Journal of Geochemical Exploration 182 (2017) 70–79

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Influence of the geological setting on the REE geochemistry of estuarine sediments: A case study of the Zrmanja River estuary (eastern Adriatic coast)

Željka Fiket*, Nevenka Mikac, Goran Kniewald

Division for Marine and Environmental Research, Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia

ARTICLE INFO

Keywords:
Rare earth elements
Soil
Bauxite
Geochemistry
Estuarine sediments
Adriatic coast

ABSTRACT

Increasing use of rare earth elements (REE) in many new technologies results in their increasing presence in the environment and consequently in natural water systems. The Zrmanja River estuary represents a small, semi-closed system located in a karstic landscape of the eastern Adriatic coast characterised by the prevailing red soil (*terra rossa*) cover, numerous bauxite pits and the proximity of a decommissioned alumina plant, i.e. sources of geomaterials enriched in rare earth elements. To study the influence of such a substrate on estuarine sediment geochemistry, distribution of REEs in the surface sediments of the Zrmanja River estuary and surrounding soils were investigated. Both sediment and soil samples displayed significant variation in terms of REE concentrations as well as their normalised patterns, with overall highest REE levels measured in bauxitic soils (ΣREE 333–596 mg kg^{-1}); up to an order of magnitude higher than in other samples. In estuarine sediments, ΣREE ranged from 29.7 mg kg^{-1} to 180 mg kg^{-1}, and displayed an increase along the estuary transect. Highest levels of rare earths in sediments of the Zrmanja River were observed in locations closest to the former alumina plant, indicating a transfer of particles rich in REE from the anthropogenically degraded environment in the vicinity of the factory and its influence on the geochemistry of the estuarine sediments. Sediment REE normalised patterns and associated fractionation parameters (ΣLREE/ΣHREE, $(La/Nd)_{NASC}$, $(La/Yb)_{NASC}$) showed similarity to those observed for soil samples, confirming a significant influence of local lithological and pedological setting on the sediment REE composition. Moreover, spatial changes in these parameters in sediments clearly followed the changes in nearby soils and can be differentiated on a relatively small scale.

1. Introduction

The growing number of current or emerging alternative energy technologies (e.g. electric and hybrid vehicles, energy-efficient lighting, wind power) and digital equipment (e.g. flat panel displays, disk drives, digital cameras) contain REE-bearing components such as glass, magnets, metal alloys, catalysts and phosphors (Haxel et al., 2002; Long et al., 2010). The latter are the cause of increasing trends in the annual demand for REEs, leading to the increasing exploitation of rare earth minerals (Chen, 2011; Haxel et al., 2002; Livergood, 2010). Consequently, more and more REEs enter the soils and water systems, mainly through microelement fertilizers and mine tailing wastes, and subsequently accumulate in soils and sediments, bioaccumulate in biota (Wang et al., 1997; Wang et al., 2008), and enter the food chain, causing serious environmental problems (Zhang et al., 2013).

In soils and sediments, levels of REEs can be influenced, therefore, not only by parent material, history and weathering state of the soil, contents of organic matter, and present clay minerals (Aubert et al., 2001; Compton et al., 2003; Davranche et al., 2011; McLennan and Taylor, 2012), but also by diverse anthropogenic activities (Zhang et al., 2001; Hannigan et al., 2010; López-González et al., 2012; Fiket et al., 2016). Despite the coherent character of the group of rare earth elements, once entering the natural water systems, they are prone to changes depending on existing environmental conditions. Ongoing sedimentary processes can also affect their mobility and fractionation, which makes them widely applicable for monitoring processes in different geochemical environments (Goldberg et al., 1963; Goldstein and Jacobsen, 1988; Elderfield et al., 1990; German et al., 1991; Sholkovitz, 1995; Johannesson et al., 1996; Van Middlesworth and Wood, 1998; Zhang et al., 1998; Johannesson and Zhou, 1999; Leybourne et al., 2000; Nozaki et al., 2000; Haley et al., 2004). In estuaries, zones of intense mixing of freshwater and seawater, distribution of trace elements, including rare earths, is primarily determined by coagulation of colloidal material along the salinity gradient, adsorption and desorption processes or remobilization from the sediment (Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Sholkovitz, 1993; Sholkovitz and

* Corresponding author.
E-mail address: zeljka.fiket@irb.hr (Ž. Fiket).

http://dx.doi.org/10.1016/j.gexplo.2017.09.001
Received 27 April 2016; Received in revised form 23 January 2017; Accepted 5 September 2017
Available online 06 September 2017
0375-6742/

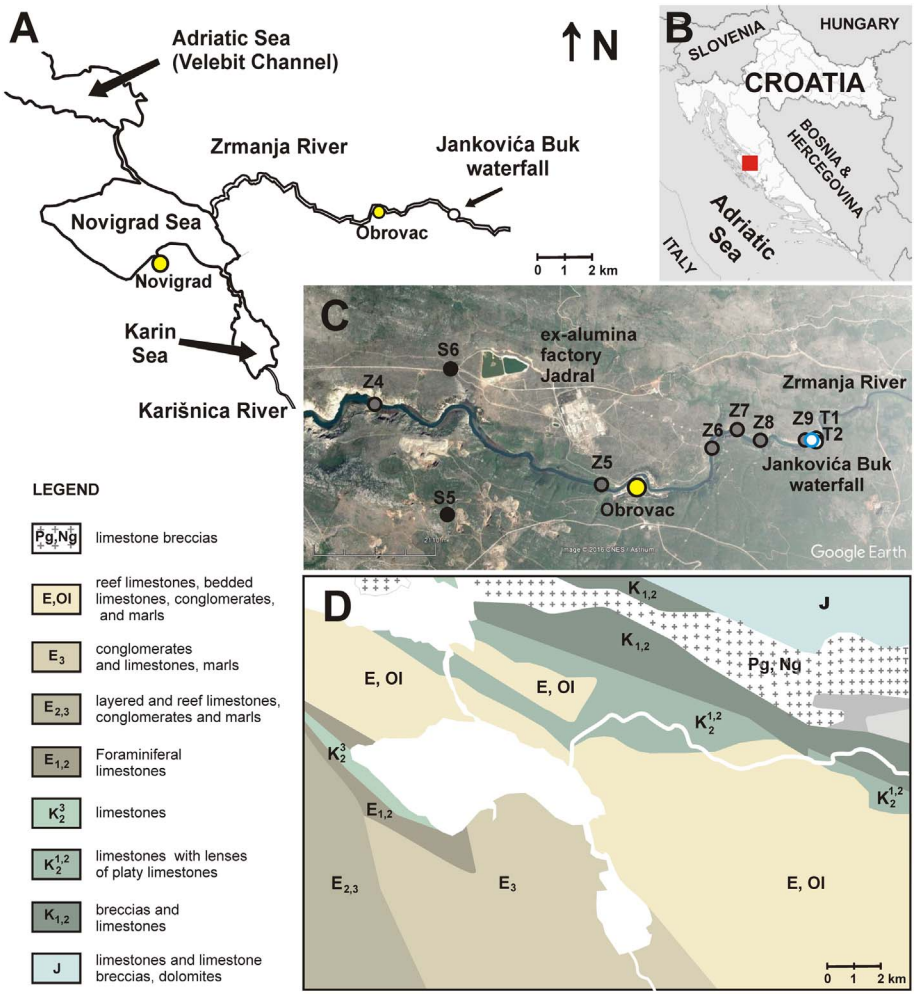

Fig. 1. a) The Zrmanja River estuary; b) Location of the Zrmanja River estuary; c) Detailed view of the Zrmanja River with indicated locations of the ex-alumina factory Jadral and the Jankovića Buk waterfall. d) Simplified geological map of the study area (Fiket et al., 2016).

Szymczak, 2000; Hannigan et al., 2010). Distribution of REEs in estuarine sediments depends, therefore, not only on provenance (Taylor and McLennan, 1985; Sholkovitz, 1993; Sholkovitz et al., 1999; Chunye et al., 2013), but also on the physical and chemical processes that take place within the estuary (Taylor and McLennan, 1985; Sholkovitz, 1990; Sholkovitz et al., 1994; Sholkovitz et al., 1999).

