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The geochemistry model of the surface sediment determined by using ED-XRF technique: a case study of the Boka Kotorska bay, Adriatic Sea

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Abstract The spatial distribution of major oxides (Na_2O, K_2O, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, MnO, TiO_2, P_2O_5) and numerous elements (Cr, Co, Ni, Cu, Zn, As, Se, Pb, Sn, Sb, Ba, Sr, Br, Rb, Zr, Mo, Cs, Y, V, Ga, La, U, Th, Nb, W, Sc, Ge, Gd, Yb, Hf, and Ce) was determined by using energy dispersive X-ray fluorescence spectrometry on the basis of previously measured organic matter and carbonates. The optimal measuring variables for the investigated oxides and elements were determined by using five standard reference materials. The carbonated sediment type can be determined on the basis of the highest Sr, Sc, La, Nb, Hf, and Yb concentrations followed with the lowest concentrations of the remaining elements and the negative Ce anomaly. The complexity of the obtained data was also examined by principal component analysis (PCA) and cluster analysis (CA) in the identifying geochemical composition of the surface sediment. Boka Kotorska bay's geographical position, orographical configuration, and hydrographic characteristics influence the geochemistry model of the surface sediment, quite different from the open sea.

Keywords Surface sediment · Oxides · Minor and trace elements · ED-XRF analysis · Boka Kotorska bay

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Introduction

There are numerous areas in which humans negatively affect coastal zones of marine ecosystems, including industrial, agricultural, and municipal activities. More recently, the impact of aquaculture on coastal environments is becoming an increasingly significant problem. Aquaculture production has experienced rapid growth, mainly due to greater demand for more food products (Tovar et al. 2000a). An intensive aquaculture can affect water and sediment chemical conditions in coastal areas. Intensive aquaculture also has the potential to modify natural concentrations of metals in local sediments (Tovar et al. 2000b).

Boka Kotorska bay is on the UNESCO's World Heritage List located in Montenegro, the southeastern Adriatic Sea, with a complex geohydrological structure, consisting of four embayments naturally divided into smaller bays: the Herceg Novi, Tivat, Risan-Morinj, and Kotor bay. They are connected and interact with the sea through narrow straits, and the bay can be considered one of the main freshwater inputs into the southern Adriatic Sea (Bellafiore et al. 2011). The bottom of the bay, whose mean depth varies from 30 to 40 m, has the form of a plateau filled with deposits. On average, the Boka Kotorska bay situation presents a surface outflow and a bottom inflow of water (Bellafiore et al. 2011). The deepest and narrowest part of the bay is the small Kotor bay (70 m)

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surrounded by high mountains and with highest precipitations in Europe, with terrestrial and different physical and chemical and anthropogenic impacts. The shallowest and the widest bay is the small Tivat bay with high anthropogenic impacts.

Studies investigating metal content in the southeastern Adriatic Sea sediments have mostly focused on the coastal areas (Rivaro et al. 2004, 2011; Stanković et al. 2014), with the exception of the work undertaken by Dolenec et al. (1998) examining elements in surficial sediments in the open Adriatic Sea. Therefore, the aim of this work was to investigate the surface sediments composition in Boka Kotorska bay, ten oxides and 31 elements analyzed by energy dispersive X-ray fluorescence spectrometry (ED-XRF) at 12 locations, including organic matter and carbonates, in order to determine their origin and type of sediment. At the same time, the surface sediment composition was compared with the values reported for the central southern Adriatic Sea (Dolenec et al. 1998) and Albanian and Montenegrin coastal areas (Rivaro et al. 2004, 2011; Tanaskovski et al. 2014; Stanković et al. 2014).

Material and methods

Study area

Boka Kotorska bay is located in Montenegro, Adriatic-Mediterranean country (Fig. 1). Sediment samples were collected in April 2013 at the 12 locations at a depth of 6–42 m: L1. Igalo, L2. Kumbor, L3. Lipci, L4. Dražin Vrt, L5. Orahovac, L6. Institute of Marine Biology (IBM), L7. Kotor bay (central), L8. Kalardovo, L9. Ostrvo cvijeća, L10. Obala Đuraševića, L11. Tivat bay (central), L12. Herceg Novi bay (central), as it is shown in Fig. 1. Samples L1–2, L7, and L11–12 were taken from deeper water, from 25 to 42 and 900 to 2400 m from the coast and L6 at a depth of 22 and 50 m from the coast. The remaining sediment samples (L3–5 and L8–10) were taken close to the mussel farms, i.e., 50 m from the bay coast and at different depths: L3–5 was taken from 15 to 31 m and L8–10 from 6 to 7 m. In Table 1, the characteristics of sediment sampled locations are shown.

Sample collection and analytical method

About 1.5 kg of each sample was taken from the upper 15 cm by a grab sampler from the boat. Samples were taken from 6 to 42 m depth. To ensure the representativeness of the sample, three replicates were collected from each site with the distance of 3 m between each other and the fresh samples were placed in plastic boxes. Before oven drying at 105 °C for 24 h, each sample was combined after removal of the coarse fraction (>2 mm) by wet sieving. Sediment samples for ED-XRF analyses were prepared as follows: after oven drying, grinding, homogenizing, and sieving (particle size less than 0.071 mm

in diameter), the pellets were finally formed by pressing 1.0 g of each powdered sediment samples and 5 g of boric acid was added in the mold and pressed into pellets of 32 mm diameter (15 tons pressure, 30 s dwelling time). The standard reference material samples were prepared in the same way as sediment pellets and directly measured by ED-XRF under an air conditioner. The presented results are based on dry weight for all measured samples.

Measurement conditions

Concentrations of ten oxides and 31 elements were measured by the ED-XRF method using a PANalytical MiniPal 4 (Almelo, Netherland) ED-XRF spectrometer, equipped with a 30-kV Rh anode tube (maximum power: 9 W; window: 75 μm Be; maximum high voltage: 30 kV; maximum current: 750 μA; cooling medium: air), with a high-resolution silicon drift detector (SDD), a spinner, and a 12-position removable sample changer. The resolution of the SDD is 145 eV for Mn-Kα.

To obtain the best possible performance of the spectrometer, the following instrumental variables had to be adapting to each of the measured elements and oxides: tube-current, voltage, type of excitation (continuous or monochromatic which could be reached with the application of appropriate filter), measurement time, and path of the X-ray between the sample and detector (air). Five reference materials were selected for calibration: NIM-GBW 07428, NIM-GBW 07427, NIM-GBW 07430, NIM-GBW 07419, and NIM GBW 87102.

The measurement was done primarily by measuring components in four MC (China) standard samples (NIM-GBW 07428, NIM-GBW 07427, NIM-GBW 07430, and NIM-GBW 07419) in order to find optimal measuring variables for each investigated oxide and element. The standard reference material NIM GBW 07428 was included in the calibration, and after, calibration was used as unknown sample for the first check, while the second check was done by the measurement of the NIM-GBW 07402 standard which was not included in the calibration and represented a "real unknown sample." In order to reduce the background and to improve the element of interest intensity, different filters with different thickness were used during the element analysis between the X-ray source and samples to filter out unwanted X-ray peaks. Optimal measurement variables for each group of elements were determined and presented in Table 2. Spectral data were analyzed by MiniPal/MiniMate software version 3.0.–63(2.64) (PANalytical, Almelo, Netherlands).

