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The influence of fly and bottom ash deposition on the quality of Kastela Bay sediments

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Abstract The objective of this study was chemical and radiological characterization of Kastela Bay sediments exposed to numerous anthropogenic sources like deposition of fly and bottom ash enriched in radionuclides and heavy metals, chemical plant, cement plant, iron plant, shipyard, electroplating facility, untreated industrial and domestic waste waters as well as heavy traffic. Totally, 33 samples of the mixture of fly and bottom ash, 12 sediment cores ranging from 0 to 40 cm and nine surface sediment samples were analyzed. Enrichment in heavy metals in the mixture of fly and bottom ash was ranging from 1.5 to 36 times compared to flysch soil while ^{226}Ra and ^{238}U were up to 50 times enriched compared to average activities characteristic for surrounding soils developed on the Middle and Upper Eocene flysch. Maximum ^{238}U activity was approximately 32 times higher and ^{226}Ra approximately 40 times higher in the Kastela Bay sediment compared to mean value determined for Adriatic sediments. The highest enrichment in sediment cores compared to background values were found for Zn (35.6 times), Pb (16 times), Cr (9.1 times) and Ni (4 times)

Keywords Fly and bottom ash · Heavy metals · Radionuclides · Sediments leaching

Introduction

The purpose of this paper was chemical, radiological and mineralogical characterization of the Kastela Bay sediments under the influence of past industrial activity and its waste by-products. The Kastela Bay is situated in the Middle Adriatic and represents a semi-enclosed low energy environment with total area of 60 km^2, average depth of 23 m (maximum depth of 45 m at the inlet of the bay), and the volume of 1.4 km^3 (Ujević et al. 2000) (Fig. 1). Until the early 1990s of the 20th century, this was densely populated and the most industrialized area along the eastern Adriatic coast. The major sources of pollution were ex-chemical factory called 'Jugovinil', cement plant, iron plant, shipyard and electroplating facility. Heavy traffic across the main road located close

to the shoreline also contributes to the pollution of the Bay. Besides, most of the outlets of industrial and domestic wastewater, located in the eastern part of the Bay, discharge their untreated or partially treated effluents into the Bay either directly or through the Jadro River.

As a result of almost five decades of 'Jugovinil' factory operation, large amount of the mixture of fly and bottom ash, by-products of coal burning in thermo-electric unit of the factory, remained. All of the used coals have elevated concentrations of uranium and its natural decay series radionuclide products. During the combustion process and depending on the inorganic portion of the coal, content of ^{226}Ra and ^{238}U in fly and bottom ash was elevated several times. Bottom and fly ash were, as a produced waste, deposited in the vicinity
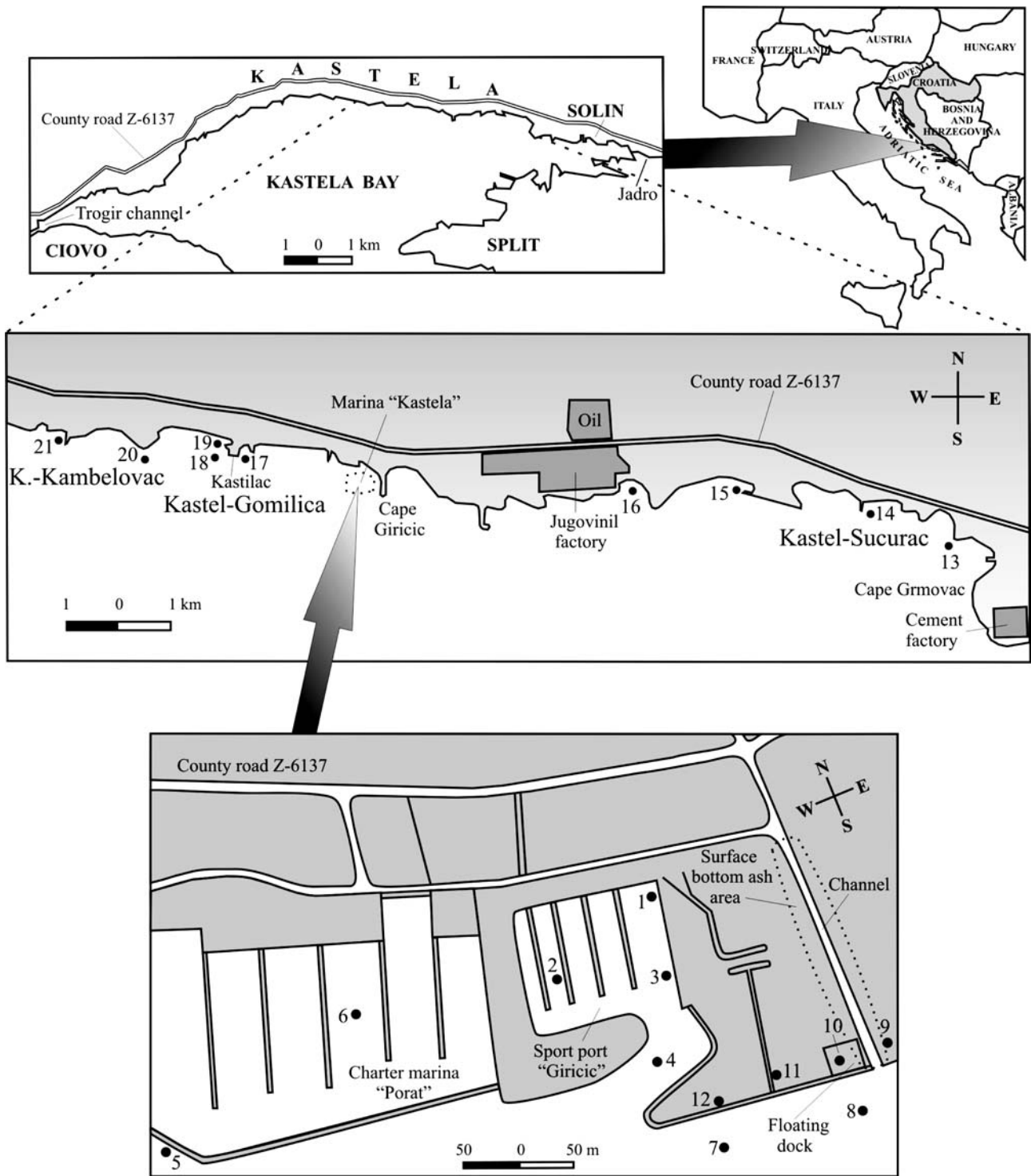
Fig. 1 Geographical location of the study area and sampling points

of facility and remained there until 1973 when a proper deposition location was defined. The material was removed on selected location few hundred meters farther away at the border of town Kastel Gomilica and protected with plastic foil, layer of clay and humus. The area was fenced in and the grass was sown. That way the

'old' depot was formed. In time, the area between the factory and the 'old' depot was covered up with waste materials, among it with mixture of fly and bottom ash. At the end of 1980s and the beginning of 1990s, fly and bottom ash were dumped directly into shallow seawater in the south-western part of the facility. In the southern part, a little bit more to the west of the present fence of former 'Jugovinil', a floating dock is situated. Most of its parts are buried into the deposited material, which is in direct contact with the sea. In north–south direction a channel is also buried into the fly and bottom ash. At both sides of the channel the mixture of fly and bottom ash is exposed on the surface. In south-western part of the area of the factory a pool separated from the sea is situated. Seawater in the pool is in direct contact with the waste material. It is visible from all documents that natural activity of both uranium isotopes (^{238}U and ^{235}U) as well as of ^{226}Ra and their decay products is elevated both in fly and bottom ash (personal communications, data not published). Therefore, this waste material can be characterized as TENORM (technologically enhanced naturally occurring radioactive material) because concentrations (activities) of natural radionuclides (^{238}U, ^{235}U and ^{226}Ra) are elevated by a technological procedure. To obtain a preliminary data about the present state of new unregulated part of the depot, 33 samples of TENORM were collected and analyzed in spring 2004.