The Zrmanja River estuary is a semi-closed bay (Fig. 1a) located in the central part of the eastern Adriatic coast (Fig. 1b), and according to estuary classification (Hansen and Rattray, 1966) can be described as a highly-stratified estuary. It represents a highly indented system comprising of three parts: the upper part (downstream part from Jankovića Buk to Novigrad Sea), the middle part (Novigrad and Karin Sea) and the lower part (strait that connects the Novigrad Sea and the Velebit Channel) (Viličić et al., 2008). The Zrmanja River is a tufa bearing karst river (Pavlović et al., 2002), with the last travertine barriers at the Jankovića Buk waterfall (Fig. 1c). Studies on phytoplankton communities and nutrient cycle (Viličić, 1989; Burić et al., 2005; Burić et al., 2007) indicate only minor anthropogenic influence in the Zrmanja river estuary. Geological background of the wider study area mainly consists of sedimentary Mesozoic (Jurassic and Cretaceous limestones, dolomites and limestone breccias) and Paleogene (Eocene limestones, dolomites and clastites and Oligocene conglomerates and limestones) rocks (Fig. 1d). The area is also characterised by a number of bauxite deposits of different geological age, while the most common soils are red soil (*terra rossa*), sands and soils with high content of lime debris. On the right bank of the river canyon, about 8 km upstream from the mouth of the Zrmanja River into the Novigrad Sea, the decommissioned alumina factory Jadral is situated (Fig. 1c). The plant was in operation since 1978 but was closed in 1981 due to its unprofitable production and lack of own resources, leaving behind pools filled with alkaline sludge (650,000 m^3) and red mud (850,000 m^3) enriched with metals (Kutle et al., 2004). Remediation of residues and removal of the factory began in 2006 and during the field study in 2010 has not yet been completed.

Carbonate rocks, i.e. limestones and dolomites, typically contain very small amounts of accessory minerals which are the most common carriers of the REEs. On the contrary, *terra rossa* and bauxite contain significantly higher concentrations of rare earths. Bauxite represents raw material for the alumina production, while the waste of such production is red mud, enriched in REE from the original bauxite ore (Ochsenkühn-Petropoulou et al., 1994). Red mud is usually deposited in holding ponds near factories, which was also the case with the former alumina factory Jadral. Due to the weather conditions in the study area, dominated by a strong bora winds (Dorman et al., 2006), transport of particles from the vicinity of the former alumina plant to the Zrmanja River estuary is expected, which prompt the idea for here presented study. So far, a number of authors investigated distribution of rare earths in *terra rossa*, attempting to assess its origin (Whitehead et al., 1993; Miko et al., 1999; Durn, 2003; Ji et al., 2004; Cooke et al., 2007; Muhs and Budahn, 2009), but with inconclusive results.

The aim of this study was to investigate the influence of lithological and pedological setting (enriched in rare earth elements) on sedimentation within the estuarine system. Following the above, objectives of this study were: 1) to assess the levels of rare earth elements in surface sediments of the Zrmanja River estuary and surrounding soils and sedimentary rocks; 2) to get an overview of spatial variations in

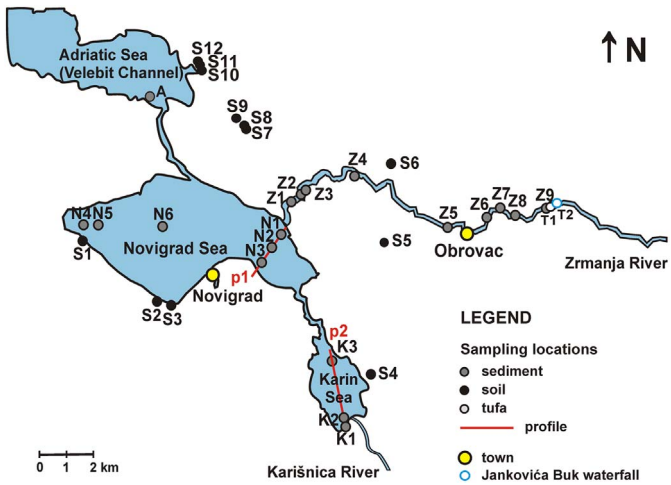

Fig. 2. Spatial distribution of sampling locations in the study area with indicated profiles (p1 and p2).

REE abundances and fractionation patterns; 3) to determine the influence of surrounding setting on the distribution of REEs in the estuarine sediments, 4) to determine the major processes and factors controlling the levels of these elements in estuarine sediments.

2. Materials and methods

2.1. Sample description

For purpose of this study, surface sediments were taken at 19 locations in the Zrmanja River estuary, including the Zrmanja River, the Novigrad Sea, the Karin Sea and the Velebit Channel. Additionally, soils were sampled at 12 locations in the surrounding area taking into account that they represent a cross-section of local soils. In the study area, because of the war activities in 1990's, a number of explosives were left behind which limited the field study. Sampling locations were indicated in Fig. 2, while a brief description of collected samples is given below. For each sediment sampling location, the water depth is given in brackets. The GPS coordinates of the sampling locations are listed in Supplement 1.

The Zrmanja River sediments were sampled downstream from Jankovića Buk at 9 locations (Fig. 2). At locations Z1 (6 m), Z4 (4.5 m), Z7 (1 m) and Z8 (4 m) single surface sediments were sampled, while at locations Z2 (5.5 m), Z3 (6 m), Z5 (6.5 m) and Z6 (6.5 m) sediment cores were taken. At location Z9 coastal surface sediment was sampled, while nearby two tufa samples (T1 and T2) were taken. The Novigrad Sea sediments were sampled along a profile p1, at locations N1 (2 m), N2 (15 m), and N3 (21 m) and in the deepest part of the basin, at locations N4 (17 m), N5 (34 m), and N6 (34 m). Karin Sea sediments were sampled along the profile p2, at locations K1, K2 (1.2 m) and K3 (13 m), while sediment from the Velebit Channel was sampled at location A (38 m). Sediment from locations K1 represents coastal surface sediments, while at location N2 single surface sediment was taken. At remaining locations, sediment cores were sampled.

Coastal surface sediments (upper 10–15 cm of sediment) were sampled with a sampling shovel and stored in plastic bags. Sediment cores were sampled by gravity corer (UWITEC, Austria) and subsequently divided into 2 cm slices. For purposes of this study composite sample of the first 10 cm (i.e. top 5 slices) of each sediment core was used. Because of the depth and characteristics of the bottom, at some locations, it was not possible to retrieve sediment cores and samples were transferred into plastic bags and processed further as single surface sediment sampled up to 10 cm depth.

Soil samples include one sample of black soil (S1), 4 samples of red soil (*terra rossa*, S2, S3, S4 and S10), 5 samples of bauxitic soil (S5, S6, S7, S8, S9), and two samples of sandy soil (S11, S12). Samples of bauxitic soils S5 and S9 represent surface soils sampled in the immediate vicinity of the former bauxite pits, sample S6was taken in the vicinity of the former alumina plant Jadral, while samples S7 and S8 were taken along pathways of bauxite transportation. At each location, upper 10–15 cm of soil was sampled with the sampling shovel and stored in a plastic bag.

Table 1
Description of sediment and soil samples.

Sediments			Soils		
Sample	Location	Textural class	Sample	Description	Textural class
A	Velebit channel	Sandy silt	S1	Black soil	Loam
K2	Karin Sea	Silt	S2, S3	*Terra rossa*	Sandy loam
N3	Novigrad sea	Silt	S4, S10	*Terra rossa*	Silty loam
N6	Novigrad sea	Silt	S5, S9	Bauxitic soil	Sandy loam
Z2	Zrmanja river	Silty sand	S6	Bauxitic soil	Loam
Z5	Zrmanja river	Sandy silt	S7, S8	Bauxitic soil	Sandy loam
Z6	Zrmanja river	Silty sand	S11, S12	Sandy soil	Sand

A brief description of textural characteristics of studied samples is presented in Table 1.

2.2. Sample preparation

All samples were air-dried, homogenised using an agate mill, and stored until further analysis.

Prior to analysis subsamples (0.1 g) were subjected to total digestion in the microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) in a two-step procedure consisting of digestion with a mixture of 4 mL nitric acid (HNO_3, 65%, *pro analysis*, Kemika, Zagreb, Croatia) - 1 mL hydrochloric acid (HCl) - 1 mL hydrofluoric acid (HF, 48%, *pro analysis*, Kemika, Zagreb, Croatia) followed by addition of 6 mL of boric acid (H_3BO_3, 40 g L^{-1}, Fluka, Steinheim, Switzerland). Prior to analysis samples were diluted, acidified with 2% (v/v) HNO_3 (65%, *supra pur*, Fluka, Steinheim, Switzerland) and In (1 μg L^{-1}) as an internal standard was added. Detailed method description is given elsewhere (Fiket et al., 2016).

2.3. ICP-MS analysis

Multielemental analysis of prepared samples was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) using an Element 2 instrument (Thermo, Bremen, Germany). Instrument parameters are given elsewhere (Fiket et al., 2007). External calibration was used for the quantification. Standards for multielement analysis were prepared by appropriate dilution of a multielement reference standard (Analytika, Prague, Czech Republic) containing Ce, La, Nd and Pr (100 ± 0,2 mg L^{-1}), and Dy, Er, Eu, Gd, Ho, Lu, Sc, Sm, Tb, Tm and Yb (20 ± 0,4 mg L^{-1}).