Before the ED-XRF analysis, to obtain the accurate value of the examined elements in the investigated samples, the residual ("dark") matrix was measured in sediment samples as a loss-on-ignition (LOI) 1 upon sample heating in a muffle furnace at 450 °C, and LOI 2 at 950 °C, for 4 h. The loss on

ignition—*LOI* was calculated on the basis of difference between a mass of dry sample at 105 °C and mass loss after firing at 450 and at 950 °C (Heiri et al. 2001). The organic matter content listed in the standard reference materials (SRMs) was used in the instrument calibration and CaO measurement. The *LOI 1* (organic matter content) and *LOI 2* (carbonate mineral content) were experimentally determined in the all investigated sediment samples, Table 1.

The obtained results of measured elements in the standard reference material as unknown sample, NIM GBW 07428, were in good agreement with the certified values of the element concentrations in this standard. The calibration of ED-XRF instrument was appropriate with above used certified standards. The relative standard deviation (RSD) of the elements determined on the basis of ten consecutive measurements of the same element in the standard reference material NIM-GBW 07402 under determined parameters are compared with the certified value for the same element. The highest RSDs were calculated for Rb, W, Nb, P, Th, Cu, As, U, Cr, and V (the highest was for Rb, 19 %, and the lowest for V, 5 %), and for the remaining elements and oxides, RSD was less than 1.0 %. Bromium, Cs, Sc, Ge, Yb, Gd, Hf, and Ce

were not included in checking by NIM-GBW 07402, as there are no these elements in this standard.

Statistical analysis

The basic statistical analyses (mean, SD, min., max., and variance) were calculated for the presented *LOI 1*, *LOI 2*, oxides, and elements. Various multivariate statistical techniques have been employed for evaluation and characterization of environmental data (Stanković et al. 2014). Principal component analysis (PCA) is a commonly used multivariate method mainly utilized for data reduction, but it is also used to classify and discriminate between various samples. Cluster analysis (CA) was also performed to classify the samples. All samples were grouped in a multidimensional factor space and the dendogram was plotted, representing the similarities and/or dissimilarities of surface sediments in chemical composition.

PCA was used to allow easy representation of trace elements and samples in a two-dimensional diagram. The rotation of the principal components was executed by the Varimax method with Kaiser normalization. The results showed good discrimination capabilities between the samples taken from

Table 1 Coordinates and depths of the sampling stations

	Location	Depth (m)	Distance from the cast (m)	*LOI 1* (%)	*LOI 2* (%)	Latitude (N)	Longitude (E)
L1	Igalo	25	800	7.36	17.04	42° 27′ 1.1″	18° 30′ 54.9″
L2	Kumbor	42	900	7.72	16.59	42° 25′ 58″	18° 35′ 20.2″
L3[a]	Lipci	15	50	2.84	37.29	42° 29′ 40.3″	18° 40′ 26.2″
L4[a]	Dražin Vrt	31	50	5.50	21.12	42° 28′ 59.6″	18° 43′ 41.4″
L5[a]	Orahovac	22	50	11.51	25.35	42° 29′ 14.6″	18° 45′ 47.2″
L6	IMB	22	50	7.87	17.88	42° 26′ 18.8″	18° 45′ 29.6″
L7	Kotor bay (central)	34	1500	12.93	19.54	42° 28′ 51″	18° 44′ 47″
L8[a]	Kalardovo	6	50	4.08	10.94	42° 24′ 41.3″	18° 42′ 34.1″
L9[a]	Ostrvo cvijeća	7	50	3.41	12.34	42° 24′ 13.6″	18° 42′ 22.4″
L10[a]	Obala Đuraševića	7	50	6.83	12.21	42° 24′ 26.1″	18° 40′ 43.6″
L11	Tivat bay (central)	39	2400	7.84	16.06	42° 25′ 9.7″	18° 39′ 53″
L12	Herceg Novi bay (central)	41	1400	6.73	17.40	42° 26′ 28″	18° 32′ 6.8″

[a] Mariculture

Table 2 The optimal parameters and measured conditions

Elements	Line name	Electric potential difference (V)	Electric current (μA)	Tube filter	Filter thickness (μm)	Mass density (g cm^{-3})	Medium	Measuring time (s)
Ba, V	Lα, Kα	12,000	750	Al thin	50	2.7	Air	100
P, Sc	Kα, Kα	12,000	750	Al thin	50	2.7	Air	200
As, Cu, Zn, Sn, La, Sr, Zr, Nb, W, U, Br, Cs, Ge, Gd, Yb, Hf	Kα, Kα, Kα, Lα, Lα, Kα,Kα, Kα, Lα, Lα, Kα, Lα, Kα, Lα, Lα, Lα	30,000	300	Ag	100	10.5	Air	100
Co, Cr	Kα, Kα	20,000	300	Al	200	2.7	Air	200
K$_2$O, Ce	Kα, Lα	13,000	650	Al thin	50	2.7	Air	400
Ti, CaO	Kα, Kα	15,000	540	Al thin	50	2.7	Air	200
Ga, Th, Y	Kα, Lα, Kα	30,000	200	Al	200	2.7	Air	400
Mn, Ni, Fe$_2$O$_3$	Kα, Kα, Kα	20,000	405	Mo	100	10.22	Air	200
Rb, Pb	Kα, Lα	30,000	270	Mo	100	10.22	Air	200
MgO, SiO$_2$, Al$_2$O$_3$	Kα, Kα, Kα	8000	750	none	0	0	Air	500

different locations. PCA was applied to analyze the similarities at the sampling sites and to identify the source and apportionment of trace elements in surface sediments. The first two PCs were extracted and utilized in bivariate plots; loadings were considered to evaluate correlations between variables. The analysis is used to achieve maximum separation among clusters of parameters. CA was performed to classify the samples of surface sediments. In this study, single-linkage algorithm and city-block (Manhattan) distance measurement was calculated. In addition, linear correlation coefficients were calculated to understand the inter-element relationships. Data were analyzed by Statistica software (Data Analysis Software System, v.10.0, StatSoft, Inc, Tulsa, OK, USA). Prior to PCA and CA, the data sets were examined for outliers (Grubbs 1969).

Results

The elemental composition of surface sediment from Boka Kotorska bay was determined by measuring ten oxides (SiO$_2$, CaO, Fe$_2$O$_3$, Al$_2$O$_3$, K$_2$O, MgO, TiO$_2$, Na$_2$O, MnO, and P$_2$O$_5$) and 31 elements (Cr, Co, Ni, Cu, Zn, As, Se, Pb, Sn, Sb, Ba, Sr, Br, Rb, Zr, Mo, Cs, Y, V, Ga, La, U, Th, Nb, W, Sc, Ge, Gd, Yb, Hf, and Ce) with the energy dispersive X-ray fluorescence. The results of the investigated oxides and elements are shown in Supplementary Table A.