Materials and methods

At each location, 1 kg of the mixture of fly and bottom ash was sampled, put in a plastic bag and transported to a laboratory. Material was dried at 105°C and fraction < 0.5 mm was disaggregated in an agate mortar and prepared for the determination of total elemental composition, selected radionuclides, XRD analysis as well as for leaching tests.

Twelve sediment profiles and nine surface samples were collected in Kastela Bay. Surface samples were collected by divers while sediment cores were taken by gravity corer. Cores were divided into segments of 0–5, 5–10, 10–20, 20–30, 30–40 and 40–50 cm. All sediment samples were dried to a constant weight, sieved, ground and pressed into pellets in order to prepare tick targets.

Concentrations of Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Y, Zr, Pb and U in bulk samples of ash and sediments were determined using energy dispersive X-ray fluorescence, EDXRF method (Oreščanin et al. 2004a).

After XRF analysis all remaining fly and bottom ash were mixed and homogenized. One gram of homogenized sample was extracted either by distilled water according to DIN 38414-S4 standard or by seawater (solid to liquid ratio = 1:10) for 24 h. At the end of the contact time, solid part was separated from the leachate

by filtration through the white ribbon-filter paper. The extracts were diluted to 100 mL with double-distilled water, divided in two sub samples, and adjusted to pH 3 and 11, respectively by the addition of concentrated HNO_3/NH_4OH. After the pH adjustment, samples were preconcentrated by 1 mL of freshly prepared 1% w/v solution of ammonium-pyroloidinedithiocarbamate (APDC). After the complexation lasted 20 min, the suspension was filtered through a Millipore filter (0.45 μm) and irradiated for 10,000 s.

All samples were analyzed by energy dispersive X-ray fluorescence (EDXRF). Samples were irradiated by X-rays generated from a ^{109}Cd annular source. The angle between the sample and a source was 89°. Detection of characteristic X-ray radiation from the sample was conducted with a Si (Li) detector (Canberra) cooled with liquid nitrogen with the following characteristics: detector size = 30 mm^2, Si thickness = 3 mm, Be window = 25 μm, FWHM for 5.9 keV ^{55}Fe 165 eV. The angle between the sample and a detector was 1°, and the distance was 1.5 cm. Spectra were collected by a Genie-2000 software (Canberra). Collecting time was 10,000 s for thin targets and 7000 s for thick targets (solid ash samples and sediment samples). Spectral data were analyzed by WinAxil software (Canberra). Calibration file for thin targets (water samples) was created on the basis of measurements of the standard solutions (Merck) prepared and analyzed in the same way as unknown samples. Elemental concentrations in thick targets were calculated with the 'Fundamental parameters' method from a WinFund package using ECH (coal burning fly ash) as a standard reference material for the mixture of fly and bottom ash and IAEA SRM SL-1 and SOIL-7 for sediment samples.

All sediment segments from 0 to 5 cm were also prepared for XRD analysis. Powdered samples were examined at room temperature using a Philips PW 1830 X-ray diffractometer with Cu tube (current = 40 mA; voltage = 40 kV), graphite crystal monocromator and a proportional counter. Diffraction data were processed by Philips X'Pert software. The relative intensities of X-ray diffraction lines were compared with literature values (Oreščanin et al. 2004b).

Ash samples were placed in the counting vessels of 125 cm^3, sealed and stored for at least a 4-week period to allow an ingrowth period of gaseous ^{222}Rn. At the end of ingrowth period, gamma-spectrometry measurements were performed on a HPGe semiconductor detector joined to the 8192 channel analyzer 'Canberra'. Spectra were recorded during 80,000 s and analyzed using Genie 2K 'Canberra' software. Activities of ^{40}K were calculated from the 1460.75 keV-peak, ^{226}Ra from the 609.3 keV-peak of its ^{214}Bi progeny and ^{228}Ra from 911.1 keV-peak of its ^{228}Ac progeny. Activities of ^{235}U were calculated from 186 keV-peak after subtraction of the overlapping ^{226}Ra contribution and used for calcu-

Table 1 Mean values ($\bar{X}$) and concentration ranges measured in the mixture of fly and bottom ash from Kastel Gomilica, Croatia, mean values of the elements for common flysch soil and ratio between ash and soil mean values

Element	$\bar{X}$	Range	$\bar{X}$ soil	$\bar{X}_{ash}/\bar{X}_{soil}$
Zn (ppm)	150.5	56.0–307.0	155.9	1.0
Cu (ppm)	40.3	19.0–64.0	22	1.8
Ni (ppm)	149.0	48.0–240.0	34.3	4.3
Co (ppm)	11.7	4.9–22.8	12.1	1.0
Fe (%)	3.775	1.260–7.810	4.401	0.9
Mn (ppm)	307.1	80.0–670.0	1686.2	0.2
Cr (ppm)	136.2	69.6–250.0	153.4	0.9
V (ppm)	329.9	146.6–630.0	90.1	3.7
Ti (%)	0.30	0.10–0.47	0.51	0.6
Ca (%)	9.77	4.30–17.90	12.8	0.8
Y (ppm)	73.4	28.0–133.0	50.1	1.5
Zr (ppm)	184.2	65.0–281.0	380.6	0.5
Sr (ppm)	434.6	233.0–898.0	134	3.2
Rb (ppm)	43.8	6.5–89.0	143.5	0.3
As (ppm)	21.4	14.0–42.0	27.1	0.8
U (ppm)	93.8	34.0–227.0	2.6	36.1
Pb (ppm)	42.8	24.6–74.0	26.6	1.6

lation of ^{238}U activity assuming the natural ^{235}U/^{238}U activity ratio of 0.04603 (Oreščanin et al. 2004b).