All samples were analysed for total concentration of 14 elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm and Yb).

2.4. Quality control

Quality control of analytical procedure was performed by simultaneous analysis of the blank and following certified reference materials: stream sediment (NCS DC 73309, also known as GBW 07311, China National Analysis Center for Iron and Steel, Beijing, China), estuarine sediment (IAEA 405, IAEA, Vienna, Austria), offshore marine sediment (NCS DC 75301, also known as GBW 07314, China National Analysis Center for Iron and Steel, Beijing, China) and soil (NCS DC 77302, also known as GBW 07410, China National Analysis Center for Iron and Steel, Beijing, China). Good agreement between the analysed and

Table 2
Concentrations of REEs in sediment, tufa and soil samples, expressed in mg kg^{-1}.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
Sediments															
A	26.8	50.6	5.52	23.5	4.05	0.800	3.11	0.536	2.77	0.560	1.58	0.229	1.45	0.213	122
K1	8.58	15.8	1.82	7.58	1.32	0.278	1.23	0.178	0.934	0.193	0.517	0.069	0.456	0.062	39.0
K2	13.4	23.6	2.76	11.1	2.06	0.369	1.92	0.296	1.38	0.267	0.736		0.723	0.101	58.7
K3	27.7	51.3	5.61	23.0	3.83	0.792	3.22	0.527	2.66	0.536	1.52	0.209	1.33	0.201	122
N1	17.2	34.0	4.12	18.6	3.55	0.709	1.14	0.490	2.33	0.460	1.29	0.182	1.17	0.812	86.0
N2	22.8	44.2	4.84	20.6	3.60	0.769	2.93	0.441	2.51	0.495	1.32	0.197	1.35	0.190	106
N3	34.6	67.4	7.42	32.2	5.48	1.17	4.79	0.773	3.75	0.723	2.06	0.261	2.03	0.295	163
N4	36.0	71.8	7.94	35.2	5.89	1.12	2.28	0.771	2.96	0.567	1.55	0.217	1.47	0.982	169
N5	36.6	80.3	7.80	33.4	6.05	1.24	4.74	0.699	4.27	0.761	2.36	0.362	2.16	0.307	181
N6	38.2	74.2	7.85	33.4	5.50	1.20	4.86	0.746	3.85	0.757	2.13	0.264	2.03	0.309	175
Z1	11.0	21.4	2.74	12.4	2.21	0.477	1.82	0.305	1.54	0.290	0.829	0.110	0.712	0.102	55.9
Z2	21.8	42.7	5.18	23.0	4.21	0.846	3.28	0.537	2.77	0.545	1.47	0.207	1.34	0.193	108
Z3	15.3	30.4	3.74	17.0	3.15	0.655	2.53	0.407	2.06	0.401	1.06	0.139	0.893	0.127	77.9
Z4	21.1	40.8	4.87	21.2	3.96	0.732	3.03	0.493	2.61	0.512	1.49	0.207	1.41	0.194	103
Z5	25.5	48.6	5.86	26.5	4.83	0.946	3.71	0.619	3.23	0.637	1.82	0.256	1.67	0.248	124
Z6	14.7	28.6	3.26	13.8	2.56	0.531	2.09	0.307	1.76	0.329	0.877	0.126	0.853	0.125	69.9
Z7	13.1	24.1	3.03	13.9	2.54	0.491	1.85	0.336	1.67	0.344	0.942	0.131	0.868	0.106	63.4
Z8	19.6	35.2	4.29	18.5	3.12	0.625	2.48	0.411	2.11	0.420	1.11	0.154	0.950	0.137	89.1
Z9	6.4	10.3	1.42	6.70	1.23	0.258	1.05	0.172	0.93	0.187	0.492	0.062	0.414	0.055	29.7
Tufa															
T1	4.36	9.10	0.930	4.36	0.729	0.161	0.593	0.102	0.542	0.102	0.339	0.068	0.271	0.042	21.7
T2	5.44	10.5	1.18	5.26	0.837	0.215	0.71	0.121	0.672	0.138	0.419	0.072	0.336	0.050	26.0
Soils															
S1	36.0	68.7	7.35	31.0	4.94	1.07	4.37	0.695	3.28	0.670	1.83	0.266	1.75	0.266	162
S2	38.7	82.5	7.81	31.4	4.85	1.01	3.89	0.606	2.63	0.506	1.40	0.2	1.26	0.187	177
S3	11.5	20.4	2.23	9.44	1.60	0.332	1.51	0.217	1.08	0.212	0.620	0.076	0.522	0.071	49.8
S4	14.4	27.0	2.95	13.4	2.21	0.453	1.85	0.261	1.45	0.242	0.764	0.114	0.754	0.102	66.0
S5	41.6	73.9	8.31	36.4	6.44	1.51	5.62	0.777	4.67	0.782	2.52	0.359	2.55	0.373	186
S6	53.6	151	13.2	59.8	12.1	2.88	11.1	1.69	10.8	1.85	6.40	0.958	6.45	0.929	333
S7	102	311	20.4	88.5	16.2	3.63	14.7	2.21	14.9	2.55	7.80	1.14	6.71	0.951	593
S8	101	315	20.6	88.0	16.4	3.65	14.3	2.21	14.5	2.63	8.40	1.11	7.08	0.981	596
S9	76.4	140	14.2	63.8	11.2	2.76	11.1	1.69	10.5	1.80	6.04	0.868	5.42	0.765	347
S10	12.7	30.1	3.64	16.7	3.58	0.825	3.23	0.526	3.23	0.612	2.02	0.313	2.16	0.324	80.0
S11	9.75	19.2	2.12	9.50	1.81	0.412	1.10	0.228	1.45	0.247	0.818	0.121	0.851	0.121	47.7
S12	9.15	21.6	2.00	8.78	1.61	0.347	1.15	0.199	1.23	0.221	0.681	0.099	0.714	0.084	47.9

A – Velebit Channel, K1–K3 – Karin Sea, N1–N6 – Novigrad Sea, Z1–Z9 – Zrmanja River. ΣREE – sum of all rare earth element concentrations.

certified concentrations within their analytical uncertainties for all elements was obtained (± 10%) (Fiket et al., 2016).

3. Results

Rare earth element concentrations in surface sediment samples of the Zrmanja River estuary and soil samples of the surrounding area are shown in Table 2.

Concentrations of the REEs in analysed samples ranged over four orders of magnitude, from 0.038 mg kg^{-1} to 80.3 mg kg^{-1} in sediments and from 0.044 mg kg^{-1} to 485 mg kg^{-1} in soils (Table 2). Of all the measured REE, Ce was found at highest concentrations in all studied samples, whereas concentrations of Tm and Lu were lowest. Analysed samples displayed variations in terms of REE concentrations as well as distribution patterns, with total REE (ΣREE) ranging from 21.7 mg kg^{-1} in tufa samples to 593 mg kg^{-1} in bauxitic soils. In general, soil samples displayed higher REE concentrations compared to estuarine sediments. Moreover, the range of ΣREE values in the soil samples was much wider (47.7 mg kg^{-1} to 596 mg kg^{-1}) compared to the range of values obtained for the estuarine sediments (29.7 mg kg^{-1} to 181 mg kg^{-1}).

Fig. 3 shows the spatial distribution of ΣREE in soil samples and estuarine surface sediments, including tufa samples, of the study area. Highest average ΣREE concentrations were measured in samples of bauxitic soil (ΣREE = 411 mg kg^{-1}), while lower average concentrations were measured in samples of *terra rossa* (ΣREE = 93.2 mg kg^{-1}), and other soil samples (ΣREE = 85.9 mg kg^{-1}). Tufa samples displayed overall lowest REE average values (ΣREE = 23.9 mg kg^{-1}). Estuarine surface sediments displayed differences regarding the level of REEs, with the lowest average ΣREE values observed for the Karin Sea sediments (ΣREE = 73.2 mg kg^{-1}), slightly higher in the Zrmanja River sediments (ΣREE = 80.1 mg kg^{-1}) and the highest in the Novigrad Sea sediments (ΣREE = 147 mg kg^{-1}).

In the Zrmanja River, highest REE concentrations showed sediments from locations closest to the former-alumina plant Jadral (Z4 and Z5, Fig. 3), while the lowest REE values were recorded in sediment Z9, sampled at the most upstream location (Fig. 3).

In the area of the Novigrad Sea REE concentrations in sediments displayed an increase along the profile p1, i.e. from the mouth of the Zrmanja River to the deeper part of the Novigrad Sea. Similarly, sediments of the Karin Sea sampled along the profile p2 displayed an increase in REE concentrations from the coast to the deeper part of the basin (Fig. 3). Interestingly, sediment from the Velebit Channel (sample A) displayed similar REE concentrations as the sediment from location K3. The overall highest levels of REEs in sediments were measured in samples from the deepest part of the Novigrad Sea, from locations N4, N5 and N6.