The organic matter content higher than 4 % was usually found in highly productive areas and sediments with prevailing small-size particles (Bogner et al. 2005). Also, the depth of water is an important factor in the deposition of the organic matter and carbonates (Farah et al. 1990). An organic matter in

marine sediments may be derived from terrestrial, marine, and anthropogenic sources. Organic matter (*LOI 1*) in coastal aquatic sediments derives from marine sources, such as seagrasses, micro- or macroalgae, and phytoplankton, as well as terrestrial sources that are principally delivered by rivers. Marine-derived organic matter is generally more labile than its refractory, terrestrial counterpart (Basaham 2008). Carbonates in marine sediments (*LOI 2*) are the result of both, weathering of surrounding limestone rocks (carbonate and flysch) and sedimentation of different biogenous particles (calcite and aragonite minerals) (Mihelcic et al. 1996).

Sediments taken from the Boka Kotorska bay at comparable water depths differ in the percentage of organic matter and carbonate: the organic matter content ranges from 2.84 to 12.93 % and carbonates from 10.94 to 37.29 %, Table 1. The lowest *LOI 1* and the highest *LOI 2* values were determined in the sediment sample L3 from the Morinj bay at the depths of 15 and 50 m from the shore, near by the mussel farm Lipci, Table 1 and Fig. 1. L5 and L7 had the highest and almost the same *LOI 1* values (11.51 and 12.93 %, respectively). The sample at L5 was taken close to the mariculture (22 m depth and 50 m from the coast) and at L7 from the central part of the small Kotor bay (34 m depth and 1500 m from the coast). There is a big difference between *LOI 2* values at L3–L5 (21.12–37.29 %) in Kotor bay and L8–L10 (10.94–12.34 %) in Tivat bay. Sediment samples from these locations were taken close to mussel farms, Table 1. The locations without mussel farms (L1–2, L6, L11–12) and at higher depth (22–42 m) had similar values of *LOI 1* and *LOI 2*, from 6.73 to 7.84 % and from 16.06 to 17.88 %, respectively, Table 1. The organic matter content of the sediment is a result of contribution of terrigenous materials and decomposition of marine

organisms. Phytoplankton and zooplankton are the most abundant source of the organic material in the sediments. The amount of organic matter and carbonate in the sediment is largely dependent on water depth, production from marine organic sources, and sediment type (Farah et al. 1990). In addition, high carbonate values at shallow depths may indicate increased productivity, if there is no carbonate present in the source lithology (Hasan and ul Islam 2010). Distribution patterns of *LOI 1* and *LOI 2* in surface sediments in the Boka Kotorska bay are shown in Fig. 2.

Major elements

Descriptive statistics of ten major elements measured as oxides and 31 elements (minor, trace, and rare earth elements) in the sediments of the Boka Kotorska bay are displayed in Table 3. Data are shown in wt% for oxides and in milligrams per kilogram for elements, dry weight. The oxide average content is found in the bay surface sediment in the following order, Table 3:

$$SiO_2 > CaO > Fe_2O_3 > Al_2O_3 > K_2O > MgO$$
$$> TiO_2 > Na_2O > MnO > P_2O_5.$$
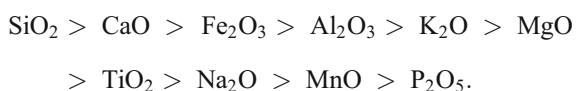
It is known that the concentration of the major elements in marine sediments varies depending on the sediment type and on the geohydrographic deposition environment (Popadić et al. 2013). Marine sediments are composed of essentially two fractions, a land-derived lithogenous fraction and a seawater-derived fraction, a biogenous fraction. Aluminum serves as a proxy for the lithogenous fraction, and this fraction hosted predominantly the alkali metals and heavy-mineral hosted trace elements, as W, Zr, Rb, Ga, Th, U (Cai et al. 2008; Piper and Bau 2013), as it is in the bay sediment (Supplementary Table A), except location L3. At this location, content of Al_2O_3 was the lowest, 2.7 %, but on the remaining, it was from 8.5 to 11.4 %. In the sediment deposits of the bay, large ranges were found for the SiO_2 and CaO concentrations, Table 3. The highest concentration of SiO_2 was in Tivat bay (41.3–49.4 %), and the lowest in L3 (9.1 %) in Morinj bay, but for the CaO content, it was opposite: the CaO concentration was the lowest in Tivat bay (8.3–8.9 %) and the highest in L3 (44.1 %). In the other locations, SiO_2 ranged from 29 to 39 % (Supplementary Table A). The value of SiO_2 indicates that it is a function of both inorganic and biogenic silica. These results indicate that SiO_2 and CaO are the main sediment components in the area and that the origins of sediments deposited in these sampling sites vary significantly.
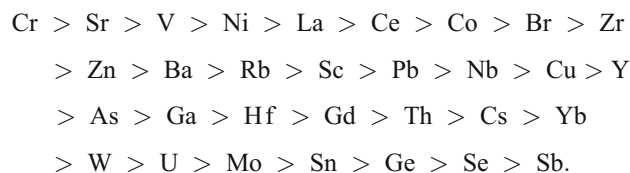
In the remaining samples from Boka Kotorska bay, the mean concentrations of K_2O and Al_2O_3 ranged from 2.3 to 3.6 and from 8.5 to 11.4 %, respectively, Table 3, and they were two times higher than those in the surface sediment from

the central and southern Adriatic Sea (Dolenec et al. 1998). The concentration of Fe_2O_3 slightly varied among the samples ranging from 11.0 to 14.1 %, with the exception of L3 where only 3.8 % of Fe_2O_3 was measured (Supplementary Table A). Generally, concentrations of Fe_2O_3 were higher in the bay than values of the central and southern Adriatic Sea and in the Albanian coastal area (Dolenec et al. 1998; Rivaro et al. 2004). Distributions of MgO, TiO_2, MnO, and P_2O_5 have a more homogeneous trend in the Bay (Supplementary Table A). The content of Mg was lower in the bay related to the Mg content in the central part of the southern Adriatic Sea, but TiO_2 and MnO were higher in the bay (Dolenec et al. 1998; Rivaro et al. 2004).

The content of Na_2O obtained in the present study ranged from 0 to 0.56 %, but in L2, Na_2O was not detected, and in L6 and L1 was close to zero (0.01–0.04 %), Supplementary Table A. On the other locations, Na_2O concentrations were detected in a slightly higher percentage with the highest Na_2O content, 0.56 %, in the central part of the Herceg Novi bay (L12), i.e., in the entrance of the bay with regard to the open Adriatic Sea. The Na_2O concentration obtained in the surface sediment in the Croatian coast was higher and ranged from 0.81 to 1.80 % (Žvab Rožič et al. 2012). The concentration of P_2O_5 was very low related to other investigated oxides, 0.1 %, or not detected at all (L1, L4, and L8–9), Supplementary Table A. Measured P_2O_5 values were similar as in the literature (Dolenec et al. 1998; Popadić et al. 2013). Distribution patterns of oxide contents in surface sediments in the Boka Kotorska bay are shown in Fig. 3.

