	4.92	503	7.10	0.18	0.08	38.4	8.25
pw 20-22 cm	22.7	0.228	2.64	850	31.4	0.10	0.06	39.5	4.50
pw 22-24 cm	23.6	0.162	3.75	869	65.4	0.10	0.03	2.53	5.41
pw 24-26 cm	24.2	0.286	3.48	882	65.8	0.12	0.06	46.8	6.70
pw 26-28 cm	35.2	0.242	5.68	830	44.1	0.10	0.09	35.5	4.98
pw 28-30 cm	19.1	0.291	1.98	924	55.0	0.08	0.04	100	4.12
pw 30-32 cm	18.1	0.160	1.10	969	105	0.05	0.02	26.6	4.00
pw 32-34 cm	20.1	0.197	2.08	822	100	0.06	0.06	26.4	5.02
pw 34-36 cm	46.9	0.055	11.7	524	49.6	0.11	0.10	29.5	9.81

Table S6. Chemical composition of the overlying water and pore water samples from the K3 sampling location (ow – overlying water, pw – pore water, numbers in the sample name indicate distance from the bottom for the overlying water or sediment layer from which pore water was extracted). Values are expressed in μg L^{-1}.

	Mo	Pb	U	Mn	Fe	Co	Cu	Zn	As
ow 15 cm	13.53	0.033	4.14	199	0.494	0.174	0.279	3.35	2.19
ow 5 cm	14.19	0.009	4.32	269	1.10	0.244	0.190	2.19	2.18
ow 2 cm	13.81	0.005	4.30	272	2.96	0.242	0.253	3.47	2.28
pw 0-2 cm	18.60	0.078	2.61	984	791	0.182	9.701	1.88	8.72
pw 2-4 cm	15.84	0.109	1.98	600	353	0.101	0.439	2.65	7.25
pw 4-6 cm	19.75	0.135	2.23	531	212	0.127	0.383	1.29	4.97
pw 6-8 cm	23.77	0.160	2.87	424	134	0.105	0.365	3.49	7.95
pw 8-0 cm	19.57	0.182	2.78	371	124	0.110	0.457	1.20	4.85
pw 10-12 cm	14.61	0.193	1.25	410	196	0.091	0.376	1.08	2.82
pw 12-14 cm	14.52	0.222	1.28	417	282	0.157	0.397	1.70	3.07
pw 14-16 cm	16.17	0.223	1.77	423	238	0.220	0.385	2.43	3.88
pw 16-18 cm	19.09	0.209	2.20	425	281	0.178	0.414	2.04	4.92
pw 18-20 cm	18.00	0.299	1.98	442	381	0.213	0.366	2.42	3.70
pw 20-22 cm	11.50	0.264	0.974	447	498	0.237	0.448	2.05	1.46
pw 22-24 cm	19.91	0.259	2.52	443	469	0.174	0.365	1.69	3.75
pw 24-26 cm	11.92	0.249	1.17	423	563	0.238	0.450	3.67	2.08

Table S7. Chemical composition of the overlying water and pore water samples from the K4 sampling location (ow – overlying water, pw – pore water, numbers in the sample name indicate distance from the bottom for the overlying water or sediment layer from which pore water was extracted). Values are expressed in μg L^{-1}.

