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CHARACTERIZATION OF TENORM AND SEDIMENTS OF KASTELA BAY AND THE INFLUENCE OF TENORM ON THE QUALITY OF SEDIMENTS

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ABSTRACT

The objective of this study was set on three goals: (i) Chemical and radiological characterization and leaching properties of the mixture of fly and bottom ash, (ii) Chemical, radiological and mineralogical characterization of the Kastela Bay sediments, and (iii) Estimation of the influence of TENORM deposition on the quality of sediments. Samples of the mixture of fly and bottom ash, sediment cores ranging from 0 to 55 cm and surface sediment samples were analyzed. Enrichment with heavy metals in the mixture of fly and bottom ash ranged from 1.6 to 36 times while ^{226}Ra and ^{238}U were up to 50 times enriched. Most of the measured heavy metals in the ash were 3-4 times those in the surrounding soil. It was found that over 37% of the total U could be removed from the ash by the sea water. The highest enrichment in sediment cores was found for Zn (35.6 times), Pb (16 times), Cr (9.1 times) and Ni (4 times). The highest concentrations of total uranium were determined at positions in the vicinity of the ash deposit site. Maximum concentrations of heavy metals were found in deeper sediment segments deposited in the period of the highest industrial production.

KEYWORDS: TENORM, fly ash, bottom ash, radionuclides, heavy metals, Kastela Bay

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 (Ujevic *et al.*, 2000). Until the early 90's of the twentieth 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 “Adriavinil” 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 “Adriavinil” 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 of the 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 “Adriavinil”, 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. Sea water 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 communication, 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. Material was dried at 105°C and fraction <0.5 mm was disaggregated in an agate mortar and prepared for determination of total elemental composition, selected radionuclides, mineralogical composition as well as for leaching tests.

Twelve sediment profiles and nine surface samples were collected in Kastela Bay. Geographical location of the study area and the sampling points are shown in Figure 1.

Sediment cores were divided into segments of 0-5 cm, 5-10 cm, 10-20 cm, 20-30 cm, 30-40 cm and 40-50 cm (or 40-55 cm if possible). Concentrations of Cr, Fe, Zn, Zr, Pb, Ni, Co and U in bulk samples of ash and sediments were determined using energy dispersive X-ray fluorescence, EDXRF method (Orescanin *et al.*, 2003). Cu was measured only in the mixture of fly and bottom ash. Samples were irradiated by X-rays generated from a ^{109}Cd annular source. The incident angle was 49.76°. Detection of characteristic X-ray radiation from the sample was conducted with a Si (Li) detector (Canberra) cooled with the liquid nitrogen and 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 emerging angle was 74.05°, and the distance was 1.5 cm. Spectra were collected by a Genie–2000 software (Canberra). Collecting time was 10000 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 the thin targets 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 the thick targets were calculated with the “Fundamental parameters” method from a WinFund package using ECH (coal burning fly ash) as a standard reference material.

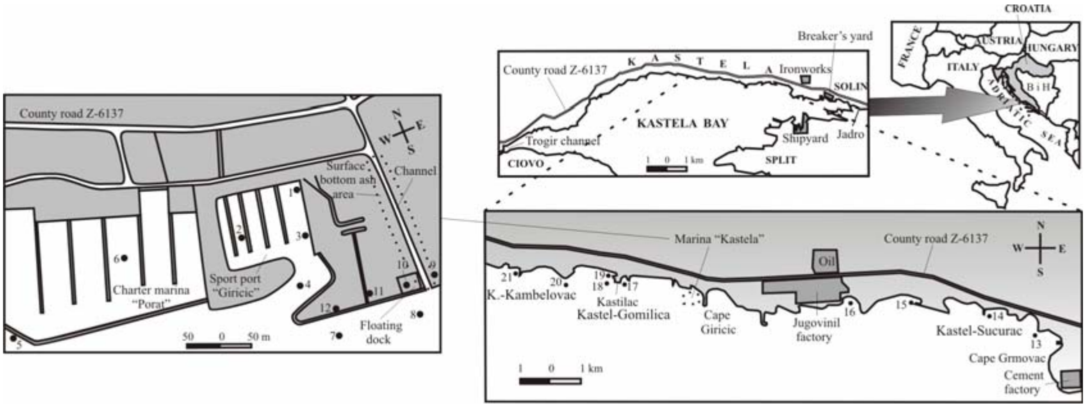

Figure 1. Geographical location of the study area and the sampling points

After the XRF analysis, 1 g of homogenized sample was extracted either by distilled water or by sea water. 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. After 20 minutes of complexation with APDC (ammonium-pyroloidinedithiocarbamate), the suspension was filtered through a Millipore filter (0.45 μm) and irradiated for 10000 s. Also, different organic acids were applied in order to simulate leaching conditions that occur naturally in the environment. 1 g of homogenized samples were extracted by 1M NH_4Ac-pH 7 for one hour or by $2x10^{-2}$ M citric acid, EDTA, ascorbic or oxalic acid for eight hours.

