GEOCHEMICAL CHARACTERISTICS AND DISTRIBUTION OF RARE EARTH ELEMENTS IN MAKIRINA BAY SEDIMENTS (N. DALMATIA, REPUBLIC OF CROATIA)

Darja Komar[1], Nastja Rogan Šmuc[1], Živana Lambaša Belak[2], Sanja Slavica Matešić[2], Sonja Lojen[3], Goran Kniewald[4], Petra Vrhovnik[1], Tadej Dolenec[1], Matej Dolenec[1]

[1]*Department of Geology, Faculty of Natural Sciences and Engineering,*
University of Ljubljana, Aškerčeva 12, 1000 Ljubljana, Slovenia
[2]*Department of Environment and Municipal Affairs,*
Trg Pavla Šubica I, no. 2, 22000 Šibenik, Croatia.
[3]*Department of Environmental Sciences, Jožef Stefan Institute,*
Jamova cesta 39, 1000 Ljubljana, Slovenia
[4]*Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*
komar.darja@gmail.com, darja.komar@ntf.uni-lj.si

A b s t r a c t: The research focuses on determination of geochemical characteristics and distribution of Rare earth elements (REEs) in Makirina Bay sediments. The overall REEs concentrations in Makirina Bay sediments samples detected during study ranged from 123.94 ppm to 188.74 ppm. REEs content showed a gradual increase towards the depth of sediments. The average UCC-normalized REEs pattern pointed out negative δCe values and positive δEu values, indicating reductive conditions prevailing in Makirina Bay sediments. Calculated enrichment factor values are in the range of natural variability with no addition of different anthropogenic components. According to sequential extraction procedure results, the studied fractions can be followed from highest to lowest percentage of REEs as: oxidizable > exchangeable > reducible+residual > reducible > water soluble fraction. The calculated transfer factor values generally confirmed the sequential extraction procedure results. The concentrations of all studied REEs are higher in above-ground than in below-ground biomass of seagrass *Cymodocea nodosa*.

Key words: rare earth elements (REE); Makirina Bay; sequential extraction; transfer factor;;
seagrass *Cymodocea nodosa*

INTRODUCTION

Rare earth elements (REEs) are a group of 15 elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Tu, Yb and Lu) that occur together in the periodic table. REEs are characterized by simmilar chemical and physical properties, owing principally to the same electronic configuration (Henderson, 1984; Taylor and McLennan, 1985; Tyler, 2004; Tranchida et al., 2011; Morgan et al., 2012; Jung et al., 2012).

REEs are divided in two subgroups; lanthanum to samarium are light REEs (LREEs); and europium to lutetium are heavy REEs (HREEs). Several of the REEs are not very 'rare' and occur widely dispersed in a variety of forms (Tyler, 2004). The abundance of Ce is almost the same as the more studied environmental Cu and Zn, and

some of them (Lu and Tm) are even more abundant in the earth's crust than Cd and Se (Tyler, 2004). REEs are mainly trivalent, with the exception of Ce and Eu, which occur also in tetra- and divalent oxidation states, and often show greater fractionation relative to the other REEs (Tyler, 2004; Mao et al., 2011; Tranchida et al., 2011; Mao et al., 2014).

REEs have been applied widely to trace geochemical processes and anthropogenic disturbance in natural systems (Taylor and McLennan, 1985; Morgan et al., 2012; Jung et al., 2012; Prego et al., 2012). In marine sediments, REEs have been confirmed as a reliable tool for determining depositional processes and sediment provenance, precisely because of their conservative behaviour

(Taylor and McLennan, 1985; Jung et al., 2012). REEs can also be used to evaluate the relative contribution of various positions of a study area, and as potential indicators of environmental pollution (Xu et al., 2012).

In the past few years, several geochemical studies of Makirina Bay (Republic of Croatia) sediments have been performed (Šparica et al., 1989; Vreča, 1998; Dolenec et al., 2002; Lojen et al., 2004; Vreča and Dolenec, 2005; Šparica et al., 2005; Miko et al., 2007; Miko et al., 2008). Vreča (1998) studied REE (La, Ce, Nd, Sm, Eu, Yb and Lu) distribution in Makirina Bay sediments, and found that the average concentration of the above-mentioned REEs in surficial sediment (0–5cm) is 148 ppm, they increase gradually with depth and there is a good correlation between REEs and clay minerals.

According to Makirina Bay sediments organoleptic properties these sediments are treated as peloid or healing mud and therefore could be used for various therapeutic and wellnes related purposes (Šparica et al., 1989). Precisely because of potential application of these sediments in balneotherapy the detailed assessment of their contamination status is needed.

When studying the environmental impacts of REEs present in sediments, the most important factor is to evaluate their mobility (Kabata-Pendias and Pendias, 2001). The physical and chemical behaviour of REEs in the environment strongly depends on their chemical forms or binding type (Tessier et al., 1979; Li et al., 2000; Yu et al., 2001; Yuan et al.,2004; Ebrahimpour and Mushrifah, 2008; Yan et al., 2010) and can be determined by various sequential extraction procedures (Tessier et al., 1979; Filgueiras et al., 2002; Sahuquillo et al., 2003; Dean, 2007; Rao et al., 2008).

A determination of the total REE concentration in sediments cannot provide sufficient information about REEs' mobility, bioavailability, and consequently, an assessment of the environmental risk to the marine ecosystem (Li et al.,2001; Ebrahimpour and Mushrifah, 2008; Gao et al., 2010; Zhang et al., 2012). Therefore, the following work is a detailed study of REEs present in Makirina Bay sediments. The objectives of this research are:

– to characterize the concentration and distribution of REEs in Makirina Bay sediments.

– to analyze REEs' chemical speciation by employing a sequential extraction procedure.

– to calculate the REEs' enrichment factor (EF) values.

– to define the REEs' transfer factor (TF) values from sediments to seagrass *C. nodosa.*

EXPERIMENTAL SECTION

Environmental setting and sampling methods

Makirina Bay is located in northern Dalmatia (Republic of Croatia), 18 km NW of Šibenik city. It is a small bay, approximately 1,250 m long and 300 m wide, and represents the SW prolongation of Pirovac Bay (Fig. 1). The depth of the sea rarely exceeds 0.5 m in the southern part of the bay and increases in the seaward direction to a depth of 4.5 m. The bottom of the bay is covered by 0–3 m thick sediment, overgrown mostly by seagrass (*Cymodocea nodosa*) and benthic algae (*Codium bursa*) (Šparica et al., 1989).