All the analysed samples showed a predominance of light rare earth elements (LREE, La-Gd) over heavy rare earths (HREE, Tb-Lu) with ΣLREE/ΣHREE ranging from 7.71 to 25.1 (Table 3). Lowest value of ΣLREE/ΣHREE was obtained for the *terra rossa* sample from location S9 (ΣLREE/ΣHREE = 7.71), while the highest value was observed for the *terra rossa* from location S2 (ΣLREE/ΣHREE = 25.1). For sediments, lowest values of ΣLREE/ΣHREE were observed for Zrmanja River sediments, ranging from 11.8 to 15.8. Similar values of ΣLREE/ΣHREE ratio, from 10.4 to 15.3, were obtained for bauxitic soils (S5–S9)

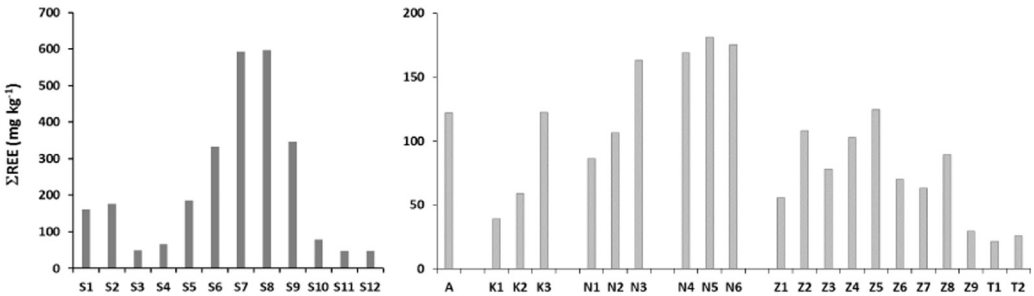

Fig. 3. Spatial distribution of ΣREE (mg kg^{-1}) in soils (S1–S12) and estuarine surface sediments (A, K1–K3, N1–N6, Z1–Z9), including tufa samples (T1 and T2), of the study area.

sampled on the river banks (Table 3). On the other hand, the highest value of this ratio in the sediments was observed for sample N4 from the Novigrad Sea (ΣLREE/ΣHREE = 20.8). In general, the ΣLREE/ΣHREE ratio values for Novigrad Sea sediments ranged from 15.6 to 20.8 (Table 3). Similar range of the ratio values was obtained for surrounding soils S1–S3, from 16.8 to 25.1. Analogously, the ratio values for sediments from the Karin Sea ranged from 15.2 to 16.5 and resembled ratio value of the soil sample S4 (ΣLREE/ΣHREE = 16.9) sampled nearby Karin Sea (Table 3). In general, ΣLREE/ΣHREE ratio values in sediments displayed an increase along p1 and p2 profiles, reflecting an increase in concentrations of LREE compared to HREE, and were found to be similar to ratio values of nearby soils.

Concentrations of REE in analysed samples, normalised with respect to the estimated average composition of the North American Shale Composite (NASC), (Gromet et al., 1984) are presented in Figs. 4 and 5. Related calculated parameters (europium anomaly, cerium anomaly, $(La/Nd)_{NASC}$, and $(La/Yb)_{NASC}$) are listed in Table 3.

Sediments exhibited slightly negative to slightly positive europium anomaly ($Eu/Eu^* = Eu_{NASC} / (Sm_{NASC} \times Gd_{NASC})^{0.5} = 0.82–1.11$), while cerium anomaly values displayed similar range of values ($Ce/Ce^* = Ce_{NASC} / (La_{NASC} \times Pr_{NASC})^{0.5} = 0.78–1.10$). In soils, both anomalies displayed a broader range of values, from 0.91 to 1.30 and from 0.92 to 1.58 for Eu/Eu* and Ce/Ce*, respectively.

Sediments from the Zrmanja River were characterised by an overall predominance of elements from Nd to Dy resulting in a convex shape of the normalised curve (Fig. 4a). On the other hand, REE distribution curves of the tufa samples (T1 and T2) significantly differed from the normalised patterns of river sediments (Fig. 5a). Although the shape of normalised curves in the Zrmanja River sediments resembled those in the Karin Sea (Fig. 4b) and the Novigrad Sea (Fig. 4c,d) sediments, including a sample from the Velebit Channel (Fig. 4b), the same differed by the slope. Convexity of the normalised curves observed in river sediments alleviated in the remaining estuarine sediments, including that of the Velebit Channel, while inclination increased. The latter is reflected in an increase of $(La/Nd)_{NASC}$ and $(La/Yb)_{NASC}$ ratio values in sediments of the Novigrad and Karin Seas compared to the Zrmanja River sediments (Table 3). Namely, the $(La/Nd)_{NASC}$ and $(La/Yb)_{NASC}$ ratio values showed, in average, lowest values for the Zrmanja River sediments ($(La/Nd)_{NASC} = 0.85$; $(La/Yb)_{NASC} = 1.61$), higher in sediments sampled at the mouth of the Zrmanja River and the Karišnica River into the Novigrad Sea ($(La/Nd)_{NASC} = 0.93$; $(La/Yb)_{NASC} = 1.64$) and the Karin Sea ($(La/Nd)_{NASC} = 1.04$; $(La/Yb)_{NASC} = 1.91$), respectively, and highest values for sediments from the deepest part of the Novigrad sea ($(La/Nd)_{NASC} = 1.01$; $(La/Yb)_{NASC} = 2.08$).

Moreover, normalised curves in estuarine sediments resembled those observed in the surrounding soil samples (Fig. 5). Soils from locations S1 and S2 (Fig. 5b), although belonging to different types of soil (black soil and *terra rossa* soil, respectively) showed very similar normalised patterns, which also resembled those in the surface sediments of the Novigrad Sea sampled at locations N4, N5 and N6 (Fig. 4d). Furthermore, *terra rossa* samples from locations S3 and S4 (Fig. 5c) showed similarities with normalised curves of sediments from the Novigrad Sea (profile p1, Fig. 4c) and the Karin Sea (profile p2, Fig. 4b), respectively.

Samples of bauxitic soil from locations S6 (collected near the factory) and S7–S8 (collected near former bauxite transport route) displayed similar REE normalised patterns (Fig. 5d). However, their normalised patterns significantly differed from those of other soil samples in the study area, even from the normalised pattern of the bauxitic soils S5 and S9 sampled on the opposite bank of the Zrmanja River canyon

Table 3
Calculated anomalies and fractionation indices for studied samples.

Sample	ΣLREE/ΣHREE	Eu/Eu*	Ce/Ce*	$(La/Nd)_{NASCC}$	$(La/Yb)_{NASC}$	Sample	ΣLREE/ΣHREE	Eu/Eu*	Ce/Ce*	$(La/Nd)_{NASC}$	$(La/Yb)_{NASC}$
A	15.6	1.00	0.96	1.01	1.82	Z5	13.7	0.99	0.92	0.85	1.50
K1	15.2	0.97	0.93	1.00	1.85	Z6	15.0	1.02	0.96	0.93	1.69
K2	15.8	0.82	0.90	1.06	1.82	Z7	13.4	1.00	0.89	0.83	1.48
K3	16.5	1.00	0.96	1.06	2.04	Z8	15.8	1.00	0.89	0.93	2.03
N1	13.3	0.98	0.93	0.82	1.45	Z9	11.8	1.01	0.79	0.84	1.52
N2	15.3	1.05	0.98	0.97	1.66	S1	17.5	1.02	0.98	1.02	2.02
N3	15.5	1.01	0.97	0.95	1.68	S2	25.1	1.03	1.10	1.09	3.02
N4	20.8	1.03	0.98	0.90	2.41	S3	16.8	0.95	0.93	1.07	2.17
N5	15.6	1.03	1.10	0.97	1.67	S4	16.9	0.99	0.96	0.95	1.88
N6	16.4	1.03	0.99	1.01	1.85	S5	14.4	1.11	0.92	1.01	1.61
T1	13.8	1.09	1.05	0.88	1.58	S6	10.4	1.10	1.32	0.79	0.82
T2	13.4	1.24	0.96	0.91	1.59	S7	15.3	1.04	1.58	1.02	1.50
Z1	13.4	1.05	0.90	0.78	1.52	S8	11.8	1.10	0.99	1.06	1.39
Z2	14.3	1.01	0.93	0.84	1.60	S9	7.71	1.08	1.03	0.67	0.58
Z3	14.3	1.03	0.93	0.79	1.69	S10	11.4	1.30	0.98	0.90	1.13
Z4	13.8	0.94	0.93	0.88	1.48	S11	13.8	1.13	1.17	0.92	1.26

ΣLREE/ΣHREE - ratio of sum of light rare earth and heavy rare earth element concentrations.
$(La/Nd)_{NASC}$ - ratio of normalised concentrations of La and Nd.
$(La/Yb)_{NASC}$ - ratio of normalised concentrations of La and Yb.
Eu/Eu* - europium anomaly ($Eu/Eu^* = Eu_{NASC}/(Sm_{NASC} \times Gd_{NASC})^{0.5}$).
Ce/Ce* - cerium anomaly ($Ce/Ce^* = Ce_{NASC}/(La_{NASC} \times Pr_{NASC})^{0.5}$).

