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Rare Earth Elements in the Seagrass *Zostera noltei* Hornemann 1832 from the Black Sea Coast of Crimea

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Abstract: Due to the expansion of applications of rare earth elements (REE) in various technological processes, increasing amounts of these metals enter the environment, including the marine one, as pollutants. Very little is known about the bioaccumulation and toxicity of REE in marine organisms. In the present work, we assessed the contents of these metals, including yttrium and scandium, in rhizomes and leaves of the widespread seagrass *Zostera noltei* and in the nearby sediment from the Black Sea coast. The total REE content in the sediment was found to be much higher than in *Z. noltei*. The relative abundance of light REE (Sc, Y, La - Sm) in the sediment was comparable with that in the upper continental crust, unlike relative abundance of heavy REE (Eu – Lu), which was higher in the sediment than in the upper continental crust. The order of decrease in the major REE contents in the sediment and the seagrass rhizomes was identical, except for La and Y: La was the most abundant in the sediment and Y in the rhizomes. The contents of all REE in rhizomes of *Z. noltei* were 1.5–10 times higher than in leaves. The greatest difference in the REE contents was found for the minor heavy elements (Sm–Lu). Translocation factors for Sc and the minor elements (excluding Tb) from sediments to rhizomes and from rhizomes to leaves turned out to be pairwise equal, which indicate the similarity of the REE translocation mechanisms. Comparing our results with the literature data, it is possible to conclude that the seagrass *Z. noltei* does not have an advantage in the REE accumulation over marine macroalgae. However, large coastal deposits of this seagrass after storms allow it to be considered as a possible resource of REE.

Keywords: rare earth elements; seagrass *Zostera noltei*; leaves; rhizomes; sediments; Black Sea

1. Introduction

Environmental pollution with various types of toxic inorganic, organic and organometallic compounds is one of the most serious environmental issues in the world. Rare earth element pollution in the marine environment is an emerging problem that has unpredictable consequences for marine ecosystems.

According to the definition of International Union of Theoretical and Applied Chemistry (IUPAC), rare earth elements (REE) are a group of 17 elements, including 15 lanthanoids (metals from lanthanum to lutetium), scandium and yttrium [1]. All rare earth elements are widespread but scattered in the earth's crust, and they are found in more than 200 minerals, such as carbonates, silicates, and phosphates. The exception is the radioactive promethium, which is extremely rare in nature as it has no stable or long-lived isotopes [2]. Due to their unique physical and chemical properties, REE are of decisive importance for the development of a multitude of industrial technologies and products encompassing the range from cell phones and TVs to LEDs and wind turbines. These elements are indispensable components of magnetic, optical, and electronic devices used in the defense and aerospace industries for the production of unmanned aerial vehicles, guided missiles, laser guidance devices for satellite communications, etc. [3-5]. REEs are used in agriculture as supplements to fertilizers to improve crop growth and production and thus are accumulated in the soil [6,7]. As the use of rare earth elements increases, their release into the biosphere will inevitably grow [8,9].

There are a large number of studies on adverse effects of notoriously toxic elements, such as As, Pb, Cd and Hg [10,11] on biota. However, many other elements, including rare earth elements, are increasingly used in industry, and dumping of huge amounts of waste contributes to their ingress into the soil and groundwater. The background REE levels in waters vary greatly and depend mainly on local geology. Under natural conditions, REE are transferred only in small amounts through groundwater and the atmosphere, but their widespread use in recent times has increased the REE pollution and created new routes of REE bioaccumulation (in plants, animals and humans). Use of modern analytical methods, such as inductively coupled plasma mass spectrometry (ICP-MS), helps improve our understanding of reactivity and mobility of REE in the near-surface environment, their bioavailability and possible risks to human health [12-14]. At the same time, the information on REE effects on human health is very limited at present [15,16].