Results and discussion

Characterization of the mixture of fly and bottom ash

Table 1 presents the mean values and the concentration ranges of major, minor and trace elements determined in 33 samples of the mixture of fly and bottom ash, and Fig. 2 activities of the radionuclides ^{226}Ra and ^{238}U determined in the same samples. The analyzed mixture of fly and bottom ash showed significant variability in its chemical composition as well as in the activities of selected radionuclides due to different origin of coal used in a thermoelectric unit of the ex-'Jugovinil' factory. Mean elemental concentrations in the ash were elevated from 1.5 to approximately 36 times compared to the common soil concentrations. The highest enrichment was found for uranium, nickel, vanadium and strontium. Fortunately, extractable heavy metal portion (Table 2) was found to be low either by distilled or seawater, except for total uranium which showed high leachability in the seawater. The predominant minerals

present in a composite sample of the mixture of fly and bottom ash are calcite, quartz, monteponite (CdO), and bassanite (CaSO$_4$·0.5H$_2$O).

Activities of ^{226}Ra and ^{238}U in the ash were approximately 50 times higher than those in the common soil. In the majority of the samples of the ash ^{238}U activity was up to 30% lower compared to ^{226}Ra, while in the coal samples their average activities were similar. This could be explained with the fact that most of the samples were taken from the surface of the deposit with

Table 2 Elemental concentrations measured in the extracts of the composite sample of the mixture of fly and bottom ash. 1- extracted with distilled water according to DIN-38414-S4 standard; 2- extracted with sea water (solid:liquid = 1:10)

Element (ppb)	1	2
Pb	58.4	46.8
U	882.0	29732.0
V	109.2	212.4
Cr	50.4	61.2
Fe	134.4	151.2
Ni	21.4	14.4
Cu	31.1	24.81
Zn	49.11	34.6
Co	9.2	ND

Fig. 2 Activity of ^{226}Ra and ^{238}U in 33 samples of the mixture of fly and bottom ash from Kastel Gomilica
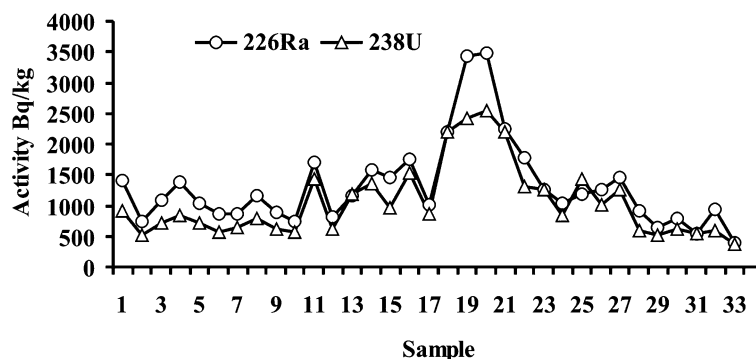
Table 3 Activity of ^{226}Ra and ^{238}U in Bq/kg measured in 12 sediment profiles, nine surface samples of Kastela bay sediments and mean values of selected radionuclides determined for open Adriatic and coastal Adriatic sediment

Profile	Depth (cm)	^{226}Ra	^{238}U
1	00–5	155.7 ± 3.3	157.7 ± 10.7
	5–10	540.7 ± 7.0	378.7 ± 20.6
	10–20	260.7 ± 3.5	184.2 ± 10.4
	20–30	117.3 ± 2.2	108.3 ± 6.8
	30–40	176.9 ± 3.0	170.9 ± 9.1
	40–55	647.1 ± 7.2	446.9 ± 20.4
2	00–5	123.4 ± 2.1	75.9 ± 6.0
	5–10	214.5 ± 2.7	145.1 ± 8.1
	10–20	262.3 ± 3.3	214.5 ± 10.1
	20–30	484.9 ± 4.7	357.3 ± 13.9
	30–40	773.0 ± 6.3	605.6 ± 17.9
3	00–5	19.6 ± 0.8	19.2 ± 2.8
	5–10	13.2 ± 0.6	11.4 ± 2.1
	10–20	24.7 ± 0.9	21.4 ± 3.0
	20–30	30.6 ± 1.0	22.4 ± 3.4
	30–40	16.8 ± 0.7	16.7 ± 2.7
4	00–5	25.1 ± 1.1	22.3 ± 3.4
	5–10	50.2 ± 1.3	32.3 ± 4.0
	10–20	27.3 ± 1.0	17.7 ± 3.3
	20–30	24.1 ± 0.9	21.2 ± 3.0
5	00–5	16.5 ± 0.8	20.4 ± 3.0
	5–10	14.4 ± 0.8	18.6 ± 3.0
	10–14	13.8 ± 0.7	17.9 ± 2.6
6	00–5	24.5 ± 1.1	23.9 ± 3.7
	5–10	19.9 ± 0.9	20.3 ± 3.2
	10–20	22.7 ± 1.0	26.0 ± 3.3
7	00–5	39.1 ± 1.9	45.6 ± 6.8
	5–10	22.1 ± 0.9	27.0 ± 3.5
	10–20	19.4 ± 0.9	24.1 ± 3.4
	20–30	15.8 ± 0.8	20.0 ± 2.9
	30–40	16.7 ± 0.8	20.6 ± 3.0
8	00–5	20.9 ± 0.9	22.2 ± 3.4
	5–10	21.6 ± 0.9	20.5 ± 3.3
	10–20	18.0 ± 0.9	20.0 ± 3.1
	20–30	19.2 ± 0.9	19.8 ± 3.3
	30–40	20.8 ± 0.9	18.8 ± 3.1
9	00–5	68.3 ± 1.9	52.9 ± 5.7
	5–10	74.9 ± 1.7	55.5 ± 5.2
	10–20	74.4 ± 1.7	54.6 ± 5.1
	20–30	58.3 ± 1.5	36.7 ± 4.3
	30–40	34.0 ± 1.1	42.7 ± 4.0
10	00–5	59.7 ± 1.5	52.5 ± 4.7
	5–10	132.9 ± 2.6	100.3 ± 7.9
	10–20	61.0 ± 1.7	57.7 ± 5.3
	20–30	79.6 ± 1.6	72.6 ± 5.2
	30–40	48.3 ± 1.3	45.1 ± 4.1
11	00–5	47.5 ± 1.5	43.4 ± 5.2
	5–10	26.6 ± 1.0	26.1 ± 3.5
	10–20	48.8 ± 1.3	43.0 ± 4.2
	20–30	138.6 ± 2.2	89.3 ± 6.5
12	00–5	92.2 ± 2.3	79.4 ± 7.4
	5–10	34.6 ± 1.1	29.2 ± 3.6
	10–20	45.9 ± 1.3	33.3 ± 4.0
	20–30	35.3 ± 1.1	30.2 ± 3.6
	30–40	28.7 ± 1.0	26.8 ± 3.4
13	00–5	15.8 ± 0.9	19.0 ± 3.3
14	00–5	16.3 ± 0.8	23.2 ± 3.1
15	00–5	14.2 ± 0.8	29.9 ± 3.3
16	00–5	192.0 ± 3.2	169.1 ± 9.6
17	00–5	13.2 ± 0.7	24.4 ± 2.8
18	00–5	17.0 ± 0.8	22.1 ± 3.2

Table 3 (Contd.)