The bay's surroundings are cultivated (olives, gardens, vineyards) and sparsely populated. The only larger settlement near Makirina Bay is Pirovac city, with approximately 2,000 inhabitants, located on the eastern side of Pirovac Bay.

The wider area of Makirina is built mostly of early and late Cretaceous carbonate rocks and Quaternary sediments (Šparica et al., 1989). According to the lithological features and microfossil assemblages, Ivinj dolomites (Albian–Cenomanian), Makirina limestones and dolomites (Cenomanian–Turonian), Kamena rudist limestones (Early Senonian), and Ivinj Draga deluvial deposits (Quaternary) lithostratigraphic units have been discerned (Šparica et al., 2005).

Sediment core samples (○) were collected in summer 2010, from 10 different sites in the central part of the bay (Fig. 1), with hand-driven plexiglass core samplers (40cm long, 3.5cm inner diameter). They were immediately frozen until further analysis. In the laboratory, cores were first divided into 5-cm-long sections and air-dried. Before the geochemical analyses, non-representative debris (large rocks and organic debris) were removed with sieving, and samples were homogenized to a fine powder (< 63 μm) in an agate mortar.

Samples of seagrass *C. nodosa* were handpicked in the same location as sediment cores; i.e. in the central part of the bay (Fig. 1) at a depth of about 0.5 m, and transferred to polyethylene bags. In the laboratory, seagrass samples were washed with distilled water, and sediment particles were

removed carefully with a nylon brush. Seagrass individuals were dissected into two different compartments: below-ground and above-ground biomass. Afterwards, samples were dried to a constant weight and then ground and homogenized to a fine powder in an agate mill.
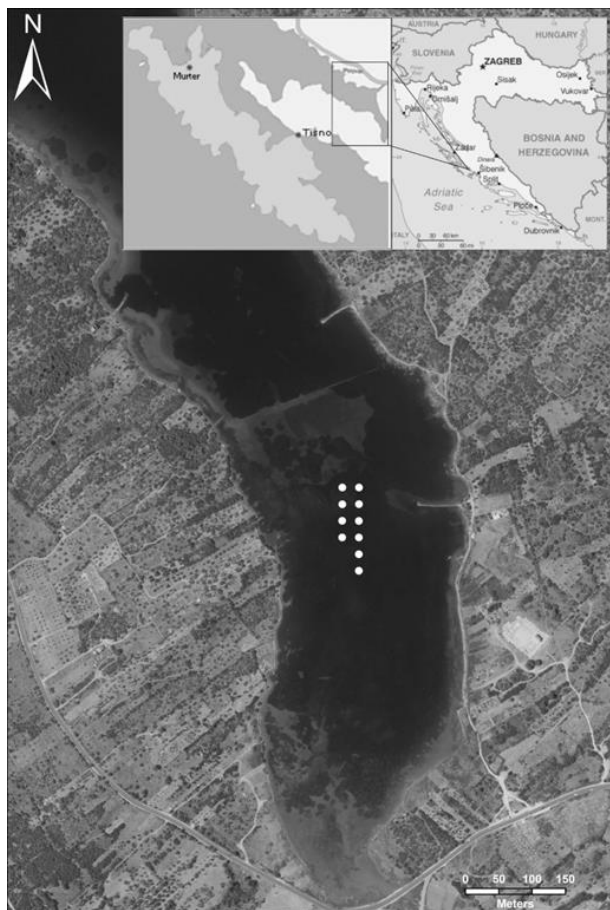

Fig. 1.

REE concentrations in sediments and seagrass

Sediments samples were analyzed for REE concentrations in a certified commercial Canadian laboratory (Acme Analytical Laboratories), by Inductively Coupled Plasma mass spectrometry (ICP-MS), following an extraction for 1 h with 2-2-2-HCl-HNO$_3$-H$_2$O at 95 °C. The analytical precision and accuracy were better than ± 5% for the investigated elements. This was assessed with in-house reference materials (STD SO-18) and by the results of the duplicate measurements of six sediment samples, as well as duplicate measurements of reference material samples.

REE concentrations in seagrass samples were determined in the certified commercial laboratory Actlabs (Activation Laboratories, Canada) by high-resolution ICP-MS and microwave digestion. Dry

ash samples were dissolved in acid (Aqua Regia solution). The quality of the analysis was assessed using standard materials, NIST 1575a and SLRS-5. Measurements of samples were also duplicated. The results indicated that the analytical precision and accuracy were within ±10% for the analyzed elements.

Main statistic parameters (mean, median, minimun, maximum and standard deviation) and Pearson R correlation analyses were performed, using the STATISTICA 10 software program.

Sequential extraction procedure

One sediment core was analyzed for the chemical partitioning (binding forms) of REEs, by employing a sequential extraction procedure devised by Acme Analytical Laboratories, Canada.

Within this procedure the sequential extraction scheme included a water-soluble fraction F1, an exchangeable and carbonate fraction F2, an organic (oxidizable) fraction F3, a reducible fraction F4 and a residual + reducible fraction F5. Reagents used per one gram of sample are:F1) - demineralized water, F2 – 1M ammonium acetate, F3 – 0.1 M sodium pyrophosphate, F4 – 0.1 M (cold) hydroxylamine hydrochloride and F5 – 0.25 M (hot) hydroxylamine hydrochloride.

After the sequential extraction procedure, the concentration of the analyzed elements in the solutions was measured by ICP-MS. A QA/QC protocol incorporated a sample duplicate to monitor the analytical precision, while a reagent blank was used to measure the background, and an aliquot of in-house reference material to monitor appropriate accuracy.

For sketching the graph, values below the detection limit were replaced with $LOD/\sqrt{2}$ (Verbovšek, 2011).

Enrichment and transfer factor calculation

In order to evaluate the contribution of REEs to Makirina Bay sediments from other than natural origins, the enrichment factors were calculated (Salomons and Forstner, 1984; Grousset et al., 1995; Ravichandran et al., 1995; Saraee Khadijeh et al., 2009). In this study, concentrations of average Upper Contintental Crust (UCC), adopted by Taylor and McLennan (1985), were used as the background values, since average UCC is an appropriate general estimate of average source rock composite (Mao et al., 2014). EF values for REEs were calculated by equation:

$$EF = (REE/Al)_{sample} / (REE/Al)_{UCC}$$

(Salomons and Forstner, 1984; Ravichandran et al., 1995; Saraee Khadijeh et al., 2009). In this study, aluminium (Al) was used as the reference element, because the concentrations of Al in weathering products and their parent material are generally comparable (Zhang and Liu, 2002). An EF value ranging between 0.5 and 2 can be considered in the range of natural variability, while an EF value greater than 2 indicates the addition of anthropo-

genic component and/or a biogenical enrichment procesess (Grousset et al., 1995).