The determination of REE in marine aquatic organisms is an important aspect of studying the distribution of these elements in the environment. Currently, the REE levels in flora and fauna of aquatic systems are not considered hazardous, but with the increasing use of these elements, the situation may change for the worse in the near future [17]. High degrees of REE bioaccumulation were found in phytoplankton [18] and in mussel shells in rivers of Europe and North America [19], proving their bioavailability and ability to accumulate along the food chain. A possible risk to the environment lies in the bioavailability of REEs and their tendency to fractionate depending on environmental conditions, especially on the water pH and the nature of the solids [17]. Sediment characteristics such as Fe content can limit the transport of rare earth elements due to complexation reactions [20]. Currently, there is evidence of elevated levels of REE in various natural systems, for example, of an anomalously high contents of Ce mainly in the warm surface layer of the Black Sea [21] and Gd near densely populated areas with developed medical care facilities due to the use of Gd as a contrast agent in magnetic resonance imaging [17].

The quantitation of REE in marine biota is important for determining their levels in the environment. Along with other macrophytes, seagrasses are an important link in the matter and energy cycles in coastal ecosystems [22,23]. Therefore, seagrasses can serve as efficient bioindicators of REE pollution in the marine environment [24]. Moreover, they can be useful in the REE extraction from natural waters and wastewater with the prospect of REE recycling and water bioremediation [25,26].

Seagrasses act as important natural archivers of anthropogenic activity. By accumulating and immobilizing contaminants from sediments, they can be used as an indicator of short- and long-term changes in metal fluxes to the coastal ecosystem [27-29]. There is currently very little information on interactions between seagrasses and pollutants, including REE, as well as estimates of the REE transfer from sediments to seagrass [29]. The purpose of this work is to study the distribution of REE in rhizomes and leaves of the seagrass *Zostera noltei* as a possible indicator of REE pollution in coastal areas of the Black Sea and a potential agent for the REE recovery and bioremediation.

2. Materials and Methods

The seagrass *Zostera noltei* was collected in Kazachya Bay (Black Sea coast of Crimea) in June at a depth of 0.5–1 m (Figure 1). After removal of visible epiphytes, the leaves and rhizomes of *Z. noltei* were rinsed with distilled water, crushed and dried to constant weight at 105 °C. For the REE quantitation, 20 mg samples of dry biomass were used. The sediment was sampled from different, randomly selected, nearby sites and thoroughly mixed to eliminate local heterogeneities in the content of elements. The sediment was also dried to constant weight, ground in a porcelain mortar, and sifted through a sieve with a mesh size of 0.5 mm. All samples were prepared in 4–5 replicates.

The sample digestion was performed for two hours using analytical-grade nitric acid purified by sub-boiling distillation in an acid purification system DST-1000 (Savillex, USA) in capped PTFE tubes in an autoclave at 2.2 bar. The digested samples were diluted with deionized water to 1000 $mL\cdot g^{-1}$ d.w. The REE concentration was measured on an ICP-MS instrument PlasmaQuant® MS Elite (Analytik Jena, Germany) using multielement standards IV-ICPMS-71A,D (Inorganic Ventures, USA). The limits of REE detection on this instrument at this dilution are no higher than 0.03 $\mu g\cdot kg^{-1}$

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d.w. [30]. Quality assurance and quality control of this analysis was provided by trace element quantitation in certified reference materials ERM®-CD200 (seaweed Fucus vesiculosus) and BCR®-670 (duckweed Lemna minor) after digestion in nitric acid according to the above procedure.