	Mo	Pb	U	Mn	Fe	Co	Cu	Zn	As
ow 15 cm	9.60	0.086	2.83	3.18	0.529	0.019	0.655	4.31	1.13
ow 5 cm	11.7	0.176	3.40	5.11	0.433	0.017	0.797	1.96	1.62
ow 2 cm	12.6	0.266	3.48	6.89	0.422	0.025	0.531	3.52	1.30
pw 0-2 cm	39.4	1.30	3.20	5501	431	0.539	0.439	3.11	4.97
pw 2-4 cm	15.6	1.22	2.66	1593	603	0.066	0.334	3.57	5.91
pw 4-6 cm	47.4	1.49	3.17	1578	329	0.040	0.343	2.76	5.89
pw 6-8 cm	9.84	2.59	1.30	2173	65.2	0.045	0.417	2.34	0.870
pw 8-0 cm	14.2	2.00	1.29	2684	166	0.072	0.298	2.24	1.23
pw 10-12 cm	8.77	3.25	1.56	2921	50.4	0.085	0.328	2.94	1.71
pw 12-14 cm	6.27	2.74	1.30	3113	47.3	0.081	0.252	2.85	1.89
pw 14-16 cm	8.35	3.81	1.95	2701	29.8	0.061	0.322	2.15	1.68
pw 16-18 cm	141	4.29	4.94	1633	75.8	0.058	0.270	30.7	3.15
pw 18-20 cm	73.2	2.12	3.79	1361	76.4	0.036	0.146	1.39	4.22
pw 20-22 cm	221	1.05	4.89	944	114	0.082	0.503	2.64	7.41

Table S8. Chemical composition of the overlying water and pore water samples from the K5 sampling location (ow – overlying water, pw – pore water, numbers in the sample name indicate distance from the bottom for the overlying water or sediment layer from which pore water was extracted). Values are expressed in μg L^{-1}.

	Mo	Pb	U	Mn	Fe	Co	Cu	Zn	As
ow 15 cm	12.7	0.784	3.43	23.1	0.634	0.057	0.993	17.6	1.63
ow 5 cm	13.0	0.811	3.52	23.0	0.580	0.055	0.977	17.0	1.46
ow 2 cm	12.7	0.755	3.45	32.2	0.831	0.051	0.977	16.8	1.57
pw 0-2 cm	17.5	1.35	3.32	3836	186	0.915	1.06	27.7	12.7
pw 2-4 cm	16.7	0.856	2.95	3235	1202	0.628	0.586	11.5	18.4
pw 4-6 cm	17.6	0.833	2.02	2582	369	0.210	0.260	2.92	10.5
pw 6-8 cm	23.7	3.62	2.09	2039	48.4	0.136	1.26	6.96	21.2
pw 8-0 cm	36.0	6.48	1.70	1490	238	0.513	5.56	21.1	30.6
pw 10-12 cm	42.7	4.22	1.93	1238	20.1	0.078	0.935	4.90	2.39
pw 12-14 cm	70.4	4.65	2.64	1136	60.3	0.081	1.08	12.4	2.84
pw 14-16 cm	61.6	4.40	3.97	1077	63.0	0.075	1.11	5.03	6.22
pw 16-18 cm	70.5	3.56	5.74	1005	17.0	0.102	1.10	4.50	9.10