Profile	Depth (cm)	^{226}Ra	^{238}U
19	00–5	20.6 ± 1.1	30.6 ± 3.8
20	00–5	15.4 ± 0.8	20.4 ± 3.0
21	00–5	18.8 ± 0.9	24.8 ± 3.4
$\bar{X}_{\text{open Adriatic}}$,[a] ($n = 48$)	00–5	19.9	19.1
$\bar{X}_{\text{Croatian coast}}$,[a] ($n = 51$)	00–5	19.2	18.2

[a]Presented on the International Seminar on the Use of isotope techniques in marine environmental studies, held in Athens, Greece; 11–22 November 1996 (data not published)

damaged protective cover or from the channel exposed to the rainwater circulation. Water circulation through the ash caused leaching of uranium that was more susceptible to the extraction from the ash by rainwater compared to ^{226}Ra causing obtained ^{238}U/^{226}Ra ratio being shifted toward radium. Alkaline solutions promote dissolution of the glassy components of fly ash that are unidentified host of uranium which increases uranium solubility as uranium carbonate species. On the other hand, leachates of fly ash are rich in dissolved sulfate, and this minimizes the solubility of radium, which forms highly insoluble sulfates.

Characterization of sediment samples

Radiological characterization

The activities of ^{226}Ra and ^{238}U measured in 12 sediment profiles ranging from 0 to maximum depth of 55 cm, nine surface samples of Kastela Bay sediments and mean values of selected radionuclides determined for open Adriatic and coastal Adriatic sediment were presented in Table 3. Dumping the mixture of fly and bottom ash directly into the sea resulted in extremely high activities of ^{226}Ra and ^{238}U in sediment profiles 1 and 2 reaching maximum values in the deepest segment. Maximum ^{238}U activity was approximately 32 times and ^{226}Ra activity was approximately 40 times higher than the mean value determined for Adriatic sediments. Quite expectedly, elevated values of these two radionuclides were also found in the profiles 9, 10, 11 and 12 which were placed near to the ash deposit.

Elemental characterization

The concentrations of selected elements measured in 12 sediment profiles ranging from 0 to maximum depth of 55 cm and nine surface samples of Kastela Bay sediments were presented in Table 4. According to Shapiro–Wilks W test, U, Sr, Pb and Zn deviated significantly from the normal distribution in all sediment segments, while the elements Br, Zr, Ti, Cr and Fe showed disturbance in

Table 4 Concentrations of the elements in 12 profiles and nine surface samples of Kastela bay sediments determined by EDXRF. Depth in cm; Ca, Fe, Ti in %wt, other elements in ppm

Profile	Depth	Pb	U	As	Br	Rb	Sr	Zr	Y	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1	00–5	80	14.1	15	210	37	436	125	46	10.5	0.185	74	110	400	3.211	10.5	90	51	422
	5–10	93	33.9	27	260	37	427	144	57	8.4	0.239	200	140	490	3.795	12.3	100	50	391
	10–20	96	16.5	19	250	52	500	159	57	12.3	0.212	210	130	490	3.221	10.6	140	70	527
	20–30	97	9.7	16	120	45	432	133	37	14.8	0.175	110	100	410	2.572	8.3	70	54	595
	30–40	75	15.3	20	180	43	426	148	45	14.5	0.185	130	140	300	3.069	10.1	90	54	432
	40–55	62	40.0	18	410	16	529	130	50	6.3	0.213	140	110	320	3.456	10.9	120	40	196
2	00–5	35	6.8	26	120	64	620	124	40	17.7	0.154	110	110	540	1.945	7.4	140	41	187
	5–10	32	13.0	26	150	57	696	127	43	17.9	0.177	190	120	500	2.260	8.0	140	41	117
	10–20	58	19.2	17	170	58	653	169	59	14.8	0.233	150	120	390	3.072	10.6	100	42	184
	20–30	53	32.0	25	190	54	547	173	70	9.3	0.266	210	140	350	3.524	12.4	110	45	157
	30–40	43	54.3	26	180	51	610	207	90	8.0	0.287	150	160	440	4.254	14.0	140	48	117
3	00–5	63	1.7	31	71	50	397	150	37	20.6	0.164	160	100	440	1.808	6.4	80	45	339
	5–10	74	1.0	27	57	56	383	171	36	20.5	0.174	120	120	460	1.870	6.3	100	41	323
	10–20	49	1.9	26	73	66	444	162	43	19.5	0.190	120	90	520	2.093	8.1	100	44	283
	20–30	36	2.0	24	59	42	370	121	28	20.3	0.131	100	100	410	1.828	6.4	110	41	184
	30–40	90	1.5	27	55	46	460	113	30	25.0	0.160	90	150	680	4.023	13.4	80	79	675
4	00–5	34	2.0	24	77	61	525	119	37	20.9	0.127	84	70	520	1.647	6.1	100	49	125
	5–10	31	2.9	23	82	70	525	127	41	20.7	0.141	85	80	550	1.751	6.2	80	45	114
	10–20	21	1.6	21	47	62	461	108	33	18.3	0.142	83	110	420	1.444	5.7	120	37	92
	20–30	25	1.9	25	52	64	487	117	32	21.0	0.126	86	100	460	1.523	6.0	140	47	107
5	00–5	29	1.8	18	93	18	1,813	122	33	29.0	0.084	89	90	200	1.100	4.5	60	24	59
	5–10	27	1.7	23	70	17	1,696	110	32	27.0	0.093	150	90	190	0.960	4.0	60	19	51
	10–14	33	1.6	28	78	13	1,942	115	28	31.0	0.090	120	130	280	1.028	4.6	60	28	58
6	00–5	29	2.1	25	120	43	1,286	151	39	23.3	0.140	92	80	370	1.384	5.4	70	35	76
	5–10	21	1.8	29	99	29	1,325	148	33	22.8	0.122	90	100	230	1.077	4.2	60	24	67
	10–20	23	2.3	19	120	32	1,485	168	33	26.0	0.140	91	70	240	1.191	3.9	40	26	70
7	00–5	35	4.1	26	110	42	1,448	151	32	22.5	0.147	88	80	310	1.461	5.0	50	28	155
	5–10	26	2.4	28	110	34	1,423	131	28	21.8	0.130	110	120	240	1.247	4.6	50	22	85
	10–20	30	2.2	19	120	48	1,506	164	38	23.1	0.143	120	90	250	1.489	5.5	70	29	83
	20–30	25	1.8	22	100	50	1,580	151	37	23.1	0.157	89	70	200	1.437	6.1	70	23	68
	30–40	26	1.8	24	110	52	1,568	139	38	22.6	0.138	90	70	270	1.478	6.0	110	26	66
8	00–5	30	2.0	19	120	36	1,405	135	31	20.8	0.114	86	90	230	1.207	4.4	60	23	114
	5–10	26	1.8	21	130	41	1,588	149	34	23.2	0.173	120	110	260	1.397	5.2	90	24	86
	10–20	26	1.8	28	130	41	1,355	154	37	21.8	0.159	80	100	210	1.353	4.8	70	24	89
	20–30	28	1.8	26	140	38	1,642	150	33	23.4	0.150	91	90	230	1.373	5.4	90	32	90
	30–40	30	1.7	27	150	43	1,760	150	37	23.8	0.130	96	90	330	1.469	5.8	80	28	94
9	00–5	33	4.7	24	180	54	607	156	40	16.8	0.182	82	90	280	1.739	6.3	60	32	146
	5–10	35	5.0	21	160	58	657	164	47	16.0	0.194	120	120	270	1.903	7.1	100	37	124
	10–20	38	4.9	27	140	53	846	176	42	18.4	0.187	120	130	270	1.844	7.3	70	33	113
	20–30	29	3.3	23	120	49	880	163	40	19.9	0.195	100	150	310	1.629	5.5	50	27	88
	30–40	27	3.8	29	90	48	840	166	33	20.0	0.162	100	80	290	1.355	4.9	50	24	63
10	00–5	28	4.7	25	130	59	435	141	42	18.6	0.154	75	87	486	1.914	7.1	92	45	158
	5–10	32	9.0	25	130	53	407	137	43	15.9	0.173	90	97	525	2.193	7.3	93	44	142
	10–20	36	5.2	32	110	57	443	140	46	18.7	0.164	75	110	500	1.946	7.1	100	43	148
	20–30	39	6.5	23	110	53	408	146	43	16.0	0.180	80	87	578	2.302	7.6	95	43	202
	30–40	51	4.0	31	81	62	428	144	39	18.6	0.177	75	80	570	2.208	8.1	110	48	265
11	00–5	70	3.9	23	150	57	507	135	41	19.4	0.147	68	85	460	1.883	6.8	85	40	394
	5–10	35	2.3	23	72	56	491	129	36	22.1	0.142	110	100	420	1.548	6.3	100	40	188
	10–20	313	3.9	25	61	38	565	138	46	20.8	0.143	110	140	800	3.894	11.5	60	70	2100
	20–30	249	8.0	25	110	43	555	139	53	16.9	0.148	150	110	680	3.715	12.0	80	64	1550
12	00–5	103	7.1	24	120	54	536	163	49	17.7	0.183	180	100	610	2.909	9.8	80	56	585
	5–10	130	2.6	22	101	50	536	127	40	19.3	0.156	70	105	573	2.533	8.5	92	49	739
	10–20	173	3.0	30	101	53	538	148	47	19.3	0.149	76	90	600	2.746	8.8	100	58	1057
	20–30	112	2.7	21	76	51	537	128	40	19.3	0.139	74	100	580	2.576	8.0	100	58	695
	30–40	140	2.4	24	85	54	498	126	39	20.7	0.135	59	99	628	2.759	9.0	102	60	972
13	00–5	20	6.7	30	140	38	469	282	37	21.6	0.180	89	130	230	0.930	2.8	60	31	85
14	00–5	27	7.1	33	130	44	634	342	38	21.7	0.190	93	150	290	1.138	3.8	80	33	112