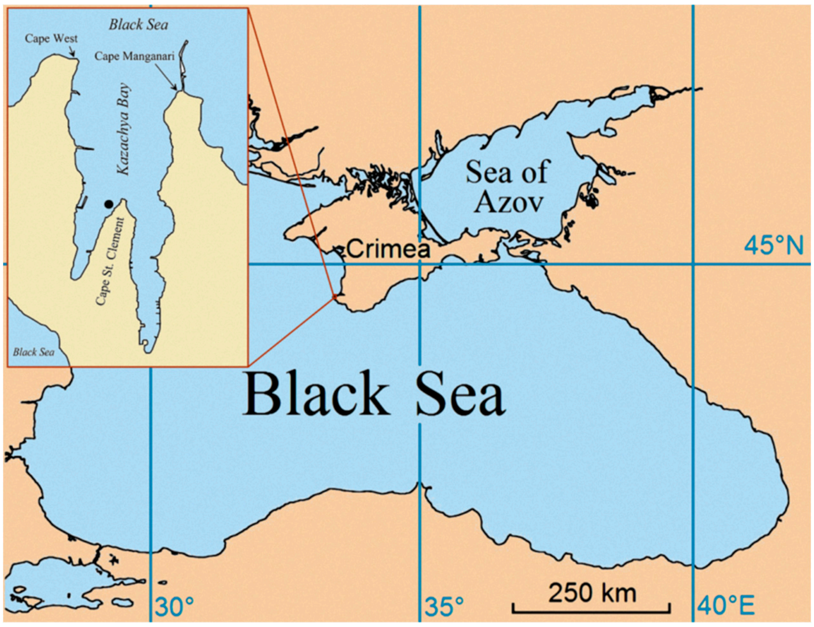

Figure 1. Map of the sampling area (inset). The sampling site is denoted by black circle.

Each analyte was measured in five replications, five scans per replicate. The plasma flow was 9.0 L·min^{-1}, and the RF power was 1.25 kW. The dwell time for each analyte was 50 ms, one point per peak in the peak-hopping mode. To ensure the insignificance of polyatomic interferences, collision reaction interface (CRI) was used as well. In the CRI, hydrogen with the flow rate 40 mL·min^{-1} was the skimmer gas. No internal standard was used. The signal drift was taken into account by measuring the element concentrations in the diluted standard IV-ICPMS-71A,D after every fifth sample.

Statistical analysis of the measurement results was carried out using one-way ANOVA in PAST 4.12 [31]. The post hoc pairwise comparison was performed using Tukey's test. In case of heterogeneity of variances detected in Levene's test, the averages were compared according to the Welch F-test and pairwise Games-Howell test in Matlab 8.2.0 [32]. Hierarchical cluster analysis was performed using PAST 4.12, with the Euclidean distance as the similarity measure and unweighted pair-group average (UPGMA) as the pairwise clustering algorithm.

To estimate whether or not REE in the sediments originate mainly from the rock weathering, the enrichment factor (EF) was calculated as follows [33]:

$$EF = (REE/Al)_{s} / (REE/Al)_{UCC} \quad (1)$$

where the subscript "s" denotes sediments and "UCC" refers to the average values in the upper continental crust. The upper continental crust values [34,35] were taken as reference because the corresponding average values represent the average source rock composition [36]. In Eq. (1), REE are normalized to the aluminium content as the ratio of REE to Al in the weathering products is approximately the same as in the source rock [37].

The REE transfer from sediments to the different parts of the seagrass and the translocation from rhizomes to leaves are characterized with the transfer factors (TF) and translocation factor (TF'), respectively, which can be expressed in a straightforward manner as

$$TF = C_{seagrass} / C_{s} \quad (2)$$

where "seagrass" stands for either seagrass rhizomes or leaves, and

$$TF' = C_l / C_r \tag{3}$$

where the subscripts "l" and "r" denote leaves and rhizomes, respectively. TF>1 indicates the REE bioaccumulation in a marine organism, and the greater TF, the more mobile and bioaccessible element forms are in the sediment environment [38].

3. Results and discussion

3.1. REE contents in the seagrass and sediments

The REE contents in sediments were much higher than those in different parts of the seagrass (Table 1). The contents of the light REE in *Z. noltei* rhizomes decreased in the following order: Y > La > Ce > Sc > Nd > Pr. For *Z. noltei* leaves, this order was different: Sc > La > Ce > Y > Pr > Nd. In sediments, the Nd content exceeded that of Sc, and the sequence changed to La > Y > Ce > Nd > Sc > Pr. Thus, the elements in rhizomes and sediments, except for La and Y, had the same decreasing order. A similar order of the element decrease was observed in Bohai Bay situated west of the Bohai Sea, but the major element was Ce [39]. The coastal region surrounding Bohai Bay is one of China's most densely populated and industrialized areas, where approximately 97% of REE are produced, and industrial and agricultural use of the elements is growing rapidly [40]. Compared to this region, the concentration of REE in the Black Sea, according to our data, was lower by a factor of 2 for La and 8-11 for all other REEs [39], which indicates a relatively low concentration of elements in the sediments of the Crimean coast of the Black Sea.