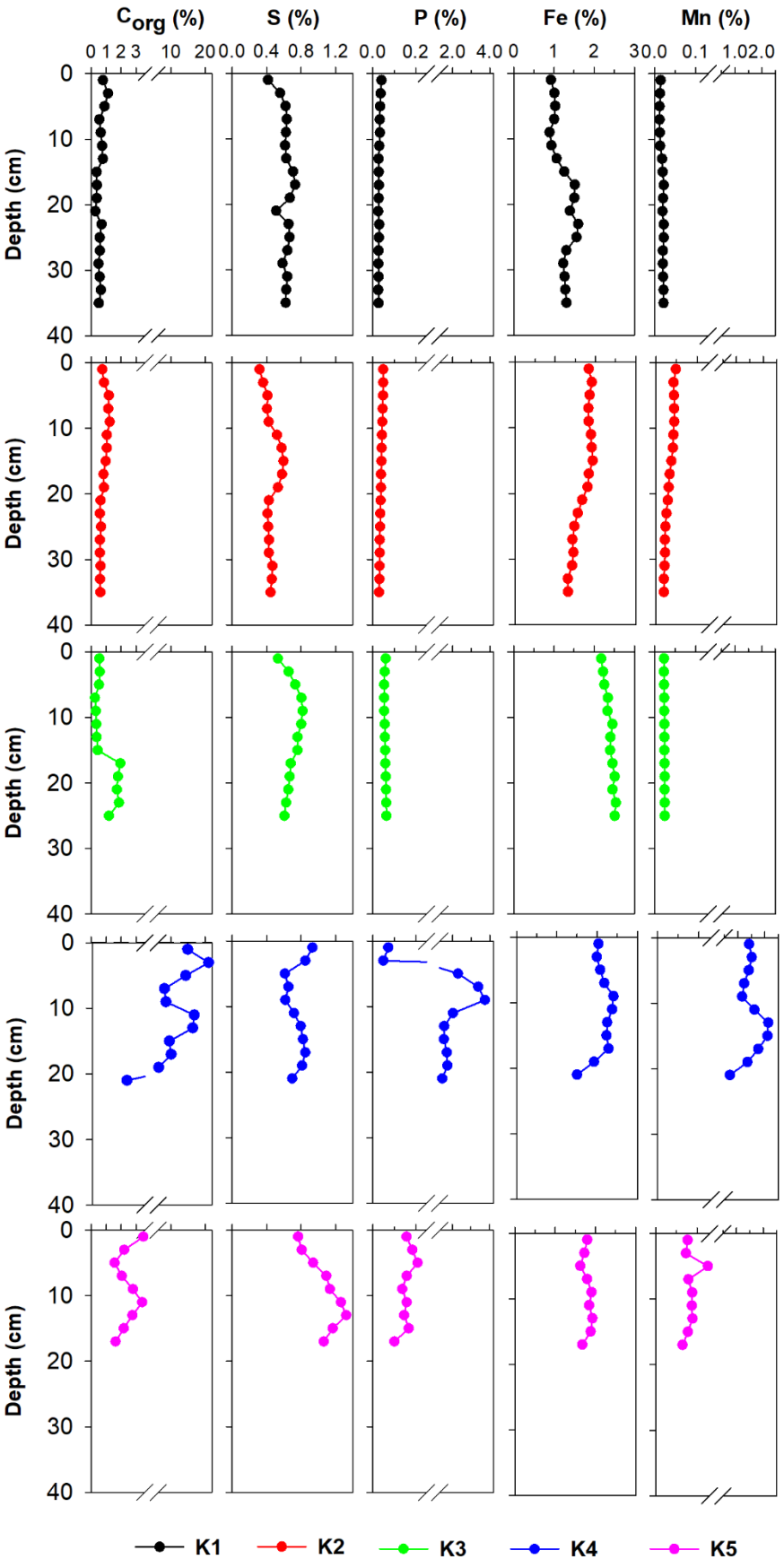

Figure S2. The vertical distribution of C_{org}, S, P, Fe and Mn in the sediment cores K1-K5.