All sediment segments from 0-5 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 proportional counter. Diffraction data were processed by Philips X'Pert software. The relative intensities of X-ray diffraction lines were compared with literature values (Orescanin *et al*., 2004b).

Ash and sediment materials were placed in the counting containers of 125 cm^3, sealed and stored for at least the 4-week period to allow an ingrowth period of gaseous ^{222}Rn. At the end of the ingrowth period, gamma-spectrometry measurements were performed on a HPGe semiconductor detector joined to the 8192 channel analyzer “Canberra”. Spectra were recorded during 80000 seconds 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 calculation of ^{238}U activity assuming the natural ^{235}U/^{238}U activity ratio of 0.04603 (Orescanin *et al*., 2004a; Marinez-Lobo and Palomares 1991; Murray and Aitken, 1988).

RESULTS

Characterization of the mixture of fly and bottom ash

Table 1 presents the mean values and the concentration ranges of selected elements determined in 33 samples of the mixture of fly and bottom ash and Figure 2 activities of the radionuclides ^{226}Ra and ^{238}U determined in the same samples. The results of the leaching tests are shown in Table 2.

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
Cr (ppm)	136.2	69.6-250.0	153.4	0.9
Zr (ppm)	184.2	65.0-281.0	380.6	0.5
U (ppm)	93.8	34.0-227.0	2.6	36.1
Pb (ppm)	42.8	24.6-74.0	26.6	1.6

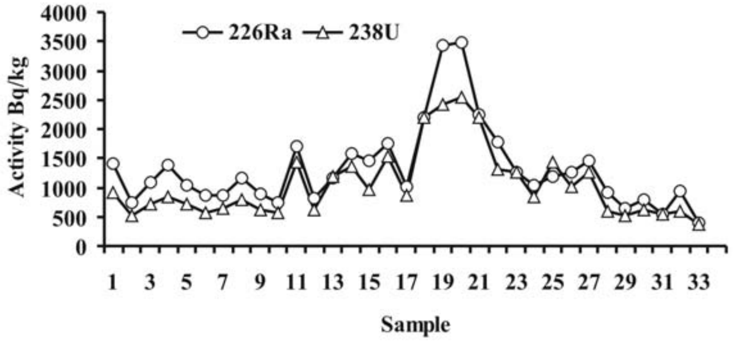

Figure 2. Activities of ^{226}Ra and ^{238}U in 33 samples of the mixture of fly and bottom ash from Kastel Gomilica, Croatia

Table 2: Elemental concentrations measured in the extracts of the composite sample of the mixture of fly and bottom ash and percentages of elements extracted by different extraction agents.

1-extracted with distilled water acording to DIN-38414-S4 standard; 2-extracted with sea water (solid:liguid = 1:10); 3-extracted with NH_4Ac; 4-extracted with ascorbic acid; 5-extracted with EDTA; 6-extracted with citric acid; 7-extracted with oxalic acid; -: test not performed

	Elemental concentrations (ppb)		**Percentage of element released from the mixture of fly and bottom ash**				
Element	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Pb	58.4	46.8	2.5	2.0	3.1	6.7	5.4
U	882.0	29732.0	1.6	26.4	17.2	43.2	51.2
Se	23.1	61.9	-	-	-	-	-
V	109.2	212.4	1.7	0.8	0.1	1.2	1.8
Cr	50.4	61.2	0.8	0.8	1.7	1.7	1.9
Fe	134.4	151.2	-	-	-	-	-
Ni	21.4	14.4	0.2	0.3	0.3	2.2	1.6
Cu	31.1	24.81	1.6	1.2	7.5	6.4	3.8
Zn	49.11	34.6	1.7	1.7	3.2	8.5	9.8
Co	9.2	n.d.	2.0	4.6	0.1	9.8	8.2

Characterization of sediment samples

Table 3 shows the activities of ^{226}Ra and ^{238}U measured in 12 sediment profiles. The activities of ^{226}Ra and ^{238}U measured in nine surface samples of Kastela Bay sediments and mean values of selected radionuclides determined for open Adriatic and coastal

Adriatic sediment are presented in Table 4. Concentrations of selected elements measured in 12 sediment profiles are presented in Table 5.