On the whole, the abundance of all REE in rhizomes was 1.5-10 times higher than in leaves. Moreover, the contents of heavy REE (Sm–Lu) differed by a factor of 7–8 (Table 1). Among all REE, the highest content was noted for Y in rhizomes of *Z. noltei*. In sediments, the highest content was registered for La. In the general case, the order of the REE decrease in different objects was as follows: sediments > rhizomes > leaves. The exceptions were Sc and La in rhizomes and leaves, where abundances of these elements did not differ significantly.

Cluster analysis of the REE contents in the seagrass (Figure 2) showed the division of elements into two groups: major (Sc, Y, La–Nd) and minor (Sm–Lu). Major REE are characterized by the levels of hundreds to thousands $\mu g \cdot kg^{-1}$ in rhizomes and tens to hundreds $\mu g \cdot kg^{-1}$ in leaves. Minor REE have the values of tens to hundreds $\mu g \cdot kg^{-1}$ in rhizomes and up to ten $\mu g \cdot kg^{-1}$ in leaves. The abundance of REE in marine organisms, excluding filter feeders, is due to the element contents in sediments and suspended particles rather than to the amount of REE dissolved in seawater [41]. In seawater, light REE are to a greater extent absorbed by organisms or adsorbed on their surfaces given that small ionic radii of heavy REE allow them to remain in solution due to the formation of stable complexes [17]. There is a small percentage of free ionic REE, mainly light REE, in the solution, which are easily incorporated into organisms [17,42] and may potentially have serious biological consequences. Another explanation for the fractionation of REE in seawater is associated with diatoms [43], which absorb these elements in the sea surface layer and transport them to the deeper waters. Light REE tends to be bound to carbonates and oxides and are thus more accumulated than heavy REE in the surficial layer of sediments. This may serve as an explanation for the enrichment of the composition of ocean waters with heavy REEs.

Table 1. REE contents (in $\mu g \cdot kg^{-1}$ d.w.) in leaves and rhizomes of *Zostera noltei* and in sediments: mean ± SD; transfer factors for rhizomes (TF_r) and leaves (TF_l); and the rhizomes – leaves translocation factors (TF'). The different upper subscript letters denote significant differences between the element contents in the objects of research: a < b < c.

	***Z. noltei* (leaves)**	***Z. noltei* (rhizomes)**	**Sediments**	**TF_r**	**TF_l**	**TF'**
Sc	373 ± 22^a	560 ± 15^a	1382 ± 77^b	0.405	0.270	0.666
Y	153 ± 9^a	1562 ± 18^b	12221 ± 646^c	0.128	0.012	0.098
La	243 ± 26^a	761 ± 112^a	17074 ± 614^b	0.045	0.014	0.320
Ce	221 ± 9^a	648 ± 25^b	6232 ± 89^c	0.104	0.035	0.341
Pr	87 ± 3^a	174 ± 11^b	1162 ± 18^c	0.150	0.075	0.499

Nd	38±3^{a}	267±49^{b}	2894±37^{c}	0.092	0.013	0.145
Sm	8.2±0.4^{a}	65±6^{b}	635±19^{c}	0.102	0.013	0.126
Eu	2.6±0.4^{a}	21.7±1.3^{b}	175±6^{c}	0.124	0.015	0.122
Gd	10.4±0.3^{a}	75±6^{b}	671±16^{c}	0.112	0.015	0.138
Tb	6±1^{a}	22±3^{b}	184±8^{c}	0.121	0.033	0.270
Dy	11±1^{a}	72±7^{b}	551±27^{c}	0.131	0.019	0.146
Ho	2.4±0.3^{a}	19±1^{b}	131±4^{c}	0.144	0.018	0.125
Er	7.3±0.6^{a}	53±4^{b}	386±13^{c}	0.136	0.019	0.139
Tm	1.5±0.1^{a}	9±2^{b}	49±2^{c}	0.190	0.031	0.164
Yb	5.1±0.7^{a}	35±2^{b}	241±13^{c}	0.145	0.021	0.146
Lu	1.7±0.2^{a}	9.3±3.4^{b}	45±2^{c}	0.206	0.038	0.183
ΣREE	1171.2	4353	44033			