To investigate the transfer values of REEs from sediments to seagrass *C. nodosa*, the transfer factors (TF) were calculated as follows: TF= $c_{seagrass}/c_{sediments}$ (Dean, 2007). According to Kalfaka-kou and Akrida-Demertzi (2000), TF > 1 indicates REE bioaccumulation in aquatic organisms. The higher the TF value, the more mobile and available the REE is in the surrounding ecosystem (Dean, 2007).

RESULTS AND DISCUSSION

REE concentrations in sediments

The concentrations of REEs in Makirina Bay sediments and average UCC (Taylor and McLen-nan, 1985) are presented in Table 1.

The concentrations of REEs in Makirina Bay sediment samples detected during this study ranged from 123.94 ppm to 188.74 ppm, indicating a gradual increase towards the depth of sediment cores. Ce, La and Nd were the most abundant ele-

ments in all sediment samples. Light REEs (LREEs) accounted for 90% of the total REE content in the investigated sediments samples, with the ratio of LREEs to HREEs (Heavy REEs) reaching up to 9.36. This is simmilar to the LREE/HREE ratio in average UCC (Taylor and McLennan, 1985), and in agreement with Tyler (2004), who reported that LREEs are usually more abundant in the earth's crust than HREEs.

T a b l e 1

REE concentrations in Makirina bay sediments and seagrass C. nodosa (Taylor and McLennan, 1985)

Depth, cm	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE	∑LREE	∑HREE	LREE/HREE
								mg/kg										
0–5	26.20	52.72	5.99	22.11	4.29	0.87	3.73	0.56	3.08	0.59	1.69	0.26	1.61	0.24	123.94	111.31	12.63	8.82
5–10	33.04	66.93	7.60	28.91	5.32	1.10	4.74	0.69	3.93	0.75	2.11	0.32	1.93	0.31	157.69	141.80	15.89	8.92
10–15	36.38	75.04	8.49	31.76	6.00	1.23	5.24	0.77	4.41	0.81	2.36	0.36	2.25	0.33	175.42	157.66	17.76	8.88
15–20	38.68	78.99	8.80	33.51	6.09	1.32	5.37	0.80	4.47	0.85	2.43	0.36	2.38	0.34	184.37	166.06	18.31	9.07
20–25	39.64	80.89	9.00	34.63	6.36	1.32	5.52	0.81	4.40	0.86	2.42	0.37	2.19	0.33	188.74	170.53	18.21	9.36
Mean	34.79	70.91	7.98	30.18	5.61	1.17	4.92	0.73	4.06	0.77	2.20	0.33	2.07	0.35	166.08	149.47	16.60	9
Med.	36.38	75.04	8.49	31.76	6.00	3.73	5.24	0.77	4.40	0.81	2.36	0.36	2.19	0.33	175.42	157.66	17.76	8.88
Min.	26.20	52.72	5.99	22.11	4.29	0.87	3.73	0.56	3.08	0.59	1.69	0.26	1.61	0.31	124.16	111.31	12.85	8.66
Max.	39.64	80.89	9.00	34.63	6.36	1.32	5.52	0.81	4.47	0.86	2.43	0.37	2.38	0.46	188.74	170.53	18.31	9.31
SD	5.43	11.49	1.23	5.00	0.83	0.19	0.73	0.11	0.59	0.11	0.31	0.05	0.31	0.06	26.28	23.98	2.32	10.34
Seagrass *C. nodosa*																		
Below-ground-biomass	0.86	1.8	0.17	0.71	0.15	0.03	0.1	0.02	0.08	0.015	0.05	0.005	0.04	0.005	4.04	3.70	0.34	10.88
Above-ground-biomass	1.47	3.05	0.29	1.16	0.25	0.05	0.16	0.03	0.15	0.025	0.08	0.008	0.06	0.008	6.80	6.22	0.58	10.72
UCC*	30.00	64.00	7.10	26.00	4.50	0.88	3.80	0.64	3.50	0.80	2.30	0.33	2.20	0.32	146.37	131.60	14.77	8.91

The REE distribution in marine sediments is a consequence of detrital fraction derived from continental land as a result of weathering processes and a biogenic/authigenic component removing REEs from the water column (McLennan, 1991; Tranchida et al., 2011). REE concentrations in most coastal sediments are also closely related to grain size; they are generally enriched in the clay and silt fraction, but depleted in the sand fraction (Gromet, 1984; Fleet, 1984; Yang et al., 2002; Jung et al., 2012) because of dilution by quartz and carbonate minerals (Fleet, 1984; Yang et al., 2002).

The granulometric analysis of Makirina Bay sediments showed that sediments are represented mostly by sandy silt. The major proportion of sand is in the top 5 cm of sediment cores, while mud (silt+clay) content indicates a gradual increase towards depth of sediment cores (Komar et al., in press). This confirms REE enrichment in lower, more muddy sediment layers, and the depletion of REEs in the top 5 cm of sediments, where there is a relatively high percentage of sand fraction and abundant carbonate bioclasts.

According to XRD analysis, the mineral composition of Makirina Bay sediments is characterized by high quantities of dolomite and quartz, followed by illite/muscovite, aragonite, halite, calcite, and pyrite (Komar et al., in press). Previous studies (Šparica et al., 2005) also revealed the small percentage of *heavy mineral fraction* (e.g. garnet, amphibole, pyroxene and zircone) originating from Eocene flysch, located approximately 6 km NE of Makirina (Šparica et al., 2005), which could be a source of HREEs, whereas the femic minerals preferentially concentrate on HREEs (Laveuf and Cornu, 2009).

The Pearson correlation analysis (Table 2) revealed a highly significant correlation among REEs themselves and between the REEs, Al and K. These findings confirm the aforementioned results, that REEs have simmilar input sources and are most probably associated with alumino-phyllosilicates (mainly clay minerals), indicating a large contribution of REEs from weathering backgrounds.