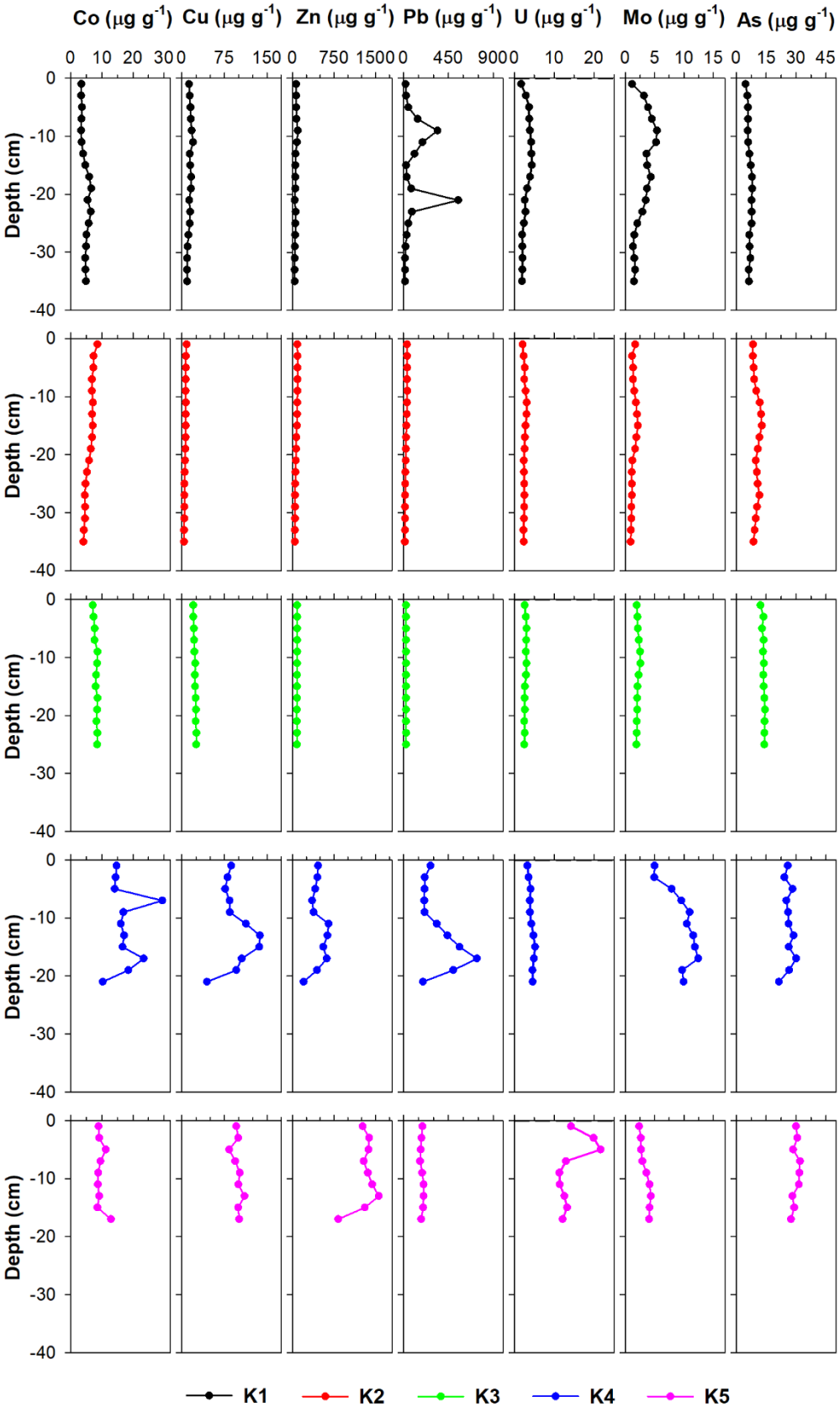

Figure S3. The vertical distribution of metals (Co, Cu, Zn, Pb, U, Mo and As) in the sediment cores K1-K5.

Table S9. Chemical composition of the K1 sediment core. Sample names indicate the sediment layer depth (cm). Values are expressed in μg g^{-1}.