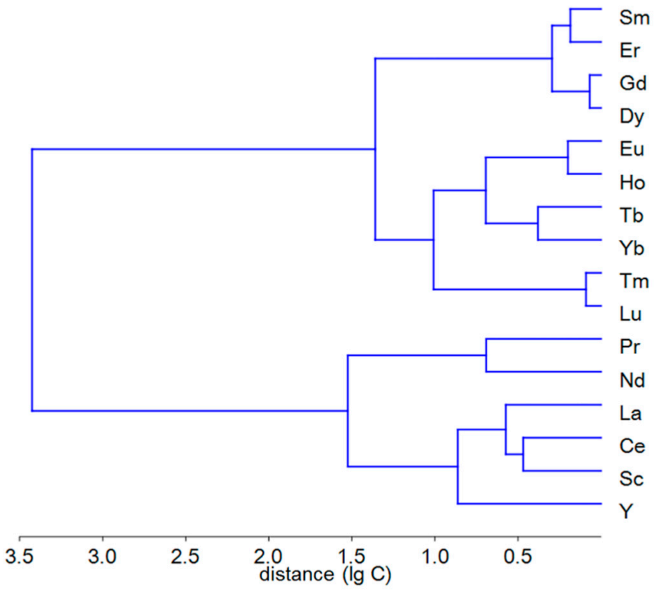

Figure 2. Dendrogram of the Euclidean distances of log-transformed REE contents in rhizomes and leaves of *Zostera noltei.*

Contemporary studies show that REE are present in almost all parts of the human body in low concentrations and may play an important biological role [44]. On the other hand, the REE concentration in drinking water exceeding the ordinary levels by a factor of seven may pose a potential risk to health [18]. There is a lack of data on the content of REE in terrestrial and marine organisms, especially in the latter. Therefore, the role of REE in marine organisms requires further research. One of a few reviews on REE in aquatic biota [17] summarized data on REE in various marine organisms, such as algae, mollusks, crustaceans, corals and fish. Low REE levels were found in wild corals and even lower ones were in fish. The highest content of these elements was found in algae; in addition, algae can accurately indicate the provenance of REE, seawater or sediments [45]. For example, the macroalga *Gracilaria gracilis* can efficiently absorb and trap REE from wastewater with low REE concentrations in it [46]. The REE accumulation in marine organisms may depend on trophic level; however, biomagnification does not appear to occur [17].

The total REE content in the seagrass *Z. noltei* from the Black Sea is 4–20 times lower than in the seagrass *Halodule wrightii* collected in Todos os Santos Bay on the east coast of Brazil [29]. It is noteworthy that the total REE content in sediments on the coast of Brazil was only 1.2–2 times higher than in the plant. This indicates that the ability of *Z. noltei* to accumulate REE is relatively low. Unlike *Z. noltei*, no significant difference in the REE contents was registered between roots and leaves of *H. wrightii*. The authors of [29] also concluded that seagrasses and their tissues have a low potential for REE bioaccumulation as the highest REE values in sediments at one of the stations did not correspond to the highest levels of REE accumulation in the plants.

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In another seagrass species, *Cymodocea nodosa,* the REE contents were significantly higher in leaves and not in the underground parts of the plant, with the light REE (La, Ce, Pr, Nd) being 1.7 times higher in abundance [33]. The contents of La–Lu in *C. nodosa* leaves were an order of magnitude higher than those obtained in the present study. In the underground parts, the REE contents were comparable to our data with the exception of Ce, Nd, Sm and Gd, which were also higher in *C. nodosa*. The contents of Pr–Lu, except for Tb, in sediments were 5.5–7 times higher, and the contents of Ce and La were 9 and 1.5 times higher, respectively. It is noteworthy that the REE in rhizomes of *Z. noltei* were almost equal to those in *C. nodosa*, with the abundance in sediments being significantly lower.

The difference in the REE contents in seagrasses can be explained, among other possible reasons, by different physicochemical properties of the sediments since the REE absorption through roots is affected by the concentration of iron oxyhydroxide, pH and redox potential in the rhizosphere and cation exchange capacity of sediments. Organic and inorganic ligands also play an important role in the REE uptake by plant roots and REE speciation, and affinity for plasma membrane affects uptake of individual elements [47]. There are two different patterns of the REE distribution: in plants and in sediments, and the contents of REE in plants do not correlate with those in the rhizosphere [47] probably due to the plant control of REE uptake [48].