Table 5 Concentrations of the elements measured in the exchangeable fraction of surface sediments (depth 0–5 cm) taken from Kastela Bay, Croatia

Sample	Element (ppm)						
	Cr	Mn	Fe	Ni	Cu	Zn	Pb
1/1	0.5	0.1	3.7	0.3	0.6	0.6	0.6
2/1	0.5	0.8	6.2	0.4	1.0	2.1	0.5
3/1	0.1	0.9	3.4	0.4	1.0	8.3	1.2
4/1	1.1	0.9	0.4	1.9	0.1	0.6	0.6
5/1	0.8	0.7	0.8	0.9	0.4	0.4	0.5
6/1	0.4	0.4	4.9	0.4	0.8	0.5	0.6
7/1	0.4	0.2	1.9	0.2	0.5	2.0	0.6
8/1	0.5	0.2	2.4	0.2	0.6	1.3	0.6
9/1	1.0	0.2	2.7	0.2	1.0	2.1	0.6
10/1	0.5	0.7	12.6	0.4	0.9	1.4	0.7
11/1	0.4	0.8	5.9	0.3	1.0	4.2	0.9
12/1	0.6	0.5	9.7	0.2	0.8	1.9	1.1
13	0.4	0.1	3.7	0.2	0.7	0.9	0.5
14	1.0	0.1	6.0	0.2	0.6	0.5	0.7
15	0.5	0.1	28.8	0.2	1.0	2.2	0.6
16	0.6	0.1	3.1	0.2	0.4	0.4	0.6
17	0.6	0.1	25.2	0.3	2.1	2.3	0.7
18	0.5	0.1	4.4	0.4	0.7	1.2	0.6
19	0.5	0.1	4.1	0.3	0.6	1.2	0.6
20	0.6	0.1	6.2	0.4	0.6	0.8	0.6
21	0.6	0.1	11.6	0.2	1.0	3.0	0.7

normal distribution only in the first segment, Mn in the second, Co in the fourth and Y in the fifth sediment segment. V concentration was normally distributed only in the second segment. According to the mean values of the elemental concentrations for each segment (Fig. 3a–c) the elements could be divided into five groups with similar distribution patterns. The elements Fe, Mn, Co, Rb and U showed linear increase with increasing depth exhibiting the greatest concentrations in the fifth segment. Cu, Ti, Br and Cr concentrations decreased from the first to the second segment and further increased linearly toward the fifth segment while concentrations of As and Ni increased from the first to the second segment, decreased toward the third segment and increased further reaching maximum concentration in the fifth segment. Pb, Sr and V showed maximum values in the second segment and decreased linearly until they reached minimum values in the fifth segment. The element Ca, Zr, Y and Zn showed the most irregular concentration patterns decreasing from the first to the second segment, reaching maximum values in the third segment, dropped to the fourth segment and increased again toward the fifth segment. Results of one-way ANOVA after logarithmic transformation of variables showed that obtained variability in the elemental concentrations among the segments was significant only for the variables Zr, Fe and Co. All the three elements showed the greatest concentrations in the fifth segment (depth 30–40 cm), which pointed to a larger input of terrestrial material like the mixture of fly and bottom ash and a flysch material into predominant carbonate sediments.

Trace elements of anthropogenic origin are easily adsorbed on the surfaces of sediment particles through relatively weak physical and chemical bonds. It has been reported (Oreščanin et al. 2003) that trace elements of anthropogenic origin are found in soil/sediments predominately as a labile and easily extractable fraction. Concentrations of the elements measured in the exchangeable fraction of surface sediments taken from Kastela Bay were shown in Table 5. Only the first segment (0–5 cm) was considered because only surface sediments were highly susceptible to leaching, remobilization and resuspension. Opposite to the elevated metal values determined in bulk samples, only small to negligible portion of metals was found in the extracts. Therefore, the considered elements can be assumed to be strongly bound to the sediment mineral particles.