	K1																	
	0-2	**2-4**	**4-6**	**6-8**	**8-10**	**10-12**	**12-14**	**14-16**	**16-18**	**18-20**	**20-22**	**22-24**	**24-26**	**26-28**	**28-30**	**30-32**	**32-34**	**34-36**
Li	26.5	28.1	30.6	28.5	25.5	27.7	29.2	33.1	34.7	33.4	27.4	34.9	36.0	32.6	35.1	36.4	36.6	36.5
Mo	1.15	3.17	3.87	4.53	5.42	5.25	3.63	3.74	4.37	3.69	3.48	2.90	2.05	1.53	1.32	1.52	1.66	1.48
Pb	19.7	25.1	48.4	141	341	191	111	25.8	32.3	76.6	550	83.6	47.8	31.1	20.8	15.3	15.4	16.1
U	1.68	2.84	3.68	3.71	3.92	4.22	4.26	4.39	3.96	3.18	2.58	2.76	2.35	1.92	1.97	2.02	1.95	1.88
Mn	150	136	127	127	130	137	182	201	227	208	197	224	225	206	203	210	221	223
Fe	9302	10114	10357	10086	8958	9397	10673	12605	15207	15071	13987	16062	15621	13084	12331	12668	12859	13121
Co	3.41	3.36	3.57	3.43	3.33	3.47	3.98	4.71	5.91	6.60	5.42	6.45	5.76	5.03	4.94	4.64	4.76	4.87
Cu	12.8	14.1	15.5	16.0	17.3	20.0	13.9	14.7	16.5	16.2	13.3	14.8	13.9	11.8	10.3	9.48	9.13	9.37
Zn	64.7	66.2	68.9	70.5	95.5	81.5	52.8	52.4	51.2	50.4	40.2	55.8	50.4	47.4	41.3	38.6	37.6	39.8
As	4.64	5.54	5.90	5.86	5.74	5.92	6.62	7.27	7.86	8.00	7.66	7.76	7.69	6.49	6.70	7.11	6.20	6.39
Corg	0.779	1.13	0.881	0.548	0.633	0.725	0.786	0.364	0.381	0.376	0.270	0.687	0.570	0.573	0.481	0.565	0.642	0.507
S	0.415	0.556	0.621	0.636	0.624	0.615	0.629	0.708	0.731	0.669	0.511	0.657	0.667	0.642	0.585	0.641	0.629	0.623
P	0.041	0.037	0.034	0.033	0.034	0.030	0.027	0.028	0.029	0.028	0.026	0.031	0.029	0.027	0.027	0.027	0.026	0.027

Table S10. Chemical composition of the K2 sediment core. Sample names indicate the sediment layer depth (cm). Values are expressed in μg g^{-1}.

	K2																	
	0-2	**2-4**	**4-6**	**6-8**	**8-10**	**10-12**	**12-14**	**14-16**	**16-18**	**18-20**	**20-22**	**22-24**	**24-26**	**26-28**	**28-30**	**30-32**	**32-34**	**34-36**
Li	60.5	61.8	59.7	58.1	60.5	53.9	60.6	60.0	58.5	58.5	54.4	51.2	49.7	48.5	47.9	46.3	43.2	42.9
Mo	1.70	1.15	1.34	1.31	1.52	1.81	1.98	2.14	1.88	1.66	1.20	1.09	1.11	1.12	1.04	1.03	0.953	0.887
Pb	35.4	35.9	36.3	35.2	37.5	35.5	33.2	27.5	24.3	23.9	21.9	19.2	17.2	15.9	15.6	15.1	14.6	14.5
U	2.03	2.30	2.55	2.46	2.76	3.05	3.02	2.76	2.60	2.51	2.34	2.38	2.45	2.49	2.43	2.36	2.24	2.33
Mn	486	431	438	442	446	427	415	378	335	310	289	257	234	222	225	214	196	197
Fe	18350	19085	18552	18267	18280	18904	19050	19295	18353	18046	16690	15572	14759	14272	14522	14212	13156	13162
Co	8.54	7.34	7.27	6.83	6.82	7.10	6.88	7.05	6.87	6.43	5.90	5.23	4.76	4.54	4.65	4.59	4.22	4.09
Cu	13.4	14.3	14.4	14.1	14.2	14.5	14.5	13.7	12.9	11.8	9.97	8.53	7.64	7.02	7.28	7.22	6.63	6.51
Zn	85.1	89.3	88.8	88.0	88.0	86.3	83.4	79.3	69.4	66.4	61.0	53.7	48.4	46.4	46.1	45.5	42.1	42.0
As	8.35	8.28	8.67	8.91	9.96	11.8	12.4	12.8	11.6	10.8	9.76	10.3	10.7	11.6	10.4	9.72	9.20	8.63
Corg	0.740	0.854	1.18	1.13	1.24	1.04	1.05	0.971	0.822	0.847	0.620	0.578	0.660	0.576	0.579	0.620	0.590	0.608
S	0.317	0.358	0.411	0.404	0.424	0.520	0.573	0.598	0.577	0.529	0.426	0.410	0.417	0.427	0.425	0.467	0.459	0.444
P	0.049	0.049	0.048	0.046	0.045	0.044	0.042	0.041	0.039	0.039	0.037	0.036	0.035	0.033	0.033	0.032	0.032	0.030