T a b l e 2

The Pearson correlation matrix analysis between REEs, Al and K
(marked correlations are significant at $p < 0.05$)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Al	K
La	1.00	1.00	1.00	1.00	0.99	1.00	0.99	1.00	0.97	1.00	0.99	0.99	0.95	0.96	0.96	0.95
Ce	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.98	1.00	0.99	0.99	0.95	0.96	0.97	0.96
Pr	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.99	1.00	1.00	1.00	0.95	0.97	0.98	0.97
Nd	1.00	1.00	1.00	1.00	0.99	1.00	1.00	1.00	0.98	1.00	0.99	0.99	0.94	0.96	0.96	0.95
Sm	0.99	1.00	1.00	0.99	1.00	0.99	1.00	1.00	0.98	0.99	0.99	0.99	0.94	0.96	0.97	0.96
Eu	1.00	1.00	1.00	1.00	0.99	1.00	0.99	1.00	0.98	1.00	0.99	0.99	0.96	0.97	0.97	0.97
Gd	0.99	1.00	1.00	1.00	1.00	0.99	1.00	1.00	0.99	1.00	0.99	1.00	0.95	0.98	0.98	0.97
Tb	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.99	1.00	1.00	0.99	0.96	0.97	0.97	0.97
Dy	0.97	0.98	0.99	0.98	0.98	0.98	0.99	0.99	1.00	0.99	1.00	1.00	0.97	0.99	1.00	0.99
Ho	1.00	1.00	1.00	1.00	0.99	1.00	1.00	1.00	0.99	1.00	0.99	0.99	0.95	0.98	0.97	0.96
Er	0.99	0.99	1.00	0.99	0.99	0.99	0.99	1.00	1.00	0.99	1.00	1.00	0.97	0.99	0.99	0.99
Tm	0.99	0.99	1.00	0.99	0.99	0.99	1.00	0.99	1.00	0.99	1.00	1.00	0.97	0.98	0.99	0.99
Yb	0.95	0.95	0.95	0.94	0.94	0.96	0.95	0.96	0.97	0.95	0.97	0.97	1.00	0.97	0.98	0.99
Lu	0.96	0.96	0.97	0.96	0.96	0.97	0.98	0.97	0.99	0.98	0.99	0.98	0.97	1.00	1.00	0.99
Al	0.96	0.97	0.98	0.96	0.97	0.97	0.98	0.97	1.00	0.97	0.99	0.99	0.98	1.00	1.00	1.00
K	0.95	0.96	0.97	0.95	0.96	0.97	0.97	0.97	0.99	0.96	0.99	0.99	0.99	0.99	1.00	1.00

In order to better understand the REE distribution patterns in the sediment samples (to eliminate Oddo-Harkins effect), the average UCC (Taylor and McLennan, 1985) has been used to normalize the REEs concentrations of Makirina Bay sediment samples. The average UCC-normalized patterns of Makirina Bay sediments are shown in Fig. 2.
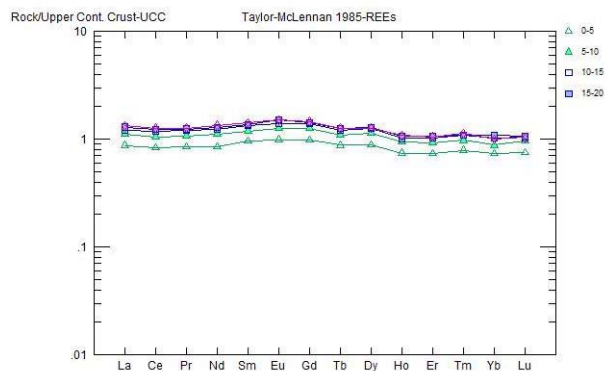

Fig. 2.

Anomalies of REEs, especially Eu and Ce, are important proxies in the normalized patterns (Mao et al., 2014). The Ce anomaly is an indicator of redox conditions (Mao et al., 2014). When insoluble Ce^{4+} is reduced to soluble Ce^{3+}, a relative depletion of Ce in sediments will occur. This leads to depletions in sediment Ce and enrichments in dissolved Ce (Hanningan et al., 2010). Therefore the sedimentary Ce anomaly is more negative within the reducing part of the sediments (Och et al., 2014). Eu anomalies may be a result of a reduction of Eu^{3+} to Eu^{2+} or simply the interaction of the solution with minerals such as feldspars (Cullers and Graf,1984). Negative δEu values reflect the oxidation of Eu^{2+} to Eu^{3+},and consequently a loss of Eu from sediments (Hanningan et al., 2010).

Eu and Ce anomalies were calculated by the formulas:

$$\delta Eu = Eu_N/(Sm_N * Gd_N)^{1/2}$$

and

$$\delta Ce = Ce_N/(La_N * Pr_N)^{1/2},$$

where Eu_N, Sm_N, Gd_N, Ce_N, La_N and Pr_N are average UCC-normalized values.

The average UCC-normalized REEs pattern of Makirina Bay sediments revealed negative δCe values (δCe = 0.96–0.98) and positive δEu values (δEu = 1.02–1.08), indicating reductive conditions in Makirina Bay sediments. Results of Eh measurement in our previous study (Komar et al., in press) showed a highly reductive sedimentary environment, even at the sediment/water interference (Eh = –430 mV), attributed to processes accompanying the decomposition of sedimentary organic matter (Lojen et al., 2004). A positive Eu anomaly in sediments was also reported by Hanningan et al. (2010), who studied Chesapeake Bay sediments, which showed similar redox (reducing) conditions as Makirina Bay sediments.

Average UCC-normalized REEs for Makirina Bay sediments are < 1 for the top 5 cm of sediments, implying REE depletion with respect to average UCC. In deeper sediment layers, average UCC-normalized REEs are > 1, meaning REE enrichment according to average UCC. These findings are most probably linked to more coarse-grained sediments in the top 5 cm of cores as had been mentioned above.

Makirina Bay sediment samples have a simmilar average UCC-normalized REE pattern, showing a simmilar provenance of sediment samples and controlling geochemical factors.

Enrichment factor (EF)

Calculated EF values for REEs in Makirina Bay sediments are presented in Table 3.

T a b l e 3

Calculated enrichment factors (EF), transfer factors (TF) and translocation factors (*TF) values

EF	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0–5 cm	1.6	1.5	1.6	1.6	1.8	1.8	1.8	1.6	1.6	1.4	1.4	1.5	1.4	1.4
5–10 cm	1.7	1.6	1.6	1.7	1.8	1.9	1.9	1.6	1.7	1.4	1.4	1.5	1.3	1.5
10–15 cm	1.6	1.6	1.6	1.7	1.8	1.9	1.9	1.6	1.7	1.4	1.4	1.5	1.4	1.4
15–20 cm	1.7	1.7	1.7	1.7	1.8	2.0	1.9	1.7	1.7	1.4	1.4	1.5	1.5	1.4
20–25 cm	1.8	1.8	1.8	1.8	2.0	2.1	2.0	1.8	1.7	1.5	1.5	1.5	1.4	1.4
TF$_{roots}$	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.02
TF$_{leaves}$	0.06	0.06	0.05	0.05	0.06	0.06	0.04	0.06	0.05	0.04	0.05	0.03	0.04	0.03
TF*	1.7	1.7	1.7	1.6	1.7	1.6	1.7	1.8	1.7	1.7	1.8	1.5	1.5	1.5

According to Grousset (1995), the calculated EF is in the range of natural variability with no addition of anthropogenic component. EF values interpreted after Birth (2003) and Chen et al. (2007), revealed minor enrichment (EF < 3). EF values show increasing trends towards depth of sediment cores, confirming the association with the granulometric composition of sediments.