The results of XRD analyses (Table 6), conducted on the surface sediment samples, pointed to a predominant carbonate sedimentation with calcite and aragonite as predominant minerals. Presence of considerable amount of quartz and traces of phyllosilicates pointed to terrigenous fluxes from the surrounding areas into the bay.

The degree of the pollution of the Kastela Bay sediments was estimated by dividing mean and maximum concentration of the elements Pb, As, Cr, Mn, Fe, Ni, Cu and Zn for each sediment segment with background

Table 6 Results of the XRD analyses of the surface sediments from Kastela Bay

Mineral	Sample no.										
	1/1	2/1	3/1	5/1	6/1	7/1	8/1	9/1	10/1	11/1	12/1
Calcite, $CaCO_3$	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +
Quartz, SiO_2	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Rodochrosite, $MnCO_3$	+							+			
Muscovite, $(K,Na)(Al,Mg,Fe)_2(Si_3Al)O_{10}(OH)_2$		+			+					+	+
Biotite, $KMg_3(Si_3Al)O_{10}F_2$			+						+		
Aragonite, $CaCO_3$				+ + +	+ +	+ +	+				
Halite, NaCl				+		+	+		+ +	+ +	
Siderite, $FeCO_3$					+						

+ + + Abundant (approximately 25–40%); + + considerable (approximately 10–25%); + subordinate to accessory (<10%); blank spaces-not present