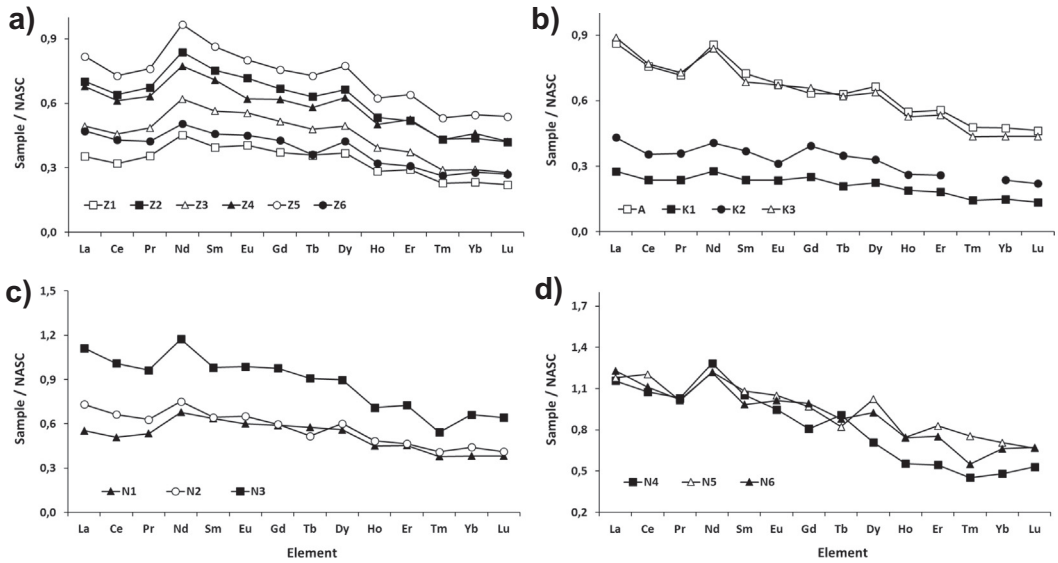

Fig. 4. NASC-normalised REE patterns of surface sediments of a) the Zrmanja River; b) the Karin Sea and the Velebit Channel; c) and d) the Novigrad Sea.

and in the immediate vicinity, respectively (Fig. 5e). This was expected given that the bauxite used in the production of the former alumina factory Jadral was not supplied from the surrounding bauxite pits (e.g. those in the vicinity of locations S5 and S9), but the same was imported from foreign countries, which may explain the differences in the observed curves. It is interesting how the samples of local bauxitic soils, S5 and S9, displayed very similar normalised curves (Fig. 5e).

Terra rossa from location S10 was the only sample which showed prevalence of HREE over LREE (Fig. 5f). Sandy soils from locations S11 and S12 displayed very similar normalised curves (Fig. 5f), significantly different from the normalised curve of *terra rossa* from location S10, sampled in the vicinity (Fig. 5f). However, normalised patterns of these samples displayed no similarities with other samples, both soil and estuarine. This was not surprising given that the latter sites are located along the coast of the Velebit channel, outside of the estuary.

4. Discussion

Studied soils and sediments showed differences in terms of rare earth concentrations as well their normalised patterns. Soils displayed a

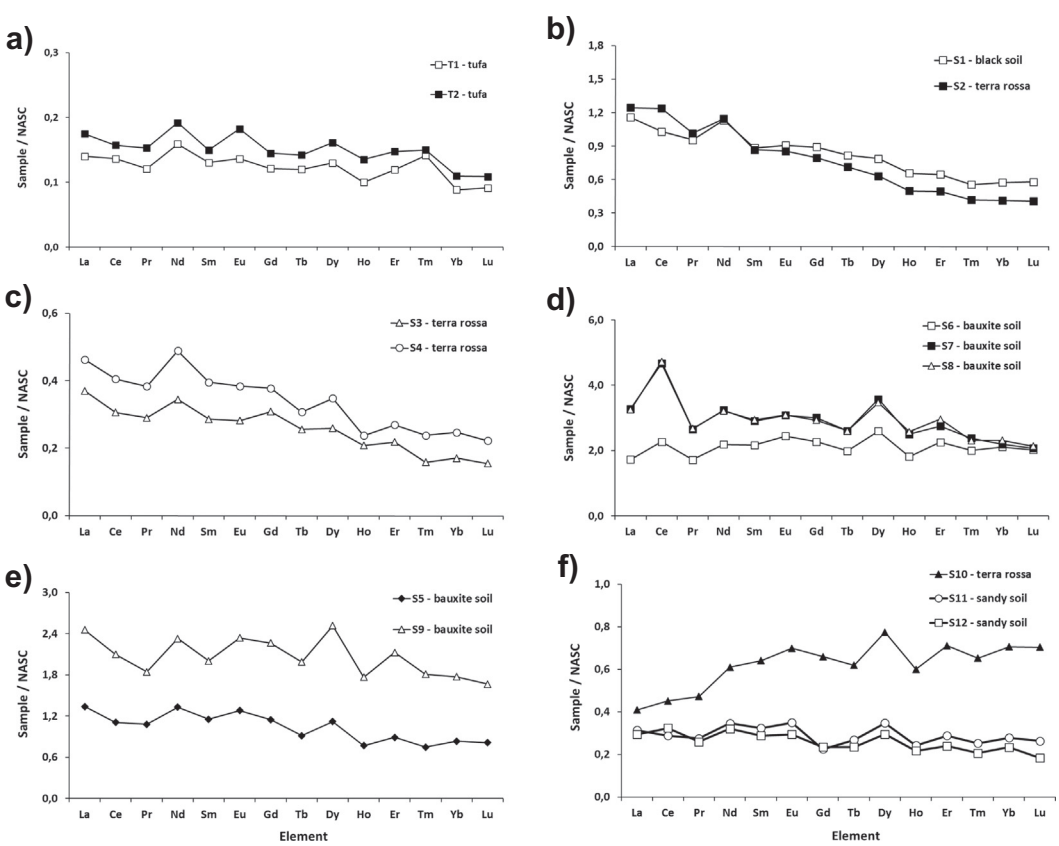

Fig. 5. NASC-normalised REE patterns of tufa (T1 and T2) and soil (S1–S12) samples.

wide range of REE concentrations, regardless of the soil type. However, overall highest levels of rare earths (ΣREE 333–596 mg kg^{-1}), up to an order of magnitude higher than in other samples, were measured in bauxitic soils (S6–S8) related to the factory and the bauxite transport route. Bauxite deposits form as a result of the intense weathering of residual clay minerals and their accumulation in topographic lows on continental surfaces (Bárdossy, 1982; Wagh and Pinnock, 1987; Gow and Lozej, 1993; Ochsenkühn-Petropoulou et al., 1995; Bland and Rolls, 1998; Deady et al., 2016). Rare earths become concentrated in such deposits due to crystallisation of authigenic REE-bearing minerals, accumulation of residual phases and the adsorption of ions on clays and other mineral surfaces (Wagh and Pinnock, 1987; Ochsenkühn-Petropoulou et al., 1995; Deady et al., 2016). For this reason, the red mud waste, generated by alumina production from bauxite through the Bayer process, becomes enriched with respect to REEs, and contains on average about 900 ppm of rare earths, up to ten times more than bauxites (< 100 ppm to ~500 ppm ΣREE, Deady et al., 2016). Thus, the highest values of the REEs in bauxitic soils sampled in the vicinity of former alumina factory were expected. Moreover, the measured concentrations of rare earths in samples of bauxitic soil were found comparable to the data reported by Calagari et al. (2010) for the Permian-Triassic Binglar bauxites and slightly lower than those reported by and Tsirambides and Filippidis (2012) for Greece bauxites of the Parnassos-Ghiona zone (Table 4). Compared with karst bauxites from southern Apennines (Boni et al., 2012), bauxitic soils nearby Zrmanja River estuary were found depleted regarding LREE, i.e. elements from La to Gd, while the levels of elements from Dy to Lu showed better agreement (Table 4).