REE mobility and bioavailability

In the applied sequential extraction procedure, the labile/residual fractions considered were: (1) water soluble fraction; (2) exchangeable fraction; (3) oxidizable fraction; (4) (easily) reducible fraction; and (5) reducible + residual fraction.

REEs extracted in the first fraction (1), by H_2O, are relatively labile, and thus may be potentially bioavailable to the surrounding ecosystem (Filgueiras et al., 2002).

The next phase, (2) exchangeable fraction, includes: weakly adsorbed REEs retained on the solid surface by relatively weak electrostatic interaction; REEs that can be released by ion-exchange processes; and REEs that can be coprecipitated with carbonates present in many types of sediments. Changes in the ionic composition which influence adsorption–desorption reactions or lower the pH could cause remobilization of REEs from this fraction (Filgueiras et al., 2002).

(3) The oxidizable fraction corresponds to REEs bound to organic matter and sulfides. REEs associated with oxidizable phases are assumed to remain in sediments for longer periods, but may be mobilized by decomposition processes (Filgueiras et al., 2002).

(4) The (easily) reducible fraction is linked to amorphous manganese hydroxides, which are thermodynamically unstable under anoxic circumstances.

The reducible + residual fraction (5) is linked to amorphous Fe hydroxides (moderately reducible part). The residual fraction includes naturally occurring crystalline Mn hydroxide minerals. REEs in this fraction are retained within their crystal lattices and are regarded as stable, and not susceptible to remobilization under normal environmental conditions (Filgueiras et al., 2002; Forghani et al., 2009).

REEs can be strongly controlled by pH, redox conditions, aqueous, and surface complex reactions. Their chemical fractions depend on redox or other environmental conditions as they will control or influence the adsorption, desorption, complexation, or co-precipitation of chemical fractions (Aubert et al., 2004; Xu et al., 2012).

In Makirina Bay sediments, all REEs were associated predominantly with the oxidizable fraction (3), followed by exchangeable fraction (2) (Fig. 3). The studied fraction can be ranked from highest to lowest percentage of REEs as follows: oxidizable (3) > exchangeable (2) > reducible+residual (5) > reducible (4) > water soluble fraction (1).
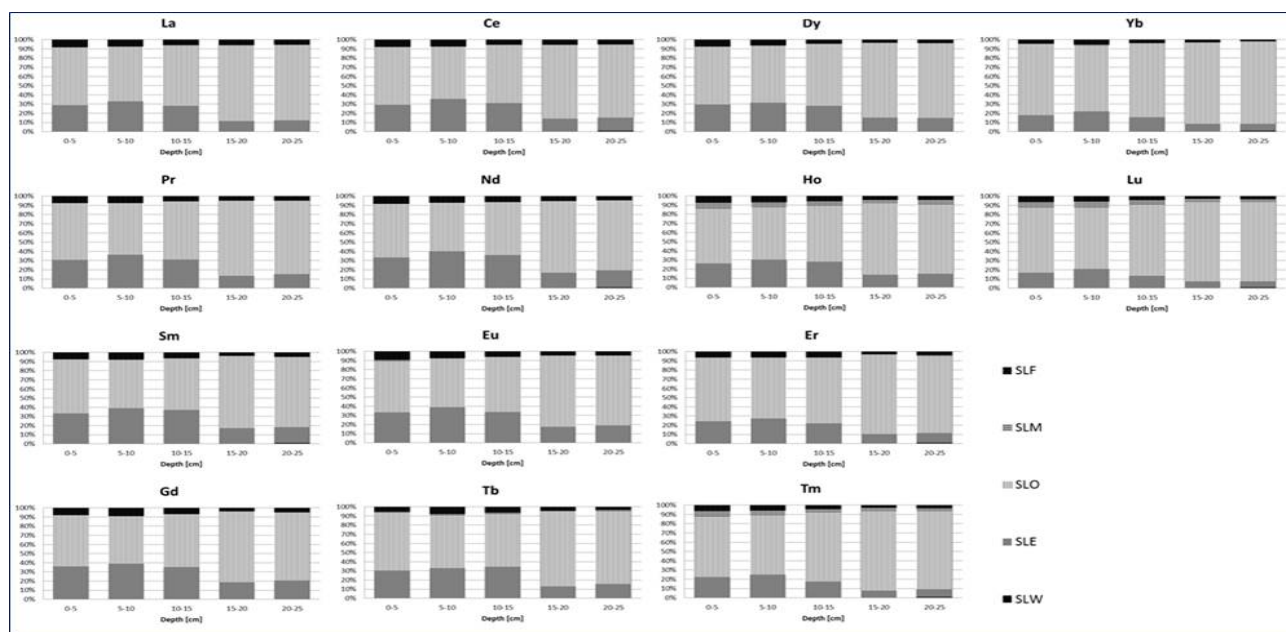
Fig. 3.

According to the sequential extraction procedure, the majority of REEs in Makirina Bay sediments are bound to the oxidizable fraction or organic matter. The C_{org} content in Makirina Bay sediments varies from 4.08 to 5.53% (Komar et al., in press). It has already been reported that REEs tend to be adsorbed by organic matter, and thus indicating their distribution in the sediments (Tyler, 2001; Nie et al., 2014). REEs can be complicated by humic substances at a near-neutral pH (Pourret et al., 2007; Morgan et al., 2012), and in Makirina Bay sediments pH ranges from 7.95 to 6.94 (Komar et al., in press).

The exchangeable fraction is unstable under natural conditions and only a change in pH could cause the remobilization of REEs from this fraction. Exchangeable REEs are most probably electrostatically adsorbed onto clay minerals, and because of their high specific surface area, clay minerals are particulary prone to adsorption (Och et al., 2014). Adsorption onto clay minerals depends on the nature of the clay mineral, the pH and the ionic strenght (Coppin et al., 2002; Laveuf and Cornu, 2009; Och et al., 2014). REEs readily sorb to clay minerals under neutral conditions, and can be released from the surface of these minerals under acidic conditions (Fleet, 1984; Morgan et al., 2012).