Table S11. Chemical composition of the K3 sediment core. Sample names indicate the sediment layer depth (cm). Values are expressed in μg g^{-1}.

	K3												
	0-2	**2-4**	**4-6**	**6-8**	**8-10**	**10-12**	**12-14**	**14-16**	**16-18**	**18-20**	**20-22**	**22-24**	**24-26**
Li	47.9	47.5	47.8	50.1	49.4	51.8	50.5	49.8	50.6	51.2	50.0	51.7	50.7
Mo	1.93	2.06	2.12	2.31	2.52	2.56	2.26	2.09	2.01	2.03	1.94	1.94	1.87
Pb	24.3	24.4	24.7	25.4	25.1	25.8	25.5	25.5	25.2	25.5	24.8	26.1	25.8
U	2.52	2.86	2.99	2.94	2.85	3.02	2.90	2.63	2.54	2.59	2.47	2.56	2.44
Mn	232	230	235	237	237	240	240	241	247	249	246	251	249
Fe	21760	22256	22528	23417	23316	24571	24039	23967	24572	25099	24554	25421	25093
Co	7.06	7.31	7.71	7.65	8.62	8.45	8.14	8.01	8.60	8.48	8.28	8.55	8.46
Cu	20.2	20.3	21.5	21.8	22.1	24.0	23.1	23.3	24.4	25.0	24.6	25.9	25.4
Zn	82.7	82.1	81.6	82.8	81.6	83.6	80.2	80.7	78.9	78.2	77.1	79.8	77.9
As	12.1	13.6	12.9	13.7	13.4	13.9	13.6	13.7	14.1	14.4	14.2	14.2	14.1
Corg	0.544	0.562	0.522	0.244	0.304	0.332	0.356	0.427	1.95	1.79	1.72	1.86	1.19
S	0.531	0.656	0.734	0.805	0.818	0.804	0.759	0.760	0.681	0.668	0.653	0.627	0.608
P	0.060	0.056	0.053	0.054	0.053	0.056	0.057	0.059	0.059	0.061	0.062	0.063	0.064

Table S12. Chemical composition of the K4 sediment core. Sample names indicate the sediment layer depth (cm). Values are expressed in μg g^{-1}.

	K4										
	0-2	**2-4**	**4-6**	**6-8**	**8-10**	**10-12**	**12-14**	**14-16**	**16-18**	**18-20**	**20-22**
Li	35.9	31.0	31.5	42.2	51.2	41.0	33.0	39.6	36.2	27.4	15.3
Mo	4.99	4.94	7.92	9.56	11.0	10.5	11.6	11.9	12.5	9.71	9.95
Pb	271	212	211	209	211	334	441	562	737	499	195
U	3.23	3.55	4.05	3.91	3.87	4.26	4.78	5.19	4.90	4.57	4.60
Mn	14225	15225	14089	12365	11641	16165	21389	21066	17650	13607	7058
Fe	20387	19946	20790	21806	24081	23743	22532	22378	22872	19268	15029
Co	14.7	14.4	14.1	29.5	16.9	16.1	17.1	16.6	23.4	18.5	10.3
Ni	71.6	63.4	68.8	71.5	88.3	90.3	97.9	80.3	71.0	66.1	46.0
Cu	86.9	80.7	76.4	84.1	84.5	113	138	136	106	95.9	44.2
Zn	461	450	410	353	380	650	631	554	618	441	201
As	25.8	24.2	28.2	25.1	26.0	26.3	28.8	26.3	30.0	26.5	21.4
Corg	14.8	21.0	14.3	8.11	8.54	16.8	16.3	9.58	10.0	6.42	2.39
S	0.933	0.850	0.613	0.654	0.618	0.719	0.798	0.822	0.850	0.814	0.697
P	0.073	0.049	2.29	3.38	3.73	2.02	1.54	1.53	1.69	1.72	1.44