Minor and trace elements

In a surface sediment, carbonate and organic matter contents are also important controlling factors on the abundance of trace metals (Alagarsamy and Zhang 2010; Popadić et al. 2013). The average content of the investigated elements obtained in the surface sediment in the Boka Kotorska bay were found in the following order, Table 3:

$$Cr > Sr > V > Ni > La > Ce > Co > Br > Zr$$
$$> Zn > Ba > Rb > Sc > Pb > Nb > Cu > Y$$
$$> As > Ga > Hf > Gd > Th > Cs > Yb$$
$$> W > U > Mo > Sn > Ge > Se > Sb.$$

Antimony concentrations were registered only at L1 and L5, while Se was not detected at L4, L8, and L9, and Sn only was not registered at the L2 (Supplementary Table A). The lower concentrations of these elements cannot be detected by the analytical method used in this study. The Sr concentration was the highest in L3 (481.8 mg/kg) and the lowest in L8–10 (58.8–77.5 mg/kg), but generally, the mean value of Sr was lower than in the surface sediment of Adriatic Sea (Dolenec
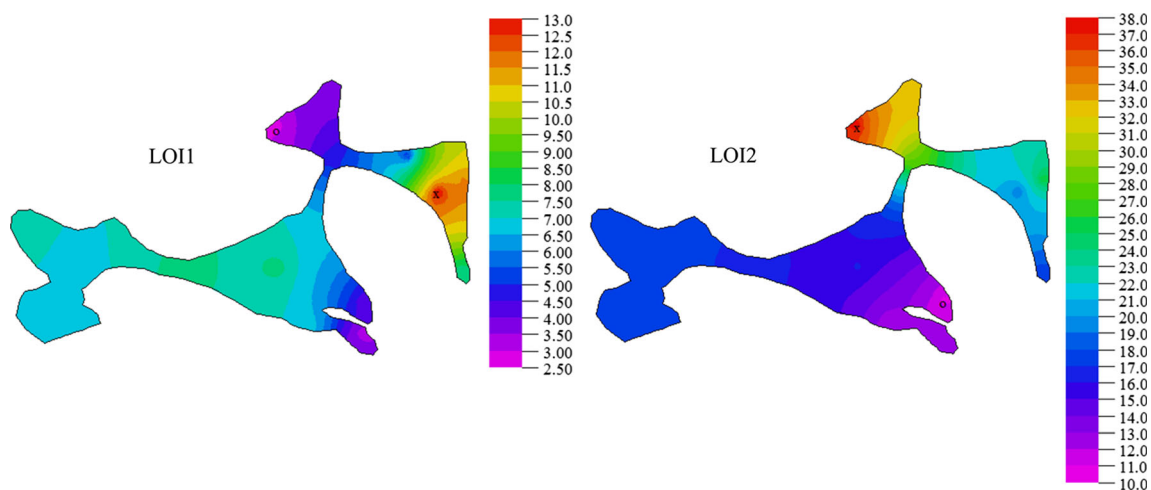
**Fig. 2** Distribution of *LOI 1* and *LOI 2* (in %) in the surface sediment of the Boka Kotorska bay

et al. 1998; Tanaskovski et al. 2014). The highest rare earth element (REE) concentrations in the karstic area of Montenegro were recorded in the form of bastnaesite carbonate minerals found mainly enriched in light REEs, e.g., Ce, La, and Y (Maksimović 1993). Concentrations of Ge, Mo, U, Yb, W, Gd, Th, Sc, Y, Nb, and La are almost homogenously distributed in the surface sediment of the bay, excepting the surface sediment examined in L3, which had the highest

concentrations of Sr, Sc, La, Nb, Hf, and Yb, and the lowest concentrations of U and Th (Supplementary Table A). Also, in L3, the content of Mo, Sb, and W was not detected, but measured Cr, Co, Ni, Cu, Zn, Ba, Br, Rb, Zr, V, and Ce were with the lowest content related to the remaining locations (Supplementary Table A). Distribution patterns of the examined element's contents in the Boka Kotorska bay are shown in Fig. 4.

Table 3 Descriptive statistics of examined oxides and element concentrations (mg/kg) in the surface sediment samples

	LOI 1	LOI 2	Na$_2$O	K$_2$O	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	MnO	TiO$_2$
Ave	7.1	18.6	0.3	2.9	36.6	9.5	12.1	15.0	2.3	0.2	1.0
SD	3.0	7.1	0.2	0.8	10.3	2.3	2.8	9.8	0.5	0.1	0.2
Min	2.8	10.9	0.0	0.6	9.1	2.7	3.8	8.3	1.0	0.1	0.3
Max	12.9	37.3	0.6	3.6	49.4	11.4	14.1	44.1	2.8	0.3	1.2
Var	9.0	50.5	0.0	0.6	105.3	5.4	7.8	96.7	0.2	0.0	0.1
	P$_2$O$_5$	Cr	Co	Ni	Cu	Zn	As	Se	Pb	Sn	Sb
Ave	0.1	146.9	69.1	84.3	15.6	64.6	13.4	0.8	25.5	1.5	0.2
SD	0.0	91.0	11.9	25.4	7.1	23.4	2.4	0.8	9.8	0.8	0.4
Min	0.0	14.7	41.2	21.7	1.2	27.0	10.5	0.0	14.2	0.1	0.0
Max	0.1	378.0	87.1	113.5	26.4	106.6	18.6	2.5	51.8	2.8	1.2
Var	0.0	8278.7	140.8	645.8	49.8	547.4	5.9	0.7	96.7	0.6	0.1
	Ba	Sr	Br	Rb	Zr	Mo	Cs	Y	V	Ga	La
Ave	55.5	139.1	66.0	55.4	65.6	1.5	3.0	15.2	109.1	8.7	81.6
SD	18.1	112.3	26.7	17.8	15.3	0.7	1.7	3.3	30.4	2.9	11.1
Min	28.4	58.8	28.9	18.4	37.2	0.0	0.8	9.7	24.3	4.3	77.0
Max	90.2	481.8	120.7	84.2	92.3	2.5	5.6	20.4	140.7	12.8	116.8
Var	329.0	12613.6	711.2	315.8	234.6	0.4	3.1	10.8	926.7	8.4	124.3
	U	Th	Nb	W	Sc	Ge	Gd	Yb	Hf	Ce	
Ave	1.7	6.2	22.3	1.8	47.1	0.9	6.6	2.9	6.8	74.3	
SD	0.6	2.1	1.0	1.3	114.2	0.1	0.1	0.2	0.9	23.4	
Min	0.1	0.9	21.2	0.0	11.1	0.8	6.5	2.8	5.6	33.5	
Max	2.5	8.3	25.0	4.3	409.5	1.1	6.7	3.5	9.3	134.8	
Var	0.4	4.3	1.0	1.7	13,031	0.0	0.0	0.0	0.9	546.5	