A very low percentage of REEs exists in the watersoluble fraction. However, a five-step sequential extraction procedure showed an important proportion of REEs in an exchangeable fraction. REEs in this fraction are not fixed in mineral lattices, and consequently have a potential impact on the environment. Cao et al.(2001) reported that the REE release increased with the decrease in pH value. The pH of Makirina Bay sediments is near-neutral, which reduces REEs' mobility. REEs bounded in oxidizable fraction are not fully mobile and bioavailable to the surrounding ecosystem, but can be released into the environment under oxidizing conditions (Filgueiras et al., 2002).

REEs concentrations in C. nodosa

REEs concentrations in below-ground (roots and rhizomes) and above-ground biomass (leaves) of *C. nodosa* seagrass are presented in Table 2.

REEs are often used in fertilizers. Therefore, their accumulation and uptake by plants have been studied more in terrestrial than in aquatic plants, and only a few investigations have been performed on the effects of REEs on the aquatic flora and fauna (Redling, 2006). In Makirina Bay it can be shown that concentrations of all studied REEs are higher in above-ground (∑REEs=6.8 ppm) rather than in below-ground (∑REEs=4.04 ppm) biomass of *C. nodosa*. This is dissimilar to the typical distribution pattern of REEs reported in plants with main accumulation in roots (Redling, 2006). Higher concentrations of REEs in the above-ground biomass of *C. nodosa* suggests their preferential uptake from the water column or can be associated with their translocation from the below-ground biomass.

Transfer factor (TF)

TF values from sediment (0–5cm) to *C. nodosa* are presented in Table 3.

Generally, low sediment-seagrass TF (0.02–0.04) values have been calculated for REEs, indicating low concentrations of REEs in seagrass, which is in agreement with Tyler (2004), who reported that transfer from soil to plant is usually low. TF_{leaves} was found to be above TF_{roots}. The TF results more or less confirmed the sequential extraction procedure results, showing the majority of REEs bounded in the oxidizable fraction.

The principal uptake routes of trace elements into seagrasses are the sediment-to-root/rhizome and water-to-leaf/epiphyte pathways (Schlacher-Hoenlinger and Schlacher, 1998; Sanz-Lázaro et al., 2012; Richir, 2012). Trace elements can be translocated after uptake among the seagrass parts (Sanz-Lázaro et al., 2012). Their uptake and translocation in seagrasses differs depending on the trace elements and plant tissue. This specificity depends on the chemical properties of each trace element (Sanz-Lázaro et al., 2012). Several studies have shown that some trace elements accumulate preferentially within the photosynthetic tissues, rather than in the below-ground plant parts of various species of seagrass (Luy et al., 2012; Sanz-Lázaro et al., 2012; Richir, 2012), and most likely, this also applies to REEs.

A plant's ability to accumulate elements from the roots to the shoots is measured using the translocation factor, which is defined as the ratio between the element concentrations accumulated in the leaves divided by the element concentrations accumulated in the roots (Yoon et al., 2006). Translocation factor values are also presented in Table 3. Translocation factors >1 indicate that the *C. nodosa* translocates REEs effectively from the roots to the shoots.

CONCLUSION

REE concentrations in Makirina Bay sediments ranged from 123.94 ppm to 188.74 ppm, indicating a gradual increase towards the depth of sediment cores. REE distribution is associated mainly with sediment mineralogical and granulometric composition. The results of EF reveal that the Makirina Bay sediments have minor enrichment and natural origins. Therefore, REE content in the sediments are not a consequence of anthropogenic activity. Results of the sequential extraction method showed the majority of REEs are bounded in an oxidizable fraction, meaning that REEs are not fully mobile and bioavailable to the surrounding ecosystem. TF values from sediment to seagrass *C. nodosa* confirmed the sequential extraction results, and were generally low, indicating a weak accumulation of REEs. REE concentrations in *C. nodosa* were higher in its above-ground biomass, linked with their effective translocation from the below-ground biomass.

REFERENCES

[1] Aubert D., Probst A., Stille P.: Distribution and origin of major and trace elements (particularly REE, U and Th) into labile and residual phases in an acid soil profile (Vosges Mountains, France). *Applied Geochemistry*, **19**, 899–916 (2004).

[2] Birth G. A.: A scheme for assessing human impacts on coastal aquatic environments using sediments. In: Woodcoffe C. D., Furness R A. (Eds): Coastal GIS 2003. University of Wollongong, Australia, 2003.

[3] Cao X., Chen Y., Wang X., Deng X.: Effects of redox potencial and pH value on the release of rare earth elements from soil. *Chemosphere*, **44**, 655–661 (2001).

[4] Chen C. W., Kao C, M., Chen C. F., Dong C. D.: Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere*, **66**, 1431–1440 (2007).

[5] Coppin F., Berger G., Bauer A., Castet S., Loubet M.: Sorption of lanthanides on smectite and kaolinite. *Chemical Geology*, **182**, 57–68 (2002).

[6] Cullers R. L., Graf J. L.: Rare earth elements in igneous rocks of the continental crust: predominantly basic and ultrabasic rocks. In: Henderson P. (ed.): *Rare Earth Element Geochemistry*, 1st edn. Elsevier, Amsterdam, pp. 237–274, 1984.

[7] Dean J. R.: *Bioavailability, bioaccessibility and mobility of environmental contaminants*. Wiley, London, pp. 292, 2007.

[8] Dolenec M., Lojen S., Ogrinc N., Lambaša Ž.: Environmentally controlled variations of $\delta^{18}O$ and $\delta^{13}C$ in mollusc shells from Makirina Bay, the Murter Sea and Pirovac Bay (Central Adriatic). *RMZ Materials and Geoenvironment*, **49 (1)**, 85–99 (2002).

[9] Ebrahimpour M., Mushrifah I.: Heavy metal concentrations in water and sediments in Tasik Chini, a freshwater lake, Malaysia. *Environmental Monitoring and Assessment*, **141**, 297–307 (2008).

[10] Filgueiras A. V., Lavilla I., Bendicho C.: Chemical sequential extraction for metal partitioning in environmental solid samples. *Journal of Environmental Monitoring*,**4**, 823-857 (2002).

[11] Fleet A. J.: Aqueous and sedimentary geochemistry of the rare earth elements. In: Henderson P. (ed.): *Rare Earth Element Geochemistry*, 1st edn. Elsevier, Amsterdam, pp 343–373, 1984.

[12] Forghani G., Moore F., Lee S., Qishlaqi A.: Geochemistry and speciation of metals in sediments of the Maharlu Saline Lake. *Environmental Earth Sciences*, **59**, 173–184 (2009).