Table S13. Chemical composition of the K5 sediment core. Sample names indicate the sediment layer depth (cm). Values are expressed in μg g^{-1}.

	K5								
	0-2	**2-4**	**4-6**	**6-8**	**8-10**	**10-12**	**12-14**	**14-16**	**16-18**
Li	23.9	22.3	21.9	28.4	32.2	32.2	31.6	30.7	27.3
Mo	2.35	2.65	2.67	2.90	3.59	4.13	4.35	4.13	4.05
Pb	190	181	173	166	187	201	202	196	177
U	14.2	19.9	21.7	13.0	11.3	11.4	12.6	13.3	12.1
Mn	771	727	1261	788	879	872	889	777	646
Fe	17982	17234	16239	17909	19026	18427	19227	18794	16740
Co	8.92	9.14	11.2	9.58	8.83	8.74	9.15	8.58	12.9
Cu	95.8	99.3	83.3	94.0	102.15	99.7	110.25	99.1	101
Zn	1269	1384	1375	1286	1363	1439	1561	1307	827
As	30.0	30.6	28.5	32.0	31.7	31.4	28.2	29.1	27.5
Corg	3.49	2.21	1.56	2.05	2.80	3.41	2.77	2.18	1.63
S	0.768	0.809	0.941	1.09	1.14	1.26	1.32	1.17	1.06
P	0.158	0.185	0.209	0.159	0.138	0.159	0.146	0.168	0.101

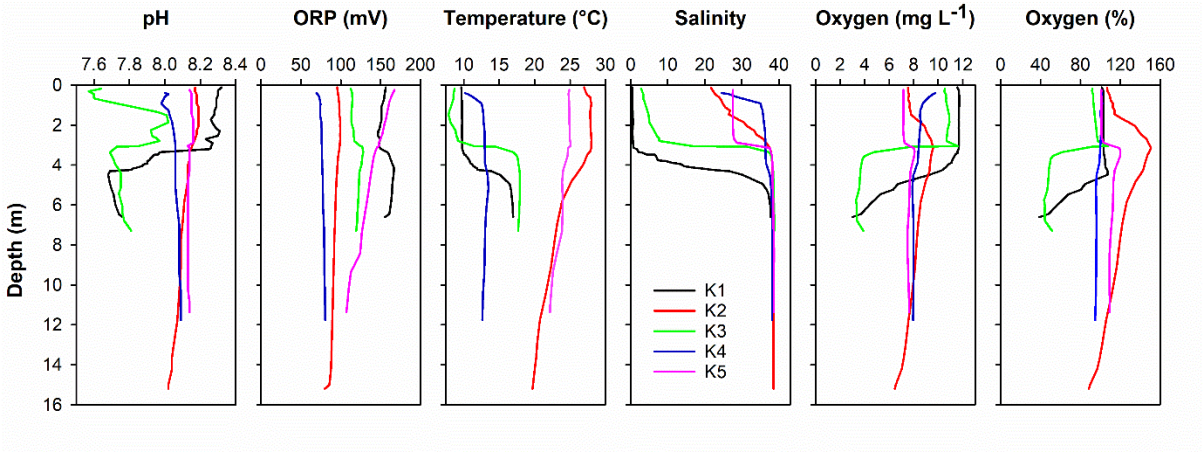

Figure S4. The physicochemical parameters measured in the water column at sampling locations K1-K5 in the Krka River estuary