Table 3. Activities of ^{226}Ra and ^{238}U in Bq kg^{-1} measured in 12 sediment profiles

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

Table 4. Activities of ^{226}Ra and ^{238}U in Bq kg^{-1} measured in nine surface samples of Kastela Bay sediments and mean values of selected radionuclides determined for open Adriatic and coastal Adriatic sediment

Surface sample	**Depth (cm)**	**^{226}Ra**	**^{238}U**
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
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
* $\bar{X}_{\text{Open Adriatic}}$, N=48	00 - 5	19.9	19.1
* $\bar{X}_{\text{Croatian coast}}$, N=51	00 - 5	19.2	18.2

Table 5. Concentrations of selected elements in 12 sediment profiles determined by EDXRF. Depth in cm; Fe in %wt, other elements in ppm

Profile	Depth	Pb	U	Zr	Cr	Fe	Co	Ni	Zn
1	00 - 5	80	14.1	125	110	3.211	10.5	90	422
	5 - 10	93	33.9	144	140	3.795	12.3	100	391
	10 - 20	96	16.5	159	130	3.221	10.6	140	527
	20 - 30	97	9.7	133	100	2.572	8.3	70	595
	30 - 40	75	15.3	148	140	3.069	10.1	90	432
	40 - 55	62	40.0	130	110	3.456	10.9	120	196
2	00 - 5	35	6.8	124	110	1.945	7.4	140	187
	5 - 10	32	13.0	127	120	2.260	8.0	140	117
	10 - 20	58	19.2	169	120	3.072	10.6	100	184
	20 - 30	53	32.0	173	140	3.524	12.4	110	157
	30 - 40	43	54.3	207	160	4.254	14.0	140	117
3	00 - 5	63	1.7	150	100	1.808	6.4	80	339
	5 - 10	74	1.0	171	120	1.870	6.3	100	323
	10 - 20	49	1.9	162	90	2.093	8.1	100	283
	20 - 30	36	2.0	121	100	1.828	6.4	110	184
	30 - 40	90	1.5	113	150	4.023	13.4	80	675
4	00 - 5	34	2.0	119	70	1.647	6.1	100	125
	5 - 10	31	2.9	127	80	1.751	6.2	80	114
	10 - 20	21	1.6	108	110	1.444	5.7	120	92
	20 - 30	25	1.9	117	100	1.523	6.0	140	107
5	00 - 5	29	1.8	122	90	1.100	4.5	60	59
	5 - 10	27	1.7	110	90	0.960	4.0	60	51
	10 - 14	33	1.6	115	130	1.028	4.6	60	58
6	00 - 5	29	2.1	151	80	1.384	5.4	70	76
	5 - 10	21	1.8	148	100	1.077	4.2	60	67
	10 - 20	23	2.3	168	70	1.191	3.9	40	70
7	00 - 5	35	4.1	151	80	1.461	5.0	50	155
	5 - 10	26	2.4	131	120	1.247	4.6	50	85
	10 - 20	30	2.2	164	90	1.489	5.5	70	83
	20 - 30	25	1.8	151	80	1.437	6.1	70	68
	30 - 40	26	1.8	139	70	1.478	6.0	110	66
8	00 - 5	30	2.0	135	90	1.207	4.4	60	114
	5 - 10	26	1.8	149	110	1.397	5.2	90	86
	10 - 20	26	1.8	154	100	1.353	4.8	70	89
	20 - 30	28	1.8	150	90	1.373	5.4	90	90
	30 - 40	30	1.7	150	90	1.469	5.8	80	94
9	00 - 5	33	4.7	156	90	1.739	6.3	60	146
	5 - 10	35	5.0	164	120	1.903	7.1	100	124
	10 - 20	38	4.9	176	130	1.844	7.3	70	113
	20 - 30	29	3.3	163	150	1.629	5.5	50	88
	30 - 40	27	3.8	166	80	1.355	4.9	50	63
10	00 - 5	28	4.7	141	87	1.914	7.1	92	158
	5 - 10	32	9.0	137	97	2.193	7.3	93	142
	10 - 20	36	5.2	140	110	1.946	7.1	100	148
	20 - 30	39	6.5	146	87	2.302	7.6	95	202
	30 - 40	51	4.0	144	80	2.208	8.1	110	265
11	00 - 5	70	3.9	135	85	1.883	6.8	85	394
	5 - 10	35	2.3	129	100	1.548	6.3	100	188
	10 - 20	313	3.9	138	140	3.894	11.5	60	2100
	20 - 30	249	8.0	139	110	3.715	12.0	80	1550
12	00 - 5	103	7.1	163	100	2.909	9.8	80	585
	5 - 10	130	2.6	127	105	2.533	8.5	92	739
	10 - 20	173	3.0	148	90	2.746	8.8	100	1057
	20 - 30	112	2.7	128	100	2.576	8.0	100	695
	30 - 40	140	2.4	126	99	2.759	9.0	102	972

The results of XRD analyses are presented in Table 6.