Ave average, *SD* standard deviation, *Min* minimum, *Max* maximum, *Var* variance
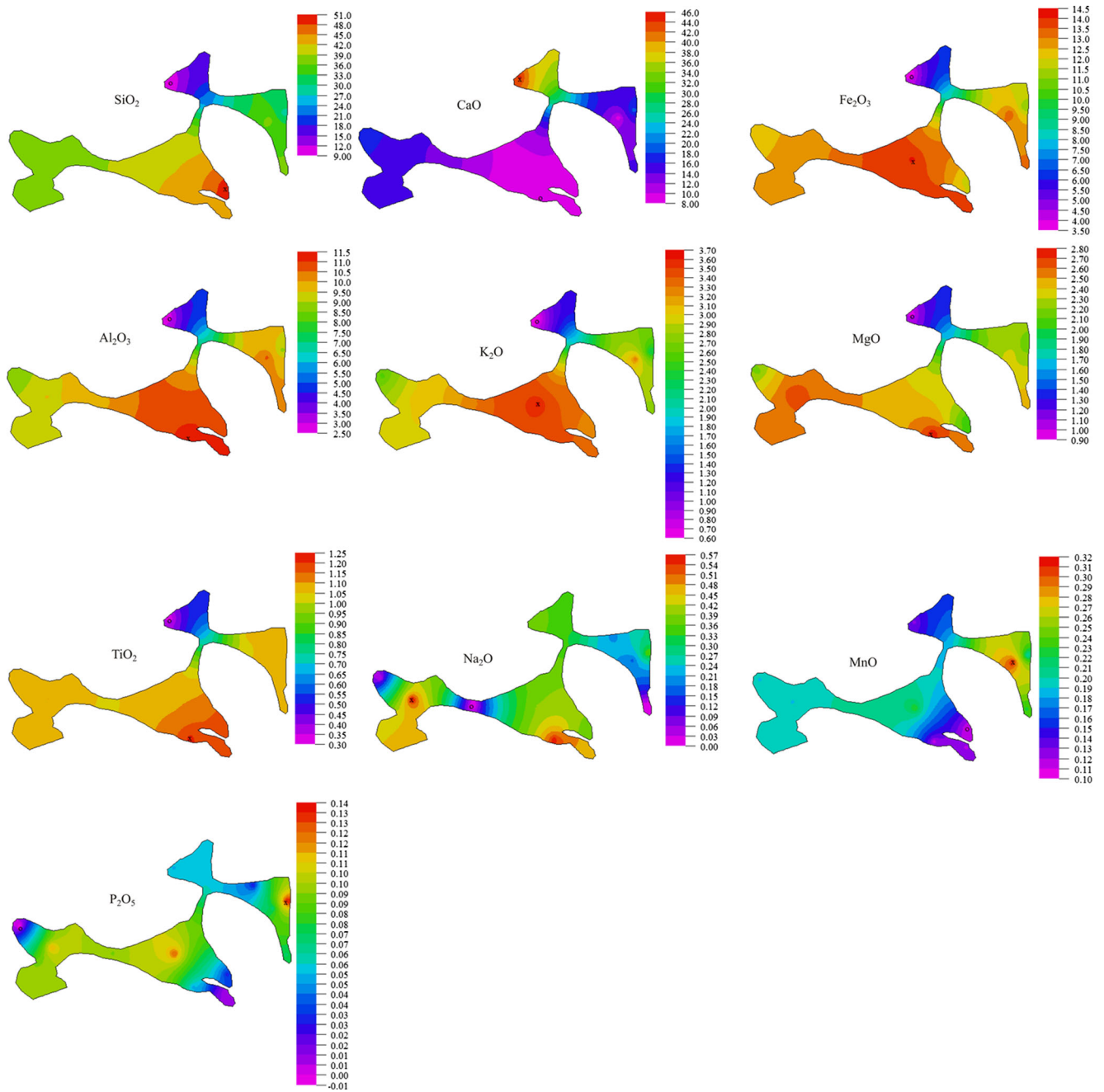
Fig. 3 Distribution of oxides (in %) in the surface sediment of Boka Kotorska bay

Discussion

The surface sediment in the Montenegrin coast is mainly sandy, except in the Boka Kotorska bay, where the proportion of a fine fraction is greater (Stanković et al. 2015). As the bay is almost a closed system, there is no possibility of a large movement or removal of sediment in relation to the open sea area (Bellafiore et al. 2011). Obtained experimental results of oxides and elements in the surface sediment of the bay are discussed in relation to the organic matter and carbonate content, as well as the depth.

The majority of investigated oxides (K_2O, SiO_2, Al_2O_3, Fe_2O_3, MgO, and TiO_2) were positively correlated with each other and with the majority of heavy metals (Cu, Ni, Co, V, Mo, Rb, Zr, U, and Th) in the investigated sediments, Supplementary Table B. The positive relationship between heavy metals and oxides indicates their common sources and association with clayey sediments (Popadić et al. 2013; Stanković et al. 2015). Furthermore, the significant correlation between Al_2O_3 and SiO_2, and with Ni, Co, Cu, V, Mo, Rb, Zr, U, and Th confirms that those elements are associated with aluminosilicate minerals in the sediment (Popadić et al. 2013).

Fig. 4 Distribution of elements (in mg/kg dw) in the surface sediment of Boka Kotorska bay
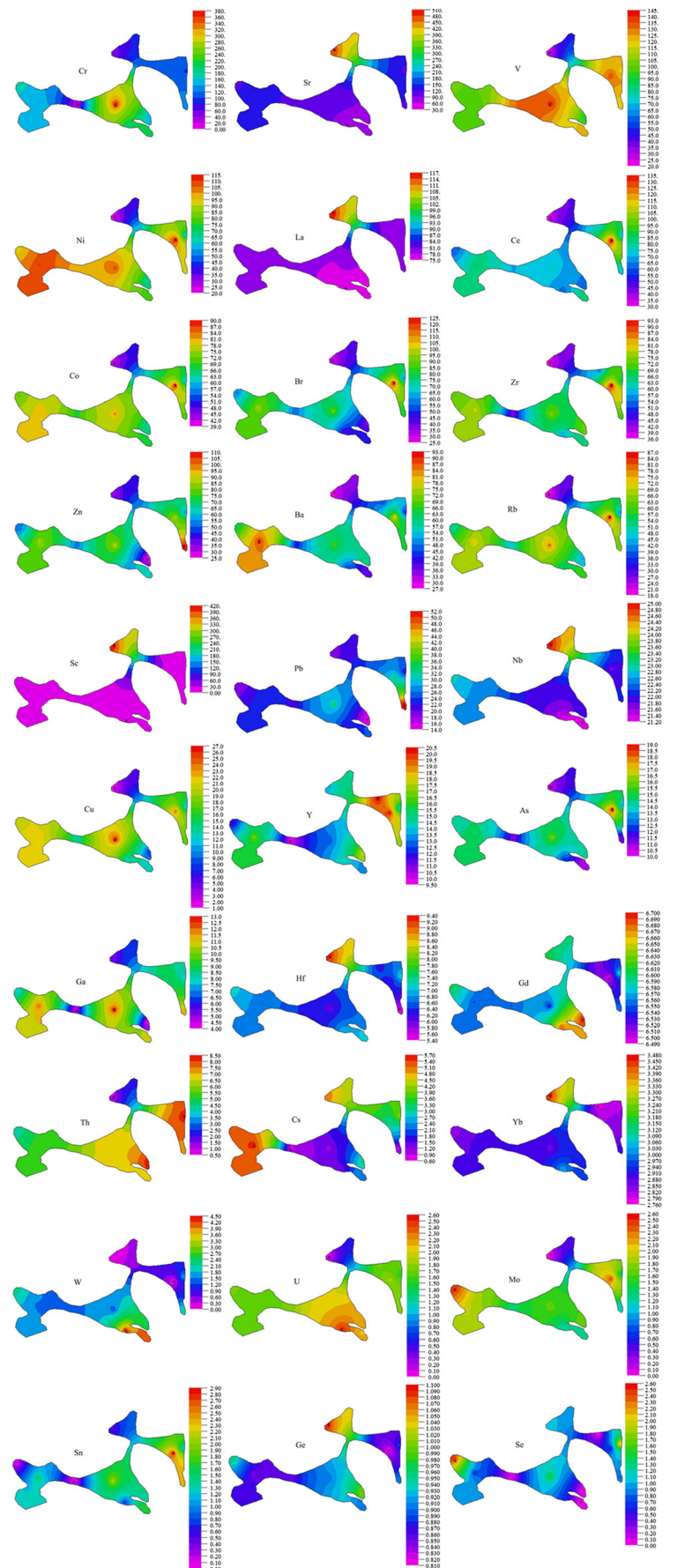
But, since CaO was negatively correlated with the remaining oxides, the lowest was with MgO ($r = -0.88$) and the highest with Al_2O_3 ($r = -0.99$), including negative correlations with Co, Ni, Cu, Rb, Zr, Mo, V, W, U, and Th content, it can be concluded that CaO is mainly derived from marine biogenic carbonate in the surface sediment of the bay (Dolenec et al. 1998; Goudeau et al. 2013). Also, as Sr was negatively correlated with Mo, V, U, Th, and W (Supplementary Table B), confirming the biogenic origin of carbonate deposits in the bay (Rubio et al. 2000). That was also supported by the negative correlation observed between SiO_2 and CaO contents ($r = -0.95$) statistically significant at $p < 0.05$ level, 95 % confidence limit (Supplementary Table B).