Some elements play an important role in the life of organisms, and they are referred to as essential macro- and micronutrients. In some cases, biochemical functions of trace elements are extremely complex as they involve interactions with other elements and can have dose-dependent effects of different signs and intensities [49]. To date, the biological role of REE remains unknown, but it was shown in some studies that they can have both negative and positive influence on animals [50,51]. As a result, it has been shown that REEs are involved in the activity of a wide range of enzymes; it was also discovered that rare earth elements, namely Ce^{3+} and La^{3+}, are necessary for some bacteria to promote methanol oxidation reaction [52]. The biochemical action of rare earth elements is largely due to the closeness of their ionic radii to those of other, essential elements. For example, the Ca^{2+} cation can be replaced by trivalent lanthanide ions at calcium binding sites in biological molecules [51]. The largest amount of Ca^{2+} is contained in the plant cell wall in the form of calcium pectinate. By replacing Ca^{2+}, REE form complexes with pectin, and their trivalency gives them a much higher charge-to-volume ratio, which means that they have a much higher affinity than Ca^{2+} for these binding sites [53,54]. REE are assimilated to a greater extent compared to other non-essential elements. For example, La^{3+} and Eu^{3+} were found in membranes of chloroplasts, mitochondria, cytoplasm and nuclei [47,55]. REE are evenly distributed in membranes of chloroplasts and thylakoids, where most of them are associated with the photosystem II complex [54].

3.2. REE enrichment and anomalies in sediments

Enrichment factors (EF) calculated according to Eq. (1) are shown in Figure 3. Heavy REE demonstrates considerable enrichment compared to primordial rock composition. They are above the natural variability ranges [56] whereas light REE are within or below (Ce, Nd) the geochemical limits. There are two other facets in the REE enrichment pattern that need to be emphasized. One of them is the clear manifestation of the “inverse Oddo-Harkins” effect: the elements that are more abundant in the crust demonstrate smaller enrichment factor and vice versa. The other one is a trend of the EF increase with the atomic number.

The “inverse Oddo-Harkins” pattern can be explained by the smoothened REE distribution in complex natural objects such as bottom sediments, which bear the imprint of a random interplay of various mineralogical, biological and chemical processes that affect their composition, with smoothing out the differences in the REE abundances. The EF growth in heavy REE can be the consequence of these processes as well, but it can also result from multiple cycles of element adsorption from the water column, enriched with heavy REE, by suspended organics (including phytoplankton), its subsequent sedimentation, resuspension and remobilization [57]. Because the sediments are not enriched with light REE with respect to the continental rock, the anthropogenic contribution to the REE accumulation in Kazachya Bay can be considered negligible.

Anomalies of Ce and Eu are important indicators of biogeochemical conditions in the environment [33,36]. Their most characteristic implication is the information on the surrounding redox conditions. A relative depletion in Ce, when insoluble CeO_2 is reduced to soluble Ce^{3+}, represents an example of the negative Ce anomaly and indicates the reductive conditions, whereas the relative Ce enrichment is the positive Ce anomaly that suggests the oxidative environment. The Eu anomalies are opposite to those of Ce in terms of reaction to redox conditions and are typically considered in mineralogy. In the reductive conditions, ions of Eu^{2+} substitute for Ca^{2+} in some minerals such as feldspars in hydrothermal, metamorphic and magmatic processes and form positive Eu anomaly, whereas in oxidative conditions Eu occurs in the form of Eu^{3+} ions, which do not have such an ability, and negative or no Eu anomaly is observed. The element anomalies can be calculated using the following relationships [33]:

$$\delta Ce = Ce_N / (La_N \times Pr_N)^{1/2} \qquad (4)$$

and

$$\delta Eu = Eu_N / (Sm_N \times Gd_N)^{1/2} \qquad (5)$$

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

In our case, $\delta Eu = 1.26$ did not essentially differ from the values for the other REE calculated according to similar relationships (0.73–1.57), which implies the absence of any Eu anomaly. However, $\delta Ce = 0.32$ was substantially lower, and this suggests the existence of negative Ce anomaly in the sediment. This anomaly is also seen in the minimum in the Ce enrichment factor in Figure 3. The negative Ce anomaly indicates the reductive environment in sediments of Kazachya Bay, which is due to the decay of organic material settling to the seafloor. A similar anomaly was detected in other sediments in reductive environments [33,58].