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 (app. 25–40%); ++ Considerable (app. 10–25%); + Subordinate to accessory (<10%); blank spaces-not present

DISCUSSION

Mixture of fly and bottom ash

The analyzed mixture of fly and bottom ash showed significant variability in its chemical composition. Mean elemental concentrations in the ash were elevated from 1.6 to approximately 36 times compared to the common soil concentrations. The highest enrichment was found for uranium and nickel.

Activities of ^{226}Ra and ^{238}U in the ash mixture were approximately fifty times higher than those in the common soil. In the majority of the samples of the ash ^{238}U activity was up to thirty percent lower compared to ^{226}Ra. This could be explained with the fact that most of the samples were taken from the surface of the deposit with 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 sulphate, and this minimizes the solubility of radium, which forms highly insoluble sulphates.

The leaching properties of the sea/rain water can be highly modified by the presence of various, naturally occurring organic complexing agents (Erdem and Tumen, 2004). Table 2 shows that only negligible amounts of V, Cr, Pb, Zn, Cu and Ni were released from flying and bottom ash either by exchangeable agent (ammonium acetate, pH 7) or the sea water (pH 7). Organic acids were more efficient in heavy metal removal compared to ammonium acetate. The high affinity of Cu, Pb and Zn for organic complexes was the reason for their higher extractability in organic acids compared to the other measured elements. The percentage of selected elements found in the extract obtained by organic acids was less than 10%. Therefore, the considered elements can be assumed to be strongly bound to the ash mineral particles under the tested conditions. On the contrary, it was found that uranium could be easily mobilized from the ash. A significant amount of the total uranium was extracted from flying and bottom ash by all leaching agents, except ammonium acetate which removed only 1.6% of the total U. Removal efficiency varied from 17.2% in the case of EDTA to over 50% in the case of oxalic acid. Results show that almost 40% of the total uranium could be mobilized from flying and bottom ash by the sea water.

Sediment samples

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 segments. Maximum ^{238}U activity was approximately 32 times higher and ^{226}Ra 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 placed near the ash deposit and in the surface sediment sample 16 located near the “Adriavinil” factory (Tables 3 and 4).

According to Shapiro-Wilks W test U, Pb and Zn deviated significantly from the normal distribution in all sediment segments, while Zr, Cr and Fe showed disturbance in normal distribution only in the first segment and Co in the fourth sediment segment. Fe, Co and U showed linear increase with increasing depth exhibiting the greatest concentrations in the fifth segment. Cr concentrations decreased from the first to the second segment and further increased linearly toward the fifth segment while concentrations of 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 showed maximum values in the second segment and decreased linearly until it reached minimum values in the fifth segment. Zr 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 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.

XRD analyses results (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, Cr, Fe, Ni and Zn for each sediment segment with background concentration determined in Punat Bay sediments (Mikulic *et al*., 2004) which have similar origin and mineralogical composition as Kastela Bay sediments. The highest enrichment compared to background values was 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 Fe was 2.9 times. As expected, the highest concentrations of total uranium were 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. Maximum concentrations of heavy metals were determined in the samples taken at the points 11, 12, 1 and 3 the most exposed 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 Mikulic and others 1994 and Lazzari and others 2004 for the Central Adriatic area. Presented results were in agreement with those reported by Bogner and others 1998 and Ujevic and others 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. 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 into Jadro River. 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.

CONCLUSIONS

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 approximately 40 times higher in the Kastela Bay sediment compared to mean value determined for Adriatic sediments, while maximum enrichment with heavy metals ranged from 4 to over 35 times compared to background values. Investigated flying and bottom ash showed a significant variability in their chemical composition. The highest values compared to soil concentrations were found for U and Ni. Extractable heavy metal portion under all tested conditions was found to be less than 10%, except for the total uranium which showed the high possibility for leaching either by the marine water or in weak organic acids.

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