[13] Gao X., Chen C. A., Wang G., Xue Q., Tang C., Chen S.: Environmental status of Daya Bay surface sediments inferred from a sequential extraction technique. *Estuarine, Coastal and Shelf Science*, **86**, 369–378 (2010).

[14] Grousset F. E., Quetel C. R., Thomas B., Donard O. F. X., Lambert C. E., Guillard F., Monaco A.: Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. *Marine Chemistry*, **48**, 291–310 (1995).

[15] Hannigan R., Dorval E., Jones C.: The rare earth element chemistry of estuarine surface sediments in the Chesapeake Bay. *Chemical Geology*, **272**, 20–30 (2010).

[16] Hendreson P.: General geochemical properties and abundances of the rare earth elements. In: Henderson P. (ed.): *Rare Earth Element Geochemistry*, 1st edn. Elsevier, Amsterdam, pp. 1–32 (1984).

[17] Jung H. S., Lim D., Choi J. Y., Yoo H. S., Rho K. C., Lee H. B.: Rare earth element compositions of core sediments from the shelf of the South Sea, Korea: Their controls and origins. *Continental Shelf Research*, **48**, 75–86 (2012).

[18] Kabata-Pendias A., Pendias H.: *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, pp. 432, 2001.

[19] Kalfakakou V., Akrida-Demertzi K.: Transfer factors of heavy metals in aquatic organisms of different trophic levels. http://biopolitics.gr/biowp/wp-content/uploads/2013/04/kalfakakou. pdf. Accessed 12.8.2014.

[20] Laveuf C., Cornu S.: A review on the potentiality of Rare Earth Elements to trace pedogenetic processes. *Geoderma*, **154**, 1–12 (2009).

[21] Li X., Shen Z., Wai O. W. H., Li Y.: Chemical partitioning of heavy metal contaminants in sediments of the Pearl

River Estuary. *Chemical Speciation and Bioavailability*, **12 (1)**, 17–25 (2000).

[22] Li X., Shen Z., Wai O. W. H., Li Y.: Chemical Forms of Pb, Zn and Cu in the Sediment Profiles of the Pearl River Estuary. *Marine Pollution Bulletin*, **42**, 3, 215–232 (2001).

[23] Lojen S., Ogrinc N., Dolenec T., Vokal B., Szaran J., Mihelčić G., Branica M.: Nutrient fluxes and sulfur cycling in the organic-rich sediment of Makirina Bay (Central Dalmatia, Croatia). *Science of the Total Environment*, **327**, 265–284 (2004).

[24] Luy N., Gobert S., Sartoretto S., Biondo R., Bouquegneau J. M., Richir J.: Chemical contamination along the Mediterranean French coast using *Posidonia oceanica* (L.) Delile above-ground tissues: a multiple trace element study. *Ecological Indicators*, **18**, 269–277 (2012).

[25] Mao L., Mo D., Li M., Zhou K., Yang J., Guo W.: The rare earth element compositions of sediments from the loess tableland in the Liyang Plain, southern China: implications for provenance and weathering intensity. *Environmental Earth Sciences*, **62**, 1609–1617 (2011).

[26] Mao L., Mo D., Yang J., Guo Y., Lv H.: Rare earth elements geochemistry in surface floodplain sediments from the Xiangjiang River, middle reach of Changjiang River, China. *Quaternary International*, **336**, 80–88 (2014).

[27] McLennan S. M.: Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. In: Lipin B. R., McKay G. A. (Eds): Geochemistry and Mineralogy of Rare Earth Elements. *Reviews in Mineralogy*. Mineral Soc Am, pp. 169–200, 1989.

[28] Miko S., Koch G., Mesić S., Šparica-Miko M., Šparica M., Vreča P., Dolenec T.: Influence of land use in small karst watersheds on the chemical status of peloid sediments on the eastern Adriatic coast. *Journal of Soils and Sediments*, **7** (5), 303–312, (2007).

[29] Miko S., Koch G., Mesič S., Šparica-Miko M., Šparica M., Čepelak R., Bačani A., Vreča P., Dolenec T., Bergant S.: Anthropogenic influence on trace element geochemistry of healing mud (peloid) from Makirina Cove (Croatia). *Environmental Geology*, **55**, 517–537 (2008).

[30] Morgan B., Rate A. W., Burton E. D., Smirk M. N.: Enrichment and fractionation of rare earth elements in FeS-and organic-rich estuarine sediments receiving acid sulfate soil drainage. *Chemical Geology*, **308–309**, 60–73 (2012).

[31] Nie Y., Liu X., Emslie S. D.: Distribution and sources of rare earth elements in ornithogenic sediments from the Ross Sea region, Antarctica. *Microchemical Journal*, **114**, 247–260 (2014).

[32] Och L. M., Müller B., Wichser A., Ulrich A., Vologina E. G., Strum M.: Rare earth elements in the sediments of Lake Baikal. *Chemical Geology*, **376**, 61–75 (2014).

[33] Pourret O., Davranche M., Gruau G., Dia A.: Rare earth elements complexation with humic acid. *Chemical Geology,* **243**, 128–141 (2007).

[34] Prego R., Caetano M., Bernárdez P., Brito P., Ospina-Alvarez N., Vale C.: Rare earth elements in coastal sediments of the northern Galician shelf: Influence of geological features. *Continental Shelf Research*, **35**, 75–85 (2012).

[35] Rao C. R. M., Sahuquillo A., Lopez Sanches J. F.: A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soil and related materials. *Water, Air and Soil Pollution*, **189**, 291–333 (2008).

[36] Ravichandran M., Baskaran M., Santschi P. H., Bianchi T. S.: History of Trace Metal Pollution in Sabine-Neches Estuary, Beaumont, Texas. *Environmental Science and Technology*, **29**, 1495–1503 (1995).

[37] Redling K.: *Rare earth elements in agriculture with emphasis on animal husbandry*. Dissertation, University of München, 2006.

[38] Richir J.: *Coastal pollution of the Mediterranean and extension of its biomonitoring to trace elements of emerging concern*. Dissertation, University of Liège, 2013.

[39] Sahuquillo A., Rigol A., Rauret G.: Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *Trends in Analytical Chemistry*, **22** (3), 152–159 (2003).

[40] Salomons W., Forstner U.: *Metals in the Hydrocycle*. Springer-Verlag, Berlin, 1984.

[41] Sanz-Lázaro C., Malea P., Apostolaki E. T., Kalantzi I., Marín A., Karakassis I.: The role of the seagrass *Posidonia oceanica* in the cycling of trace elements. *Biogeosciences*, **9**, 2497–2507, 2012.