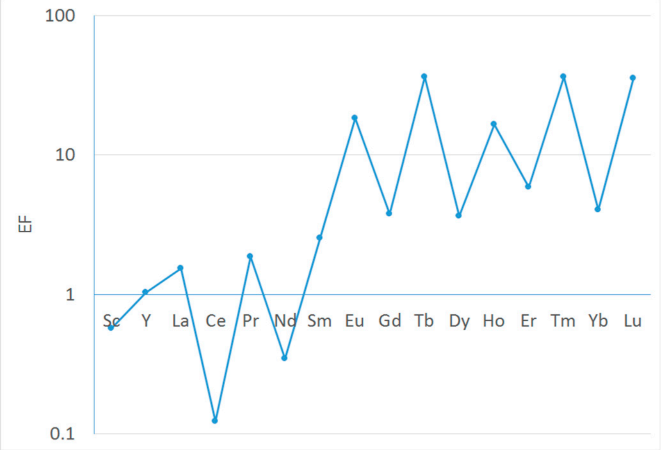

Figure 3. Enrichment factors of REE in the sediments in Kazachya Bay with respect to the upper continental crust.

3.3. REE transfer and translocation in the seagrass

Transfer factors associated with the transfer from sediment to rhizomes and leaves (TF_r and TF_l) and the rhizomes – leaves translocation factors (TF′) are presented in Table 1. All the factors are below 1, which confirm the low efficiency of REE uptake by the plant. The sediment – rhizomes transfer factors are up to an order of magnitude higher than the sediment – leaves transfer factors, with the efficiency of the REE transfer to leaves decreasing in the following order: Sc >> Pr > Lu > Ce > Tb > Tm > Yb > Dy = Er > Ho > Eu = Gd > La > Nd = Sm > Y. This fact is at odds with the data of the work [33], where the higher REE transfer to leaves of the seagrass *Cymodocea nodosa* was detected.

Consider the values reciprocal to TF′ and TF_r, namely the ratios of REE contents in rhizomes and leaves of *Z. noltei* and in the sediment and rhizomes (Figure 4). For Sc and minor REE, except for Tb, these ratios turned out to be almost pairwise equal, which fact implies the similarity of the mechanisms of their accumulation and translocation. To explain this phenomenon, it can be assumed that the differences in the REE content (ΔC) between sediments and rhizomes, rhizomes and leaves are proportional to their content (C) and differences in some factor (Δq) equal for the sediment – rhizomes and rhizomes – leaves interfaces:

$$\Delta C = kC\Delta q \tag{4}$$

In the small differences approximation, one can pass to the differential form of Eq (4), whence it follows that

$$C = C_s \exp(kq) \tag{5}$$

where C_s is the content in the sediment, and it is seen that equal intervals of q will change the content by an equal factor.

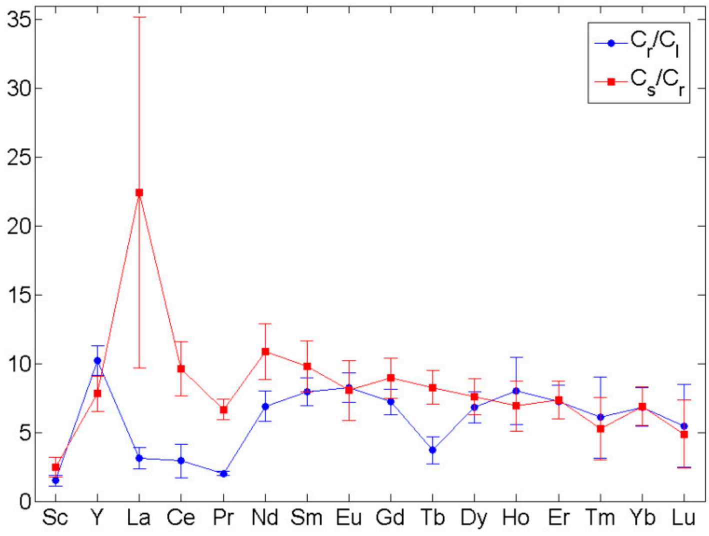

Figure 4. Ratios between the REE contents in sediments and rhizomes (C_s/C_r) and in rhizomes and leaves (C_r/C_l) of *Zostera noltei.*