Average REE concentrations in soils were found lower than the values reported by Feng (2010) and Yalcin and Ilhan (2008) for *terra rossa* from the Pingba Farm profile in the Central China and Kucukkoras Region in Turkey, respectively (Table 4). Ranges of REE concentrations obtained for sediments of the Zrmanja River estuary were found comparable with literature data for estuarine sediments in Cochin in India (Deepulal, 2012), sediments of the Gulf of Biscay in France (Chaillou et al., 2006) and those from the port of Rijeka in Croatia (Cukrov et al., 2011) (Table 4). Measured concentrations exhibited lower values than the literature data for estuarine sediments of the river Odiel in Spain (López-González et al., 2012) and sediments of the Chesapeake Bay (Hannigan et al., 2010) (Table 4). In addition to differences in geological background, higher concentrations of rare earths in the Odiel river and the Chesapeake Bay compared to the Zrmanja River estuary could probably be related to local mining activities (Hannigan et al., 2010) and intense agricultural pressures (López-González et al., 2012), reported for these two water systems.

Spatial distribution of REEs and their normalised counterparts in the studied sediments indicate a diversity of factors influencing sedimentation in the Zrmanja River estuary. In general, sediments displayed an increase of REE levels from the mouth of the Zrmanja River and the Karišnica River into the Novigrad Sea and the Karin Sea, respectively, with the highest REE concentrations (ΣREE 122–181 mg kg^{-1}) observed in the sediments sampled in deeper parts of the study area (A, K3, N3, N4, N5, N6). The latter is probably related to an increased share of clay fraction in fine-grained sediments deposited at greater depths. Overall highest levels of REEs were observed in sediments from locations N5 (ΣREE = 175 mg kg^{-1}) and N6 (ΣREE = 181 mg kg^{-1}), sampled in the deepest part of the Novigrad Sea, at depths > 30 m, i.e. below the wave base.

The Zrmanja River estuary is highly stratified system with the halocline separating upper brackish layer from bottom sea layer (Viličić et al., 1999). Studied estuary is, therefore, characterised by pronounced stratification and limited mixing processes. Thus, an increase in REE concentrations along the profiles p1 and p2 (Fig. 1) could not be solely attributed to the coagulation of river colloids in estuaries along the salinity gradient (Sholkovitz, 1992, 1995; Sholkovitz and Szymczak, 2000; Hannigan et al., 2010) but probably to a downstream increase in fine fraction in sediments. This was further supported by an enrichment of LREEs compared to HREEs and an increase of ΣLREE/ΣHREE ratio (Table 3), observed for sediments along the sampling profiles p1 and p2, and in sediments from the Novigrad and Karin Seas compared to those from the Zrmanja River. Namely, enrichment of the LREE relative to the HREE is considered to reflect greater affinity of the particles (i.e. clay minerals) for light rare earths (Vlasov, 1966; Rollinson, 1993; Sholkovitz, 1993; Sholkovitz et al., 1999).

In addition to the observed variation of rare earth concentrations in the sediments related to grain size distribution, Zrmanja River sediments displayed considerable variability regarding the REE levels, with ΣREE ranging from 29.7 mg kg^{-1} to 124 mg kg^{-1}. Highest REE concentrations in the Zrmanja River sediments, two to four times higher in comparison to other river sediments, were measured in samples from the locations closest to the former alumina plant (Z3, Z4) and slightly further downstream (Z2) suggesting the transport of the material from the plant to the water system of the Zrmanja River.

Most shales and sediments contain higher concentrations of LREE compared to HREE (Vlasov, 1966; Rollinson, 1993; Sholkovitz, 1993; Sholkovitz et al., 1999), and the predominance of light rare earth elements in studied estuarine sediments was somewhat expected. However, both sediments and soils displayed prevalence of light rare earths. The ΣLREE/ΣHREE ratio values for sediments were found to be similar to the ratio values of soils sampled nearby pointing to a direct correlation of REE distribution in the sediments and local lithology.

Rare earth element normalised patterns of the Novigrad Sea and the Karin Sea sediments were similar to those of the marine estuarine sediments reported by López-González et al., 2012. However, the REE normalised patterns of the Zrmanja River sediments showed no similarity to patterns listed in the literature for river sediments (López-González et al., 2012), and they were more similar to the distribution patterns reported by the Feng (2010) for the *terra rossa* soil, confirming the impact of the local lithology on the REE distribution in the sediments of the Zrmanja River estuary.

Thus, a spatial distribution of the REE in estuarine sediments of the study area was considered to be related to several factors, lithological and pedological background, grain size distribution, physical and chemical processes that govern the input of dissolved and particulate matter by river and coagulation of colloidal material along the salinity gradient. Furthermore, the results of this study strongly indicate transfer of particles from the immediate vicinity of the former alumina factory to the surrounding environment and their influence on the estuarine sediment geochemistry. In general, the variability of the substrate is reflected in the geochemistry of sediments, in terms of REE concentrations as well as their fractionation patterns, despite the relatively small area included in the present study. And most importantly, results showed that despite the background containing naturally elevated concentrations of REEs (i.e. *terra rossa*, local bauxite pits) it was possible to differentiate in estuarine sediments an additional input of material enriched in rare earth elements created by human activity.

These findings can also be applied for pollution tracing, remediation, assessment of habitat destruction, or in regional exploration for REE. Namely, rare earth elements are exploited in numerous applications (i.e. fluorescent lamp phosphors, permanent magnets, batteries, polishing powders, glass, ceramics, contrast agents in medicine, etc.) but can also be present in lower concentrations in a multitude of industrial process residues (i.e. phosphogypsum, bauxite residue (red mud), mine tailings, metallurgical slags, coal ash, incinerator ash and waste water streams (Binnemans et al., 2015)) or in fertilizers used in agriculture (natural phosphates can contain 0.1–1% ΣREE). Thus, they are released into the environment in many ways. On the other hand, the increasing demand for rare earth elements requires a steady supply from current and new resources as well as development of efficient REE recycling techniques from end-of-life products (Binnemans et al., 2015). For example, annual European extraction of bauxite amounts to approximately 3.5 million tons per year, resulting in approximately

Table 4
Comparison of average REE concentrations in studied sediments, local *terra rossa* and bauxitic soils with literature data, expressed in mg kg^{-1}.

	Estuarine and coastal sediments						
	Zrmanja (Croatia)[a]	Cochin (India)[b]	Odiel (Spain)[c]	Chesapeake Bay (USA)[d]	Biscay (France)[e]	Rijeka (Croatia)[f]	Daliao (China)[g]
La	24	14–52	30	15–120	7.0–28	11	33
Ce	46	28–103	49	30–240	13–57	23	64
Pr	5.1	2.8–10	8.3	3.0–26	1.7–6.6	2.9	8
Nd	22	11–39	33	11–101	6.5–25	11	29
Sm	3.9	1.9–6.9	7.7	1.9–17	1.2–4.9	2.5	5.4
Eu	0.80	0.54–1.7	1.6	0.32–3.1	0.25–1.2	0.60	1.2
Gd	3.0	1.4–5.7	7.7	1.6–14	1.1–4.4	2.6	4.2
Tb	0.51	0.19–0.89	1.1	0.23–2.0	0.13–0.58	0.38	0.78
Dy	2.6	1.0–4.9	6.3	1.1–11	0.64–3.0	2.0	4.0
Ho	0.51	0.21–1.0	1.3	0.20–1.9	0.12–0.61	0.38	0.84
Er	1.4	0.53–2.8	3.5	0.65–5.9	0.38–1.8	0.97	2.3
Tm	0.18	0.08–0.39	0.54	0.09–0.83	0.05–0.29	0.11	0.40
Yb	1.3	0.50–2.3	3.7	0.72–5.4	0.33–1.6	0.71	2.3
Lu	0.25	0.08–0.36	0.56	0.10–0.96	0.04–0.23	–	0.37

	Terra rossa			Bauxites			
	Croatia[a]	Turkey[h]	China[i]	Croatia[a]	Greece[j]	Italy[k]	Iran[l]
La	13	86	90–385	75	126	102–148	12–64
Ce	27	184	170–510	198	267	231–393	30–130
Pr	2.9	19	15–160	15	21	27–39	5.2–54
Nd	13	80	52–673	67	91	101–126	14–102
Sm	2.3	14	9.2–225	13	24	18–28	4.0–24
Eu	0.51	3.0	1.8–42	2.9	5.6	3.6–5.6	1.1–6.9
Gd	2.0	10	6.5–109	11	3.9	15–19	4.4–20
Tb	0.32	1.9	0.98–18	1.7	25	2.1–3.3	0.53–2.6
Dy	1.8	11	5.5–70	11	21	11–19	3.7–13
Ho	0.34	2.1	1.1–9.0	1.9	4.2	1.9–3.8	0.74–2.3
Er	1.1	6.0	3.2–24	6.2	11	5.3–11	2.0–6.0
Tm	0.16	0.92	0.52–4.6	0.89	1.6	0.83–1.5	0.29–0.66
Yb	1.1	5.9	3.5–35	5.6	9.8	5.4–9.8	1.6–4.8
Lu	0.16	0.89	0.55–4.9	0.80	1.5	0.84–1.5	0.25–0.77

[a] This study.
[b] Deepulal (2012).
[c] López-González et al. (2012).
[d] Hannigan et al. (2010).
[e] Chaillou et al. (2006).
[f] Cukrov et al. (2011).
[g] Chunye et al. (2013).
[h] Yalcin and Ilhan (2008).
[i] Feng (2010).
[j] Tsirambides and Filippidis (2012).
[k] Boni et al., 2012.
[l] Calagari et al., 2010.