The lowest *LOI 1* and the highest *LOI 2* values (Fig. 2) were determined in the sediment sample L3 from Morinj bay at the depths of 15 and 50 m from the shore, Table 1, near by the mussel farm Lipci, Fig. 1. The lowest *LOI 1* value at this location implied no appreciable input from anthropogenic sources since this bay is characterized with a small residential population, clean underground water from bottom springs, and with the karstic rivers which are not impacted by man (Campanelli et al. 2009), and generally, this bay exchanges little water with the sea (Bellafiore et al. 2011). The low *LOI 1* observed in this location can be attributed to the deposition of organic-poor siliciclastic terrigenous materials (Supplementary Table A), such as the rapid degradation of the newly formed, easily degradable organic matter by oxic waters could occur (Basaham 2008). In addition, this lowest value can be explained by the current located within Morinj bay which carries away the fine sediment since the seabed of the northern and western part of the Bay is characterized by natural substrata with high slopes (RAC/SPA—UNEP/MAP 2013). The highest carbonates and CaO are probably due to biogenic precipitation of aquatic organisms and due to the calcium-rich water where $CaCO_3$ is precipitated with increase of pH during photosynthesis (Hasan and ul Islam 2010). The relatively high carbonates are due to the presence of aquatic plants, phytoplankton, and corals in the area (Mohamed 2005; RAC/SPA—UNEP/MAP 2013) and partly from natural carbonates (Magaš 2002). A similar explanation for high carbonates could be used in L4 (RAC/SPA—UNEP/MAP 2013) and in L5 where *LOI 1* and CaO are also high, Supplementary Table A. Thus, the carbonate precipitation increased from the north to the west side of the bay, Fig. 2.

Very high correlations between Sr vs. *LOI 2* and Sr vs. CaO (0.91 and 0.95, respectively) obtained suggest that the sources of Sr at L3 are of a biogenic origin in relation to remaining sites. High Sr concentrations are common in marine biogenic carbonates (Basaham 2008). At this location, there is not any water mixing with the rest of the bay (Bellafiore et al. 2011), obliviously marine organisms' remains decomposed over time. Also, the highest Sc content in L3 (409.5 mg/kg dw) and Sc-positive correlations with *LOI 1*, CaO, La, Sr, and Nb

(Supplementary Table B) are indicating on the existence of karst with soil on carbonate rocks (Fedele et al. 2008) around Morinj bay. As Sr very strongly positively correlated with CaO, and both negatively correlated with SiO_2 and Al_2O_3 (Supplementary Table B), it suggests that Sr and CaO come from sources independent of aluminum silicate minerals (Rubio et al. 2000) and indicates on the biogenous carbonated nature of the L3 surface sediment since L3 has the highest content of *LOI 2* and CaO and the lowest SiO_2 and Al_2O_3, Supplementary Table A. Carbonate sediments typically contain <2 % K_2O and up to 2.5 % Al_2O_3 (De Vos and Tarvainen 2006) and L3 contained 0.6 % K_2O and 2.7 % Al_2O_3. Also, the highest *LOI 2* is associated with the lowest concentrations of trace elements in L3 (Alagarsamy and Zhang 2010; Popadić et al. 2013), but the higher *LOI 1* is directly related to a higher trace metal content, as it was on L7 (Ujević et al. 1998). It is clearly evident in Supplementary Table A. Also, the carbonate-dominant sediment type on L3 is characterized, beside the highest *LOI 2* (37.3 %), Sr (481.8 mg/kg), and CaO (44.1 %), the lowest content of aluminum silicate elements: Si, Al, Fe, Mn, Ni, Cr, V, and Ba, Supplementary Table A.

Very high positive correlations of La with *LOI 1* and Sr confirm its origin from marine organic sources, but La was also positively correlated with CaO, Nb, Sc, Ge, Yb, and Hf content (Supplementary Table B), confirming its karstic origin from bastnaesite minerals in L3. In the same time, the correlations of REEs with Al_2O_3 and SiO_2 were negative (Supplementary Table B). This attests to the fact that carbonate sediments did act as important concentrating agents for REEs (Maksimović 1993). The Ce content was the lowest and followed with the lowest Zr in L3, but the highest in L7 and followed with the highest Zr (Supplementary Table A). Further, the obtained positive correlations of Ce with *LOI 2*, MnO, Fe_2O_3, and Ba and negative with *LOI 1*, CaO and with the remaining measured REEs in this study is the result of MnO, Fe_2O_3, and barite effectiveness in adsorbing Ce more readily than carbonates (Guichard et al. 1979; Pattan et al. 2005). This positive Ce anomaly is confirmed in L1–2 and L4–12, due to the incorporation of Ce^{4+} into zircon (Thomas et al. 2003), and it is also confirmed by the high Ce and Zr correlations (Supplementary Table B). This also confirms the biogenous carbonated sediment in L3 since the biogenous fraction exhibits a negative Ce anomaly (Piper and Bau 2013).

Obviously, the obtained results of oxides and elements were depended on the organic matter and carbonates, as well as on the origins of sediments deposited in these sampling sites. Concentrations of CaO, Sr, Sc, La, Nb, Hf, and Yb have shown a significant positive correlation with *LOI 1* (Supplementary Table B), and all together were negatively correlated with the remaining oxides and elements, suggesting the presence of a biogeonus carbonate, and natural carbonate derived from the karst enriched in rare earth elements around Morinj bay (Maksimović 1993; Maksimović and Pantó 1991).

The lowest and the highest contents of organic matter were observed in L3 and L5, respectively. Both locations are close to mariculture and at the same depth, 50 m, Table 1. A very high percentage of the organic matter in L5 (11.5 %) indicates on high primary productivity (RAC/SPA—UNEP/MAP 2013), but the carbonate at this location (25.35 %) was lower than that in L3 (Table 1, Fig. 2). L5 is also characterized by a lower concentration of Sr (110.3 mg/kg) and much higher concentrations of SiO_2, Al_2O_3, and Fe_2O_3 related to L3 (Figs. 2 and 3), indicating on more terrestrial input of organic matter in L5, and therefore, the remineralization of organic matter is slower and it is a characteristic for the muddy site (Briggs 2011). If it is accepted that Al and Fe are principally of terrestrial origin, and the Sr content belongs to a marine carbonate (Basaham 2008), then L5 reflects the mixture of marine and terrestrial organic matter present.