It is likely that the q factor is related to the local pH value (more precisely, to the difference between local pH and pH of pore water), which goes down from the pore water to the juice of the plant leaves. It is well known that the pH decrease increases the solubility of sparingly soluble salts of REE and, consequently, reduces their ability to accumulate. REE can be accumulated in seagrass tissues by binding to plant matrix carboxyl or phosphate groups close in the binding energy to carbonates and phosphates in sediments; alternatively, REE can deposit on the corresponding inorganic microgranules in tissues. This assumption finds indirect confirmation in the high correlation coefficients with calcium (median $r = 0.99$), which was also noted in the algae of the genus *Cystoseira* [59].

The changes in the C_s/C_r ratio (Figure 3) represent the well-known tendency towards an increase in the solubility of lanthanide phosphates and carbonates with the atomic number increase [60,61]. The reduced values of C_r/C_l for La–Nd and Tb can be explained by the substitution for yttrium in rhizomes and/or the formation of specific soluble complexes of these elements in leaves. On the whole, the seagrass *Z. noltei* does not have an advantage in the accumulation of REE compared to other native macrophytes (*Cystoseira* spp.) [59] due to the low translocation efficiency through the root system, which was also noted for the South American species of the seagrass *Halodule wrightii* [29].

3.4. Seagrass wrack as a potential source of REE

Availability and extractability of REE from various natural sources other than minerals is an important issue associated with the commercial use of REE in the future [62]. Currently, the everincreasing number of applications of REE and high added value of REE-containing products have led to an increase in the REE production volumes. Therefore, research on minimizing industrial production losses and more cost-effective extraction of REE with the least environmentally-unfriendly consequences is in an increasing demand [63]. As a result of processing algal and seagrass biomass, including storm-cast deposits (beach wrack), it is possible to produce various types of biofuels, including biodiesel, bioethanol, biogas, biohydrogen and other valuable products [64]. As storm-cast beach wreck of algae and seagrass can be also a source of REE and bioremediate industrial wastewater, further research in this direction is strongly needed.

The Black Sea has extensive natural resources of macrophytes, including seagrasses. In late summer and early autumn, seagrasses shed their leaves and after each storm their mass deposits appear on the coastline (Figure 5). They are most widespread in Kerch Strait and in Tendra, Dzharylgach, Yegorlyk and Karkinit bays.

Figure 5. Seagrass deposits on the Black Sea coast after storm in (a) Kazachya Bay, (b) Karkinit Bay near the Portovoye settlement.

An assessment of storm-cast deposits of the seagrass as a possible source of REE can be made. According to our data, the average REE concentration in seagrass leaves is 0.4 mg·kg^{-1} w.w. After only one storm, the seagrass biomass washed ashore can be estimated at 10 tons per linear kilometer of the coast of the southern part of Karkinit Bay [65]. This biomass contains approximately 4 kg of rare earth elements. Estimating the reserves of the deposits of the seagrass on the Black Sea shoreline at hundreds of thousands of tons [66], one can arrive at REE reserves in the coastal seagrass deposits of up to 100 tons. However, a comprehensive environmental analysis is clearly needed for the large-scale use of the deposits of macrophytes for the extraction of REE and other useful materials from them.

4. Conclusions

Various factors in marine ecosystems (carbon source and content, particle size distribution, pH, salinity) play a fundamental role in the biogeochemical cycles of REE and determine their bioavailability and accumulation in sediments. Studies in local ecosystems make a significant contribution to the understanding of these processes. As the example, the significantly lower REE concentrations in *Z. noltei* compared to their content in the sediments demonstrate the low ability of the seagrass to accumulate these elements, which feature may also be related to the characteristics of marine sediments in this area.

Ratios of the contents of Sc and minor REE, except for Tb, in rhizomes and leaves of *Z. noltei* and in sediments and rhizomes turned out to be very close, which probably indicate the similarity of mechanisms of the REE accumulation and translocation and are possibly associated with the difference between the local pH value and the pH of pore waters. This work represents the first quantitative determination of a complete set of rare earth elements (except for promethium) in the seagrass *Z. noltei* and in the bottom sediments surrounding it. The obtained results can be used to further study REE in the Black Sea ecosystems and to monitor these elements in the marine environments.

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