Fig. 3 a Mean values, standard error of mean and standard deviation of the elements Pb, U, Rb, As, Sr, Br for each sediment layer of Kastela Bay sediments: 1-0-5 cm; 2-5-10 cm; 3-10-20 cm; 4-20-30 cm; 5-30-40 cm. b Mean values, standard error of mean and standard deviation of the elements Y, Zr, Zn, Mn, Cr, Co for each sediment layer of Kastela Bay sediments: 1-0-5 cm; 2-5-10 cm; 3-10-20 cm; 4-20-30 cm; 5-30-40 cm. c Mean values, standard error of mean and standard deviation of the elements Ca, V, Cu, Fe, Ni, Ti for each sediment layer of Kastela Bay sediments: 1-0-5 cm; 2-5-10 cm; 3-10-20 cm; 4-20-30 cm; 5-30-40 cm
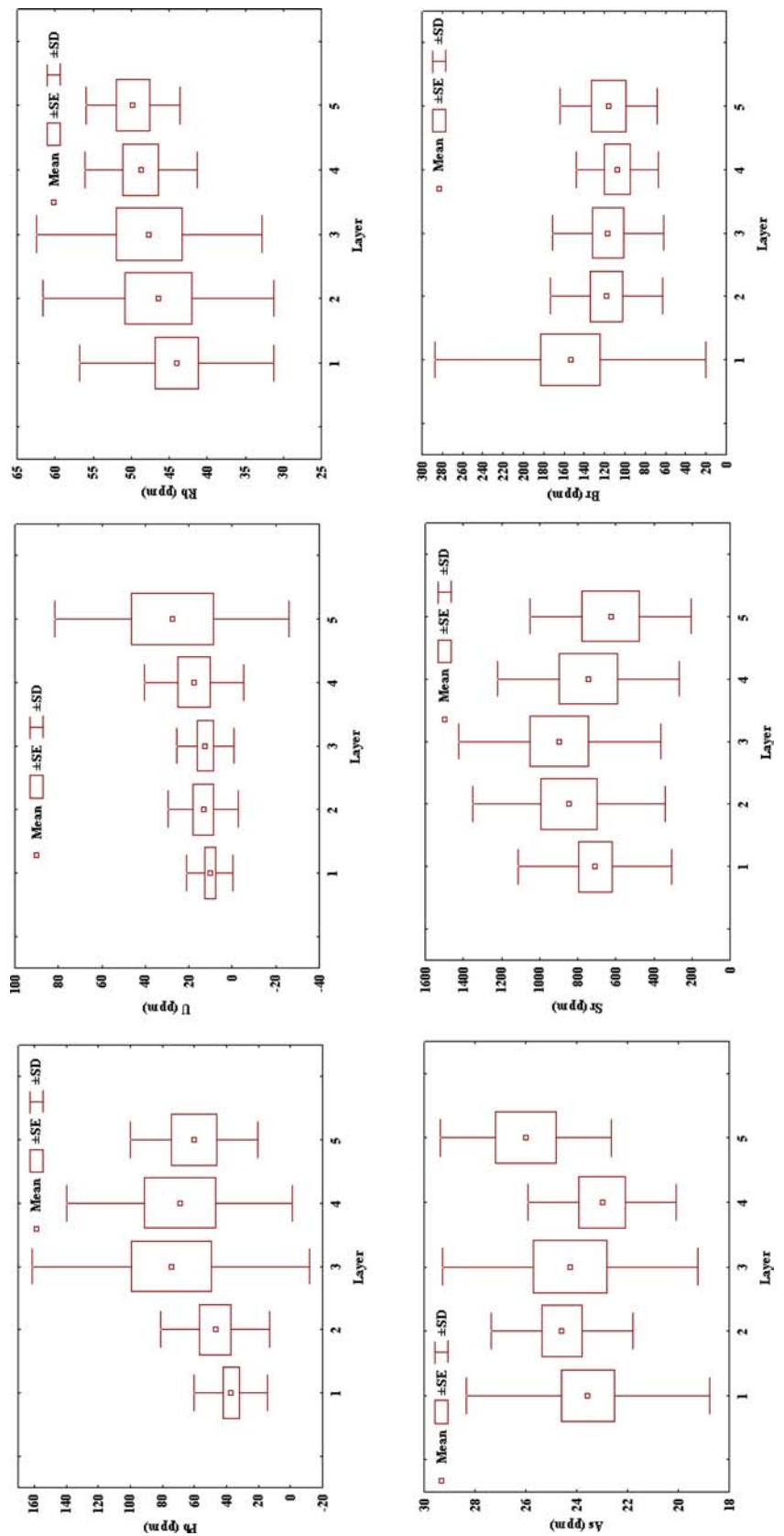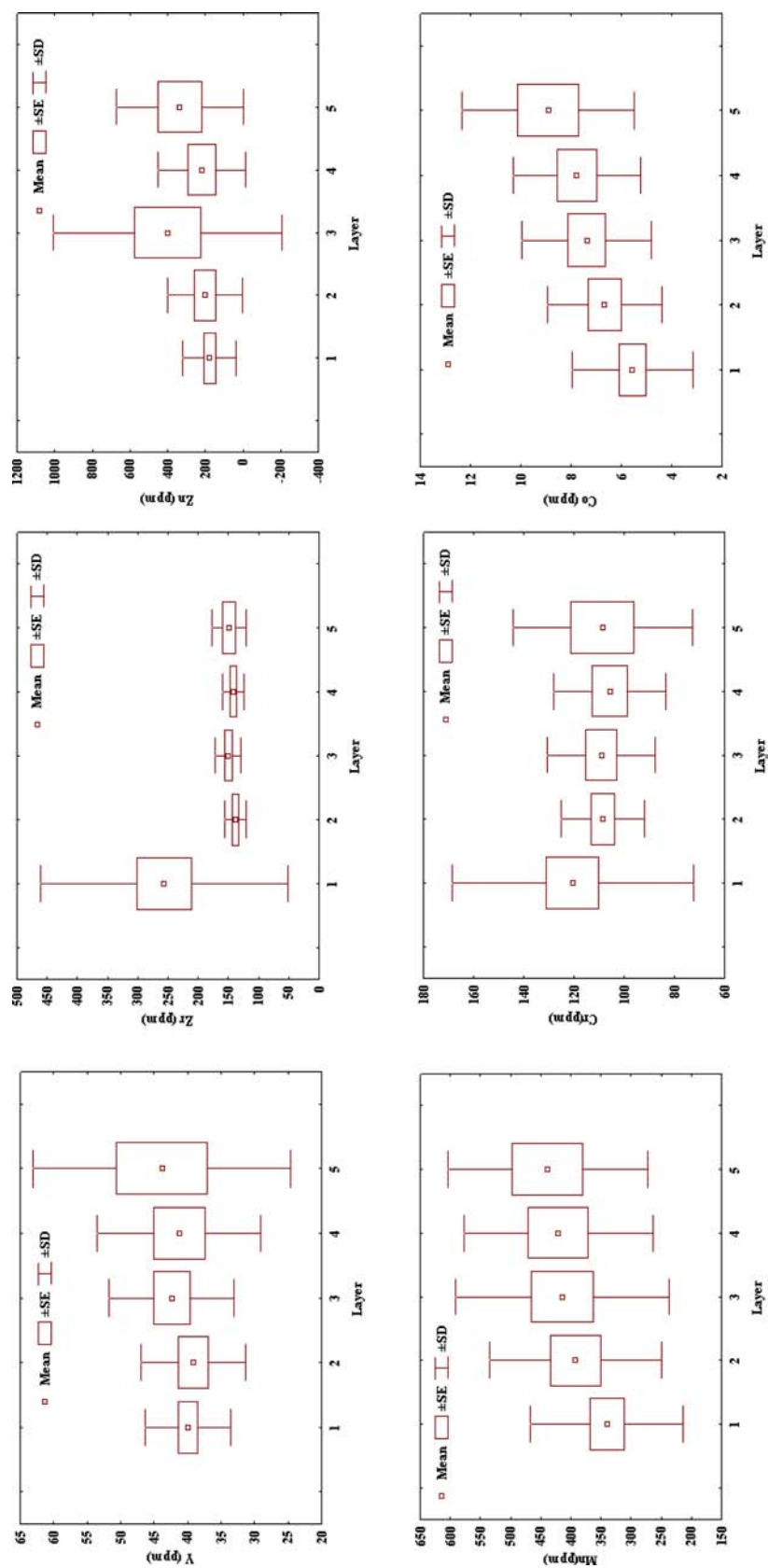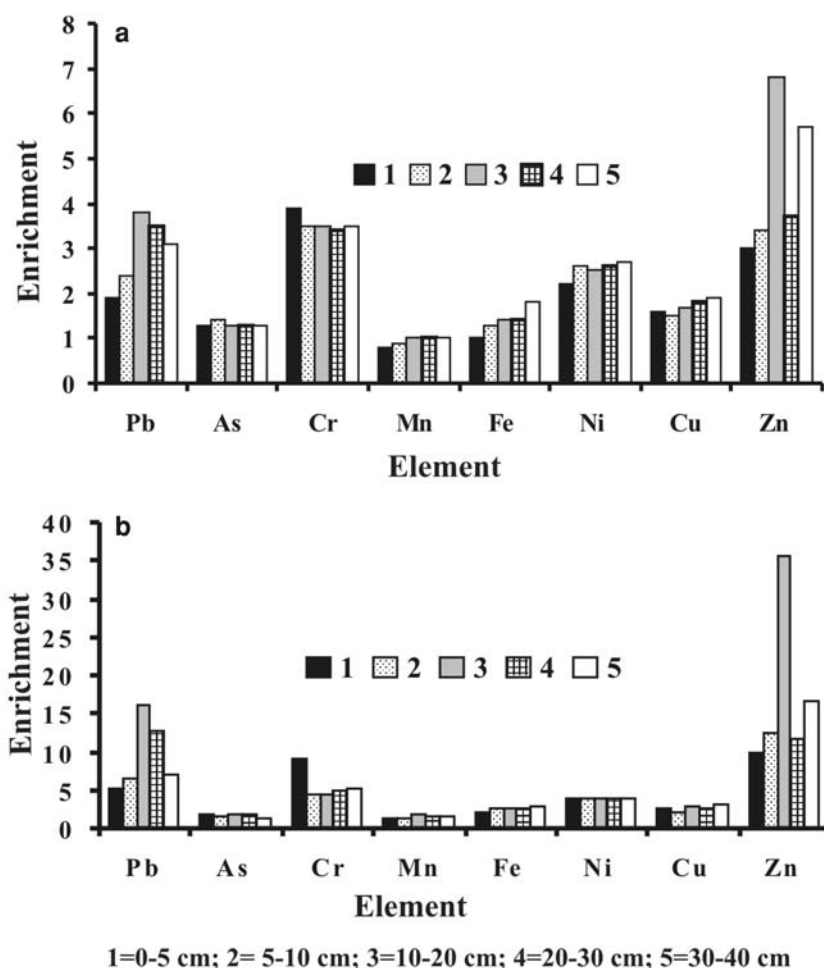
Fig. 3c (Contd.)
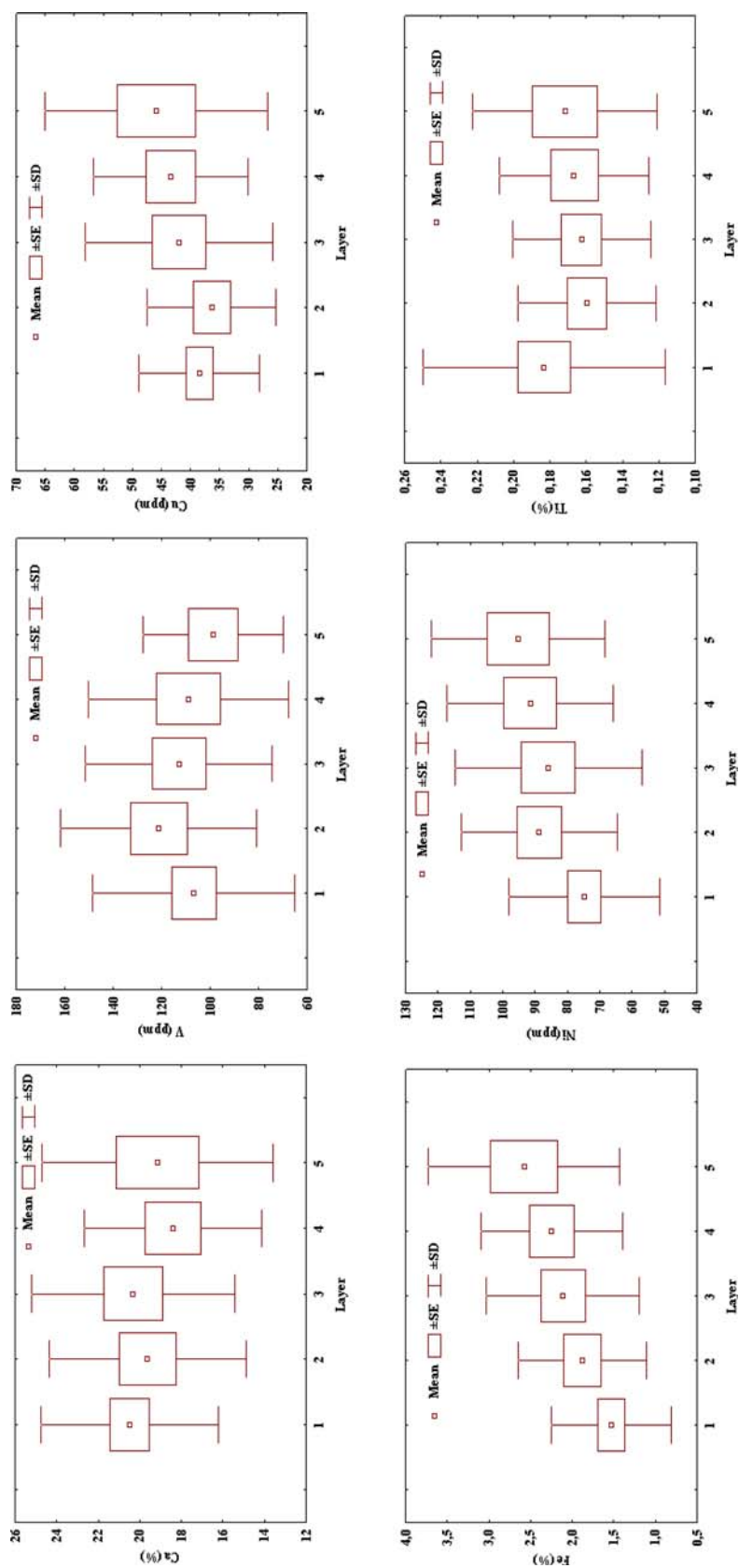
Fig. 4 a Mean enrichment of heavy metals in Kastela bay sediment compared to background values of heavy metals. b Maximum enrichment of heavy metals in Kastela bay sediment compared to background values of heavy metals