The percentage of organic matter and carbonates in locations without mussel farms showed similar values with depth, L1–2, L6–7, and L11–12, Fig. 2, obviously indicating that organic preservation increases with decreasing dissolved oxygen (Farah et al. 1990). At L7 (34 m depth and 1500 m from the coast), LOI 1 was the highest (12.93 %) and originates from marine organisms' remains and terrestrial organic matter which are accumulated over time. The share of terrestrial organic matter in L7 can be confirmed by a high presence of Al_2O_3 and Fe_2O_3 (Supplementary Table A). Also L7 is restricted with less water exchange (Bellafiore et al. 2011), and this deep area is anaerobic leading to higher organic matter (Farah et al. 1990), while L1–2 and L11–12, due to their proximity to the open sea with more water exchange (Bellafiore et al. 2011), are consequently with more organic matter oxidized. This is leading to lower organic matter in these sediments. The distribution of LOI 1 was generally characterized by the highest value in the deepest part of the Boka Kotorska bay, Fig. 2.

The lowest LOI 1, LOI 2, Sr, and CaO in L8–10 (Figs. 2, 3, and 4) can be explained by shallow depth (6–7 m) and different accumulated parent materials. L8–10 are located near the shore in the shallow part of small Tivat bay with weak currents and weak water circulations, but higher than L3–L7 (Bellafiore et al. 2011). Carbonates at shallow water (from 6 to 7 m of the depth) may indicate on increased productivity as there is no high carbonate present in the L8–10 lithology sources (8.3–8.9 % of CaO), but increased sand percentage distribution (44.8–49.4 %) in L8–10, Fig. 3, indicates on higher rates of organic matter remineralization at the sandy site, observed by Briggs (2011), where dominate more labile, marine-dominated organic matter.

Nickel, Co, and Cu contents were not only negatively correlated with Sr, La, Nb, Sc, Ge, Yb, and Hf but also positively correlated to Zn, As, Ba, Br, Rb, Zr, Mo, V, U, and Ce content (Supplementary Table B). Copper, Zn, As, and Pb are the highest heavy metal pollutants in the eastern Adriatic Sea (Obhodaš and Valković 2010). Since Ni, Co, and Cu were significantly correlated with Zn and As on one side and with Ba, Rb, Zr, Mo, V, U, and Ce on the other side (Supplementary Table B), it confirms that these elements are with the dual sources, as an anthropogenic (Jović et al. 2011; Zhuang and Gao 2014) and as a land-derived heavy mineral fraction (Cai et al. 2008; Piper and Bau 2013; Rubio et al. 2000). The main pollution sources of these elements in sediments are traffic, agriculture, and industrial sources. However, the sources of Ni, Co, and Cu in surface sediment in the Bay are mainly influenced by parent materials (Maksimović and Pantó 1991), as well as from anthropogenic activities (Jović et al. 2011; Zhuang and Gao 2014).

The sandy surface layers are relatively poor and the lower layers are relatively rich in carbonates, but the percentage of organic matter showed a higher value with depth, except L5, possibly indicating that organic preservation increases with decreasing dissolved oxygen. On the basis of Fig. 2, the distribution of the LOI 1 content was generally characterized by the highest values in the deeper part of the Boka Kotorska bay. The small Tivat bay is wider and shallower, with a greater displacement of water in the form of waves and current in relation to the Kotor and Morinj bays (Bellafiore et al. 2011). As terrestrial inputs in the Boka Kotorska bay are not so rich in organic matters (Campanelli et al. 2009), it can be concluded that LOI 1 varied between the stations due to different conditions of the bay geohydrology, production from marine organic sources, and different anthropogenic impacts (Jović et al. 2011; Stanković et al. 2015; Tanaskovski et al. 2014).

Very strong positive correlations of SiO_2 with Al_2O_3, K_2O, Fe_2O_3, and MgO (Supplementary Table B) and very strong negative correlations of CaO not only with SiO_2, Al_2O_3, and K_2O but also with other oxides coming from aluminous silicate minerals (Fe_2O_3, MgO, TiO_2) and with elements (Rb, Zr, Mo, V, U, Th, Co, Ni, and Cu) associated with heavy minerals (Piper and Bau 2013), statistically significant at $p < 0.05$ level (Supplementary Table B), point to mainly clayey provenance of the rest of the investigated sediments in the bay (Popadić et al. 2013; Stanković et al. 2015). Also, the significant correlations between Rb, V, U, Th, and SiO_2 (Supplementary Table B) attributed to higher alumosilicate minerals in the sediments and the sedimentary rocks around the bay (Lovrenčić Mikelic et al. 2013; Rubio et al. 2000).

Associations of oxides and elements in the surface sediment locations

Regarding the behavior of the investigated different sediment components, the PCA results (Fig. 5) identified three major groups which are constituents of the Boka sediments: (a) SiO_2, Al_2O_3, Fe_2O_3, K_2O, MgO, TiO_2, Cr, V, Th, U, and W clustered together indicating a similar lithogenic origin and pattern

Fig. 5 Biplot of the correlated investigated surface sediment components and locations
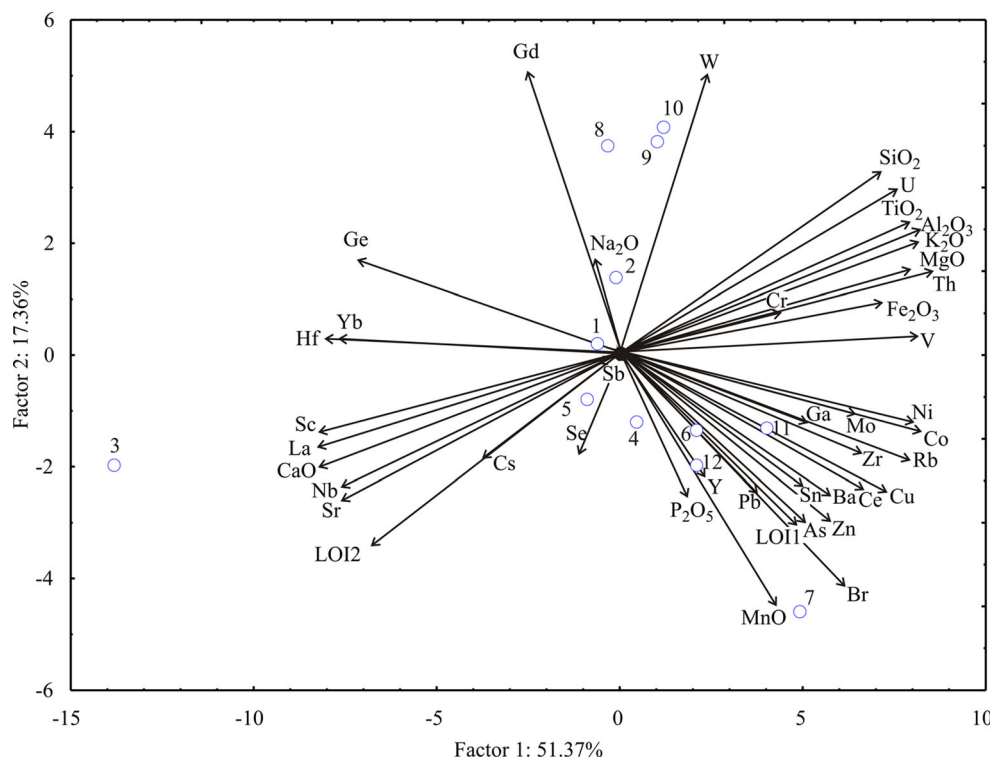
of distribution and their position on the inverse; (b) the organic matter vector which is increasing with the highest concentrations of CaO including Sr, La, Nb, Sc, Ge, Yb, and Hf contents suggesting that high CaO concentrations are implying lower concentrations of the remaining elements in the sediment at the L3; and (c) the rest of the elements showed an increasing concentration with higher concentrations of a carbonate matter and/or MnO, including Zn, Sn, As, and Pb from an anthropogenic source (L6, L7, and L12) and the heavy-mineral-hosted elements, Rb and Zr, as a major host of Ce, Ga, Ba, Ni, Co, and Cu in L11.