1.4 million tons of red mud from the production of alumina, which could be viewed as a resource rather than a waste product, and with development of efficient REE recovery techniques could account for up to 10% of the EU's annual demand for REE (Deady et al., 2016), but with the associated disposal issues. All this presupposes a number of existing, but also new and challenging environmental issues related to REE applications which require an integrated approach taking into account the REE characteristics of the study area, both natural and anthropogenic.

5. Conclusion

The results of the study indicate a significant impact of the local lithological and pedological setting on the sediment geochemistry and more importantly, the possibility of differentiation of this impact on a very small scale. In the studied estuary, the REE geochemistry of sediments varied substantially. Observed variations, however, cannot be solely attributed to grain size distribution and differences in salinity, although these processes partly determined sediment REE geochemistry. Prevalent influence on rare earth geochemistry in studied sediments could be attributed to lithological characteristics of the wider study area. Moreover, the results indicate that the imprint of material sources enriched in rare earth elements, of natural or anthropogenic origin, can be clearly recognised in REE sediment geochemistry. However, a correct interpretation of the latter should include not only the concentrations of rare earths in the sediments but also their normalised analogues and fractionation parameters. All of the above suggests the possibility of application of REEs for the purposes of tracing the origin of various geological materials in aquatic systems, assessment of pollution induced by materials enriched in rare earths or in regional exploration for REE.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2017.09.001.

Acknowledgments

Financial support from the Croatian Science Foundation through the project 7555 TRACESS is acknowledged. We would like to dedicate this article to the late Henry Elderfield who raised, years ago, an interest for REE's with one of the authors (GK).

References

Aubert, D., Stille, P., Probst, A., 2001. REE fractionation during granite weathering and removal by waters and suspended loads: Sr and Nd isotopic evidence. Geochim. Cosmochim. Acta 65, 387–406.

Bárdossy, G., 1982. Karst Bauxites, Bauxite Deposits on Carbonate Rocks. Elsevier, Amsterdam, pp. 444.

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Pontikes, Y., 2015. Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. J. Clean. Prod. 99, 17–38.

Bland, W., Rolls, D., 1998. Weathering: An Introduction to the Basic Principles. Arnold, London, pp. 271.

Boni, M., Rollinson, G., Mondillo, N., Balassone, G., Santoro, L., 2012. Quantitative mineralogical characterization of karst bauxite deposits in the southern Apennines. Econ. Geol. 108, 813–833.

Burić, Z., Viličić, D., Cetinić, I., Caput, K., Carić, M., Olujić, G., 2005. Taxonomic composition of phytoplankton in the shallow, stratified estuary (Zrmanja river, Adriatic Sea). Period. Biol. 107, 305–312.

Burić, Z., Cetinić, I., Viličić, D., Caput Mihalić, K., Carić, M., Olujić, G., 2007. Spatial and temporal distribution of phytoplankton in a highly stratified estuary (Zrmanja, Adriatic Sea). Mar. Ecol. 28, 169–177.

Calagari, A.A., Kangarani, F., Abedini, A., 2010. Geochemistry of major, trace, and rare earth elements in Biglar Permo-Triassic bauxite deposit, northwest of Abgarm, Ghazvin Province, Iran. J. Sci. Islam. Rep. Iran 21 (3), 225–236.

Chaillou, G., Anschutz, P., Lavaux, G., Blanc, G., 2006. Rare earth elements in the modern sediments of the Bay of Biscay (France). Mar. Chem. 100, 39–52.

Chen, Z., 2011. Global rare earth resources and scenarios of future rare earth industry. J. Rare Earths 29, 1–6.

Chunye, L., Shaoqing, L., Mengchang, H., Li, Ruiping, 2013. Distribution of rare earth elements in the estuarine and coastal sediments of the Daliao River system, China. J. Radioanal. Nucl. Chem. 298, 627–634.

Compton, J.S., White, R.A., Smith, M., 2003. Rare earth element behaviour in soils and salt pan sediments of a semi-arid granitic terrain in the Western Cape, South Africa. Chem. Geol. 201, 239–255.

Cooke, M.J., Stern, L.A., Banner, J.L., Mack, L.E., 2007. Evidence for the silicate source of relic soils on the Edwards Plateau, central Texas. Quat. Res. 67, 275–285.

Cukrov, N., Frančišković-Bilinski, S., Hlača, B., Barišić, D., 2011. A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea, Croatia. Mar. Pollut. Bull. 62, 154–167.

Davranche, M., Grybos, M., Gruau, G., Pedrot, M., Dia, A., Marsac, R., 2011. Rare earth element patterns: a tool for identifying trace metal sources during wetland soil reduction. Chem. Geol. 284, 127–137.

Deady, É.A., Mouchos, E., Goodenough, K., Williamson, B.J., Wal, F., 2016. A review of the potential for rare-earth element resources from European red muds: examples from Seydişehir, Turkey and Parnassus-Giona, Greece. Mineral. Mag. 80 (1), 43–61. http://dx.doi.org/10.1180/minmag.2016.080.052.

Deepulal, P.M., 2012. Behaviour of ERZs in a tropical estuary and adjacent continental shelf of southwest coast of India: evidence from anomalies. J. Earth Syst. Sci. 121 (5), 1215–1227.

Dorman, C.E., Carniel, S., Cavaleri, L., Sclavo, M., Chiggiato, J., Doyle, J., Haack, T., Pullen, J., Grbec, B., Vilibić, I., Janeković, I., Lee, C., Malačič, V., Orlić, M., Paschini, E., Russo, A., Signell, R.P., 2006. February 2003 marine atmospheric conditions and the bora over the northern Adriatic. J. Geophys. Res. 111 (C03S03). http://dx.doi.org/10.1029/2005JC003134.

Durn, G., 2003. Terra Rossa in the Mediterranean region: parent materials, composition and origin. Geol. Croat. 56 (1), 83–100.

Elderfield, H., Upstill-Goddard, R., Sholkovitz, E.R., 1990. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. Geochim. Cosmochim. Acta 54, 971–991.

Feng, J.-L., 2010. Behaviour of rare earth elements and yttrium in ferromanganese concretions, gibbsite spots, and the surrounding terra rossa over dolomite during chemical weathering. Chem. Geol. 271, 112–132.

Fiket, Ž., Roje, V., Mikac, N., Kniewald, G., 2007. Determination of arsenic and other trace elements in bottled waters by high resolution inductively coupled plasma mass spectrometry. Croat. Chem. Acta 80, 91.

Fiket, Ž., Medunić, G., Kniewald, G., 2016. Rare earth element distribution in soil nearby thermal power plant. Environ. Earth Sci. 75 (7), 1–9.

German, C.R., Holliday, B.P., Elderfield, H., 1991. Redox cycling of rare earth elements in the suboxic zone of the Black Sea. Geochim. Cosmochim. Acta 55, 3553–3558.

Goldberg, E.D., Koide, M., Schmitt, R.A., Smith, R.H., 1963. Rare earth distributions in the marine environment. J. Geophys. Res. 68, 4209–4217.

Goldstein, S.J., Jacobsen, S.B., 1988. Rare earth elements in river waters. Earth Planet. Sci. Lett. 89, 35–47.

Gow, N., Lozej, G., 1993. Bauxite. Geosci. Can. 20 (1), 9–16.

Gromet, P.L., Dymek, P.F., Haskin, L.A., Korotev, R.L., 1984. The north American shale composite: its composition, major and minor element characteristics. Geochim. Cosmochim. Acta 48 (12), 2469–2482.

Haley, B.A., Klinkhammer, G.P., McManus, J., 2004. Rare earth elements in pore waters of marine sediments. Geochim. Cosmochim. Acta 68, 1265–1279.

Hannigan, R., Dorval, E., Jones, C., 2010. The rare earth element chemistry of estuarine surface sediments in Chesapeake Bay. Chem. Geol. 272, 20–30.