[42] Saraee Khadijeh R. E., Elias S. B., Wood A. K., Reza A. M.: Rare earth elements distribution in marine sediments of Malaysia coasts. *Journal of Rare Earths*, **27** (6), 1066–1071 (2009).

[43] Schlacher-Hoenlinger M. A., Schlacher T. A.: Accumulation, contamination, and seasonal variability of trace metals in the coastal zone – patterns in a seagrass meadow from the Mediterranean. *Marine Biology*, **131**, 401–410 (1998).

[44] Šparica M., Crnko J., Belak M.: Peloid uvale Makirina (Pirovački zaljev). Elaborat **28/89**, Institut za geološka istraživanja OOUR za geologiju, Zagreb, 1989.

[45] Šparica M., Koch G., Belak M., Miko S., Šparica-Miko M., Viličić D., Dolenec T., Bergant S., Lojen S., Vreča P., Dolenec M., Ogrinc N., Ibrahimpašić H.: Recent sediments of Makirina Cove (Northern Dalmatia, Croatia): their origin viewed through a multidisciplinary approach. *Geologia Croatica*, **58** (1), 21–72 (2005).

[46] Taylor S. R., McLennan S. M.: *The Continental Crust: Its Composition and Evolution*. Blackwell, Oxford, 1985.

[47] Tessier A., Campbell P. G. C., Bisson M.: Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, **51** (7), 844–851 (1979).

[48] Tranchida G., Oliveri E., Angelone M., Bellanca A., Censi P., D'Elia M., Neri R., Placenti F., Sprovieri M., Mazzola S.: Distribution of rare earth elements in marine sediments from the Strait of Sicily (western Mediterranean Sea): Evidence of phosphogypsum waste contamination. *Marine Pollution Bulletin*, **62**, 182–191 (2011).

[49] Tyler G.: Rare earth elements in soil and plant systems – A review. *Plant and Soil*, **267**, 191–206 (2004).

[50] Verbovšek T.: A comparison of parameters below the limit of detection in geochemical analyses by substitution methods. *RMZ Materials and Geoenvironment*, **58** (4), 393–404.

[51] Vreča P.: *Isotopic and geochemical characteristics of the recent sediment of Makirina Bay (Central Adriatic)*. MSc Thesis, University of Ljubljana, 1998.

[52] Vreča P., Dolenec T.: Geochemical estimation of copper contamination in the healing mud from Makirina Bay, central Adriatic. *Environment International,* **31**, 53–61 (2005).

[53] Xu Y., Song J., Duan L., Li X., Yuan H., Li N., Zhang P., Zhang Y., Xu S., Zhang M., Wu X., Yin X.: Fraction characteristics of rare earth elements in the surface sediment of Bohai Bay, North China. *Environmental Monitoring and Assessment,* **184**, 7275–7292 (2012).

[54] Yan C., Li Q., Zhang X., Li G.: Mobility and ecological risk assessment of heavy metals in surface sediments of Xiamen Bay and its adjacent areas, China. *Environmental Earth Sciences*, **60**, 1469–1479 (2010).

[55] Yang S. Y., Jung H. S., Choi M. S., Li C. X.: The rare earth element compositions of the Changjiang (Yangtze) and Huanghe (Yellow) River sediments. *Earth and Planetary Science Letters*, **201**, 407–419 (2002).

[56] Yoon J., Cao X., Zhou Q., Ma L Q.: Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. *Science of the Total Environment*, **368**, 456–464 (2006).

[57] Yu K. C., Tsai L. J., Chen S. H., Ho S. T.: Chemical binding of heavy metals in anoxic river sediments. *Water Research*, **35** (17), 4086–4094 (2001).

[58] Yuan C., Shi J., He B., Liu J., Liang L., Jiang G.: Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environment International,***30**, 769–783 (2004).

[59] Zhang J., Liu CL.: Riverine Composition and Estuarine Geochemistry of Particulate Metals in China – Weathering Features, Anthropogenic Impact and Chemical Fluxes. *Estuarine, Coastal and Shelf Science*, **54**, 1051–1070 (2002).

[60] Zhang W., Liu X., Cheng H., Zeng EY., Hu Y.: Heavy metal pollution in sediments of a typical mariculture zone in South China. Marine Pollution Bulletin, **64**, 712–720 (2012).

Р е з и м е

ГЕОХЕМИСКИ КАРАКТЕРИСТИКИ И ДИСТРИБУЦИЈА НА ЕЛЕМЕНТИТЕ НА РЕТКИ ЗЕМЈИ ВО СЕДИМЕНТИТЕ ОД ЗАЛИВОТ МАКИРИНА (СЕВЕРНА ДАЛМАЦИЈА, РЕПУБЛИКА ХРВАТСКА)

Darja Komar[1], Nastja Rogan Šmuc[1], Živana Lambaša Belak[2], Sanja Slavica Matešić[2], Sonja Lojen[3], Goran Kniewald[4], Petra Vrhovnik[1], Tadej Dolenec[1], Matej Dolenec[1]

[1]*Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, Aškerčeva 12, 1000 Ljubljana, Slovenia*
[2]*Department of Environment and Municipal Affairs, Trg Pavla Šubica I no. 2, 22000 Šibenik, Croatia.*
[3]*Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[4]*Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*
komar.darja@gmail.com, darja.komar@ntf.uni-lj.si

Клучни зборови: елементи на ретки земји (REE); залив Макирина; секвенцијална екстракција; трансфер-фактор; морска трева *Cymodocea nodosa*

Истражувањето се фокусира на определбата на геохемиските карактеристики на дистрибуцијата на елементите на ретки земји (REE) во седиментите од заливот Макирина. Вкупната концентрација на REE во седиментите од заливот Макирина утврдена во рамките на ова проучување се движеше од 123.94 ppm до 188.74 ppm. Се покажа дека содржината на REE постепено се зголемува со зголемување на длабочината на седиментите. Средниот UCC-нормализиран модел на REE покажа негативни вредности на δSe и позитивни вредности на δEu, укажувајќи дека во седиментите од заливот Макирина преовладувале редукциони услови. Пресметаните вредности за факторот на збогатување се во рамките на природна варијабилност без додаток на разновидни антропогени компоненти. Во согласност со резултатите од процедурите на секвенцијална екстракција, проучуваните фракции можат да се проследат од највисокопроцентните до најнископроцентните REE како: оксидирачки > разменливи > редуцирачки + остаток > редуцирачки > во вода растворливи фракции. Пресметаните вредности за трансфер-фактор генерално ги потврдија резултатите на процедурата на секвенцијална екстракција. Концентрациите на сите проучувани REE се повисоки во надземната отколку во подземната биомаса на морската трева *Cymodocea nodosa*.