On the basis of Fig. 5, all sediment samples had a terrigenous group of elements from aluminosilicates and heavy minerals. The terrigenous fraction of sediments derived from the rocks weathering by rain and river erosion and biogenous part of sediments originate from biological processes such as the secretion (growth) of skeletal materials by marine organisms. The second group composed of CaO, Sr, and *LOI 1* has special characteristics and suggests that L3 sediments are composed from carbonate sources independently of aluminosilicates and heavy minerals, suggesting that their most sources are carbonate minerals of a marine origin since biogenic carbonates

Fig. 6 Dendrogram obtained by cluster analysis of elemental sediments concentrations
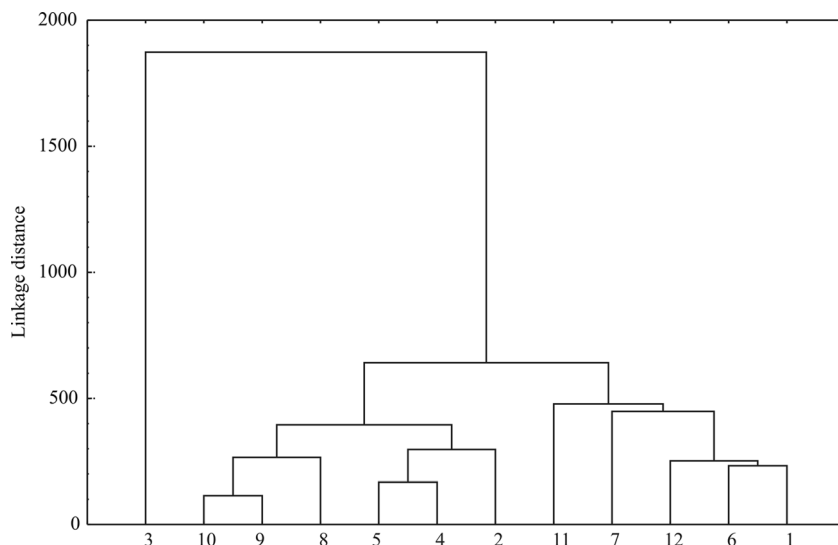
(especially carbonate shells) constitute the most important sediment fraction of such elements (Tanaskovski et al. 2014). MnO is prevalent in fine-grained sediments with higher elemental concentrations (especially of Pb, Sn, Zn, As) from anthropogenic sources in L6 (IBM Kotor), L7 (Kotor central), and L12 (Herceg Novi central), while the L11 (Tivat bay central) was with the highest elemental concentrations of aluminosilicates and heavy minerals, Fig. 5. According to Fig. 5 and based on obtained correlations in Supplementary Table B, Mn oxide and Br, Zn, Pb, Ni, Co, and Cu carbonates are the main controlling distribution factors in L6, L7, and L12, but Fe oxide is the main controlling factor of V, Co, Ni, Rb, Mo, Cu, and Ce distribution in the L11.

The tested samples of surface sediments are shown as separate dendrograms on Fig. 6. CA shows the existence of three separate groups of stations. A subsequent discriminate analysis showed that these three groups of stations are statistically different in their geochemical composition. The cluster group on the right side includes the L1, L6, L7, L11, and L12, sites distant from the coast (800–2400 m) and at the depth of 22–41 m, except L6 (the distance from the coast was 50 m), generally with higher elemental concentrations, while the cluster group on the left side includes the L2, L4, L5, L8, L9, and L10, locations with lower elemental concentrations than the group on the right side. Both cluster groups are connected with completely different third cluster, which belongs to L3.

The concentrations of investigated oxides and elements are changing with the geohydrology and the depth (L11–12) and considerably more to carbonate contents (L3). It is well-established that carbonate and also organic matter contents are important controlling factors on the abundance of trace metals. Fine-grained sediments tend to have relatively high metal contents and bind a variety of trace elements due in part to an organic matter that as a prevalent in fine-grained sediments (Rubio et al. 2000; Stanković et al. 2015). On the other hand, high carbonate contents are associated with low concentrations of trace metals. These relationships are clearly evident in L7 and L3, the central part of Kotor bay and Lipci in Morinj bay, respectively. The highest carbonate content is associated with lower concentrations to the majority of the analyzed elements, except Sr, Sc, La, Nb, Hf, and Yb, at this location. At the remaining sites are primarily aluminosilicate minerals with a share of heavy minerals and elements from anthropogenic sources contributed in higher minor and trace element contents, than in the Morinj bay.

Finally, the spatial metal distribution and chemical composition of surface sediments in the Boka Kotorska bay is primarily determined by geohydrology of the bay and the sample depth (the central part of Tivat bay L11) than by the association of metals with MnO and an organic-rich phase which has accumulated in areas of low turbulence, i.e., the innerness parts of the bay (the central part of the small Kotor bay L7) and by the carbonate content (L3 in the Morinj bay). On the

other side, sediments close to the mariculture sites (L4 and L5 in the Kotor bay and L8–10 in the Tivat bay) with different depths and geohydrology (Bellafiore et al. 2011) had a similar content of minor and trace elements.

Conclusions

The specific Boka Kotorska bay topography and geochemistry, as well as hydrogeology of the bay bottom influence the surface sediment composition. The sediment composition is dominantly determined by lithogenous material impacted by biogenic and anthropogenic materials. Obviously, the surface sediment in Boka Kotorska bay contains relatively high organic matter and carbonates. The amount of organic matter and carbonate in the sediment is largely dependent on the water depth, production from marine organic sources, and hydrographically related deposition of the bay. Obtained results of elements in the surface sediment of the bay were dependent on the organic matter and carbonate content.

The concentrations of Sr, Sc, La, Nb, Hf, Yb, Ce, and Zr on one side, and the concentrations of all other elements on the other side, clearly indicate the type of sediment in the bay and on that basis, it can be concluded that the sediment in Morinj bay is the carbonated sediment of an organic and an inorganic origin, and at the remaining locations are aluminosilicate sediments in the bay.

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