Hansen, D.V., Rattray, M., 1966. New dimensions in estuary classification. Limnol. Oceanogr. 11, 319–326.

Haxel, G.B., Hedrick, J.B., Orris, G.J., 2002. Rare earth elements: critical resources for high technology. In: U.S. Geological Survey Fact Sheet 087-02, . http://pubs.usgs.gov/fs/2002/fs087-02/.

Ji, H., Wang, S., Ouyang, Z., Zhang, S., Sun, C., Liu, X., Zhou, D., 2004. Geochemistry of red residua underlying dolomites in karst terrains of Yunnan–Guizhou Plateau II. The mobility of rare earth elements during weathering. Chem. Geol. 203, 29–50.

Johannesson, K.H., Zhou, X., 1999. Origin of middle rare earth element enrichments in acid waters of a Canadian high artic lake. Geochim. Cosmochim. Acta 61, 153–165.

Johannesson, K.H., Lyons, W.B., Yelken, M.A., Gaudette, H.E., Stetzenbach, K.J., 1996. Geochemistry of the rare-earth elements in hypersaline and dilute acidic natural soil waters: complexation behaviour and middle rare-earth element enrichments. Chem. Geol. 133, 125–144.

Kutle, A., Nađ, K., Obhođaš, J., Oreščanin, V., Valković, V., 2004. Assessment of environmental condition in the waste disposal site of ex-aluminum plant near Obrovac in Croatia. X-Ray Spectrom. 33, 39–45.

Leybourne, M.I., Goodfellow, W.D., Boyle, D.R., Hall, G.M., 2000. Rapid development of negative Ce anomalies in surface waters and contrasting ERZ patterns in groundwaters associated with Zn-Pb massive sulphide deposits. Appl. Geochem. 15, 695–723.

Livergood, R., 2010. Rare Earth Elements: A Wrench in the Supply Chain. Center for Strategic and International Studies. http://csis.org/files/publication/101005_DIIG_Current_Issues_no22_Rare_earth_elements.pdf.

Long, K.R., Van Gosen, B.S., Foley, N.K., Cordier, D., 2010. The Principal Rare Earth Elements Deposits of the United States—A Summary of Domestic Deposits and a Global Perspective. U.S. Geological Survey, Reston, Virginia, pp. 104.

López-González, N., Borrego, J., Carro, B., Grande, J.A., De la Torre, M.L., Valente, T., 2012. Rare-earth-element fractionation patterns in estuarine sediments as a consequence of acid mine drainage: a case study in SW Spain. Bol. Geol. Min. 123 (1), 55–56.

McLennan, S.M., Taylor, S.R., 2012. Geology, geochemistry, and natural abundances of the rare earth elements. In: Encyclopedia of Inorganic and Bioinorganic Chemistry. John Wiley & Sons, Ltd. http://dx.doi.org/10.1002/9781119951438.eibc2004.

Miko, S., Durn, G., Prohić, E., 1999. Evaluation of terra rossa geochemical baselines from Croatian karst regions. J. Geochem. Explor. 66 (1–2), 173–182.

Muhs, D.R., Budahn, J.R., 2009. Geochemical evidence for African dust and volcanic ash inputs to terra rossa soils on carbonate reef terraces, northern Jamaica, West Indies. Quat. Int. 196, 13–35.

Nozaki, Y., Lerche, D., Alibo, D.S., Snidvongs, A., 2000. The estuarine geochemistry of rare earth elements and indium in the Chao Phraya River, Thailand. Geochim. Cosmochim. Acta 64, 3983–3994.

Ochsenkühn-Petropoulou, M., Lyberopoulou, T., Parissakis, G., 1994. Direct determination of lanthanides, yttrium and scandium in bauxites and red mud from alumina production. Anal. Chim. Acta 296, 305–313.

Ochsenkühn-Petropoulou, M., Lyberopoulou, T., Parissakis, G., 1995. Selective separation and determination of scandium from yttrium and lanthanides in red mud by a combined ion exchange/solvent extraction method. Anal. Chim. Acta 315, 231–237.

Pavlović, G., Zupanič, J., Prohić, E., Tibljaš, D., 2002. Impressions of the biota associated with waterfalls and cascades from a Holocene tufa in the Zrmanja River canyon, Croatia. Geol. Croat. 55 (1), 25–37.

Rollinson, H.R., 1993. Using Geochemical Data: Evaluation, Presentation, Interpretation. Longman, pp. 352.

Sholkovitz, E.R., 1990. Rare earth elements in marine sediments and geochemical standards. Chem. Geol. 88, 333–347.

Sholkovitz, E.R., 1992. Chemical evolution of rare earth elements: fractionation between colloidal and solution phases offiltered river water. Earth Planet. Sci. Lett. 114, 77–84.

Sholkovitz, E.R., 1993. The geochemistry of rare earth elements in the Amazon River estuary. Geochim. Cosmochim. Acta 57, 2181–2190.

Sholkovitz, E.R., 1995. The aquatic chemistry of rare earth elements in rivers and estuaries. Aquat. Geochem. 1, 1–34.

Sholkovitz, E., Szymczak, R., 2000. The estuarine chemistry of rare earth elements: comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems. Earth Planet. Sci. Lett. 179, 299–309.

Sholkovitz, E.R., Landing, W.M., Lewis, B.L., 1994. Ocean particle chemistry: the fractionation of rare earth elements between suspended particles and seawater. Geochim. Cosmochim. Acta 58, 1567–1580.

Sholkovitz, E.R., Elderfield, H., Szymczak, R., Casey, K., 1999. Island weathering: river sources of rare earth elements to the Western Pacific Ocean. Mar. Chem. 68, 39–57.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Oxford, pp. 29–45.

Tsirambides, A., Filippidis, A., 2012. Metallic mineral resources of Greece. Cent. Eur. J. Geosci. 4 (4), 641–650.

Van Middlesworth, P.E., Wood, S.A., 1998. The aqueous geochemistry of the rare earth elements yttrium: part 7. ERZ, Th and U contents in thermal springs associated with the Idaho batholith. Appl. Geochem. 13, 861–884.

Viličić, D., 1989. Phytoplankton population density and volume as indicators of eutrophication in the eastern part of the Adriatic Sea. Hydrobiologia 174, 117–132.

Viličić, D., Orlić, M., Burić, Z., Carić, M., Kršinić, F., Jasprica, N., Smirčić, A., Gržetić, Z., 1999. Patchy distribution of phytoplankton in a highly stratified estuary (the Zrmanja estuary, October 1998.). Acta Bot. Croat. 58, 105–125.

Viličić, D., Terzić, S., Ahel, M., Burić, Z., Jasprica, N., Carić, M., Caput Mihalić, K., Olujić, G., 2008. Phytoplankton abundance and pigment biomarkers in the oligotrophic, eastern Adriatic estuary. Environ. Monit. Assess. 142, 199–218.

Vlasov, K.A., 1966. Geochemistry and Mineralogy of Rare Elements and Genetic Types of their Deposits – Vol. 1 Geochemistry of Rare Earth Elements, IPST No. 2123. Israel Program for Scientific Translation, Jerusalem, pp. 945.

Wagh, A., Pinnock, W., 1987. Occurrence of scandium and rare earth elements in Jamaican bauxite waste. Econ. Geol. 82, 757–761.

Wang, Y., Sun, J., Chen, H., Guo, F., 1997. Determination of the contents and distribution characteristics of REE in natural plants by NAA. J. Radioanal. Nucl. Chem. 219, 99–103.
Wang, L.H., Huang, X.H., Zhou, Q., 2008. Effects of rare earth elements on the distribution of mineral elements and heavy metals in horseradish. Chemosphere 73, 314–319.
Whitehead, N.E., Hunt, J., Leslie, D., Rankin, P., 1993. The elemental content of Niue Island soils as an indicator of their origin. N. Z. J. Geol. Geophys. 36, 243–255.
Yalcin, M.G., Ilhan, S., 2008. Major and trace element geochemistry of terra rossa soil in the Kucukkoras region, Karaman, Turkey. Geochem. Int. 46 (10), 1038–1054.
Zhang, X., Quine, T.A., Walling, D.E., 1998. Soil erosion rates on sloping cultivated land on the Loess Plateau near Ansai, Shaanxi Province, China: an investigation using 137Cs and rill measurements. Hydrol. Process. 12 (1), 171–189.
Zhang, F.S., Yamasaki, S., Kimura, K., 2001. Rare earth element content in various waste ashes and the potential risk to Japanese soils. Environ. Int. 27, 393–398.
Zhang, C., Li, Q., Zhang, M., Zhang, N., Li, M., 2013. Effects of rare earth elements on growth and metabolism of medicinal plants. Acta Pharm. Sin. B 3 (1), 20–24.