1=0-5 cm; 2= 5-10 cm; 3=10-20 cm; 4=20-30 cm; 5=30-40 cm

concentration determined in Punat Bay sediments (Mikulić et al. 2004) which have similar origin and mineralogical composition as Kastela Bay sediments. Results were presented in Fig. 4a, b. The highest enrichment compared to background values were found for Zn (35.6 times), Pb (16 times), Cr (9.1 times) and Ni (4 times). Pb and Zn showed the greatest enrichment in the third sediment segment (10–20 cm), Cr in the first and Ni in the fifth segment. Maximum enrichment with As was 1.8 times, Mn 1.9 times, Fe 2.9 times and with Cu 3.2 times. As expected, the highest concentration of total uranium was determined at the positions 1 and 2 located in the vicinity of the ash deposit site under the constant influence of ash dumping into the sea and leaching from the ash deposit. The maximum concentrations of heavy metals were determined in the samples taken at the points 11, 12, 1 and 3 exposed the most to the various anthropogenic sources. Measured concentrations of heavy metals Zn, Pb, Cr and Ni from that area were significantly higher than those reported by Mikulić et al. (1994) and Lazzari et al. (2004) for the Central Adriatic area. Presented results were in agreement with those reported by Bognar et al. (1998) and Ujević et al. (2000) for Kastela Bay. Anthropogenic sources contributed either through untreated waste waters or through emission into the air followed by wet and dry deposition of emitted particles containing significant amount of heavy metals. Among them cement plant, iron plant and ash deposit site were the nearest to the considered area of the bay. Besides, emission from the vehicles from the nearside main road followed by wet and dry deposition should also be considered as a source of heavy metals in the bay. Nearby shipyard activity should also be considered as a source of lead, zinc and copper originating from antifouling paints and coatings. The similar effect could be expected from the facility for boats repairing and finishing which started to operate few years ago. Elevated level of Zn, Fe and Cr was also the result of discharge of untreated electroplating waste waters from electroplating facilities situated in Vranjic. The maximum concentrations of heavy metals were found in the deeper sediment segments deposited in the period of the highest industrial production and the negligible care to the environment.

Conclusion

Presented results indicated that unregulated dumping of the mixture of fly and bottom ash enriched in radionuclides and heavy metals as well as other anthropogenic sources (industry, traffic, waste waters) caused the severe pollution of Kastela Bay sediments. Maximum ^{238}U activity was approximately 32 times higher and ^{226}Ra was approximately 40 times higher in the Kastela Bay sediment compared to mean value determined for Adriatic sediments, while maximum enrichment in heavy metals ranged from 4 to over 35 times compared to background values. Fortunately, low degree of leaching of heavy metals from sediments was found.

References

Bogner D, Juracic M, Odzak N, Baric A (1998) Trace metals in fine grained sediments of the Kastela bay, Adriatic sea. Water Sci Technol 38(11):169–175

De Lazzari A, Rampazzo G, Pavoni B (2004) Geochemistry of sediments in the Northern and Central Adriatic Sea. Estuar Coast Shelf Sci 59(3):429–440

Mikulić N, Degobbis D, Picer M, Raspor B, Šipoš L, Sobot S, Zvonarić T, Precali R (1994) Monitoring Programme of the Eastern Adriatic Coastal Area. Report for 1983–1991, MAP Technical Reports Series No. 86, UNEP, Athens

Mikulic N, Orescanin V, Legovic T, Zugaj R (2004) Estimation of heavy metals (Cu, Zn, Pb) input into the Punat bay. Environ Geol 46 (1):62–70

Orescanin V, Katunar A, Kutle, Valkovic V (2003) Heavy metals in soil grape and wine. J Trace Microprobe Techniques 21(1):171–180

Orescanin V, Lulic S, Pavlovic G, Mikelic L (2004a) Granulometric and chemical composition of the Sava river sediments upstream and downstream of the Krsko nuclear power plant. Environ Geol 46(5):605–614

Orescanin V, Barisic D, Mikelic L, Lovrencic I, Rubcic M, Rozmaric-Macefat M, Lulic S (2004b) Environmental contamination assessment of the surroundings of the ex-Sibenik's ferromanganese smelter, Croatia. J Environ Sci Health Part A A39(9):2493–2506

Ujević I, Odžak N, Barić A (2000) Trace metal accumulation in different grain size fractions of the sediments from a semi-enclosed bay heavily contaminated by urban and industrial wastewaters. Water Res 34(11):3055–3061