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Abstract

The concentrations of rare earth elements (REE) were determined by ICP-MS in dominant seaweed species, collected from three locations of the northwestern Mediterranean Sea. This is the first study to define levels and patterns of REE in macro algae from these coastal areas.

Rare elements are becoming emerging inorganic contaminants in marine ecosystems, due to their worldwide increasing applications in industry, technology, medicine and agriculture.

Significant inter-site and interspecies differences were registered, with higher levels of REE in brown and green macro algae than in red seaweeds. Levels of light REE were also observed to be greater compared to heavy REE in all samples.

One of the investigated locations (Bergeggi, SV) had higher REE and ΣREE concentrations, probably due to its proximity to an important commercial and touristic harbor, while the other two sites were less affected by anthropogenic contaminations, and showed comparable REE patterns and lower concentrations.

Capsule: rare earth elements in seaweeds

Keywords: REE, seaweeds, Mediterranean Sea, pollution tracers.

1. Introduction

Rare earth elements (REE) are a group of chemical elements including yttrium (Y), scandium (Sc) and lanthanides (from lanthanum to lutetium). Despite their name, REE are not that rare in the natural environment, being the fifteenth most abundant component of the earth's crust (USEPA, 2012). REE are further subdivided into light REE (LREE), including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd) and samarium (Sm); and heavy REE (HREE), including gadolinium (Gd), europium (Eu), terbium (Tb), dysprosium (Dy), thulium (Tm), ytterbium (Yb), holmium (Ho), erbium (Er), lutetium (Lu) and yttrium (Y) (Anastopoulos et al., 2016).

REE mainly enter into oceans through atmospheric fallout (De Baar et al., 1983) and fluvial inputs (Frost et al., 1986), and have been frequently investigated as natural tracers of biogeochemical processes (Oliveri et al., 2010). As the distribution patterns of REE in the water column are already known, it is possible to utilize these patterns for tracing water masses or to identify pollution sources in seawater (Censi et al., 2004).

In fact, in the last decade, the worldwide use of REE in industrial applications (electronics, nuclear energy, metallurgy, medicine, computer manufacturing) and in some countries (such as China) for use in fertilizer and feed additives, has increased levels of REE in water environments (Mashitah et al., 2012; Hermann et al., 2016). Thus, REE can be considered as emerging contaminants and pose a potential risk for marine and freshwater ecosystems.

The Mediterranean Sea is a semi-enclosed sea; concentrations of trace elements and REE in this basin are higher than those registered in other nutrient-depleted surficial waters (Greaves et al., 1994; Strady et al., 2015). Numerous investigations regarding patterns of dissolved and particulate REE have been performed in this basin (e.g. Censi et al., 2004; Martinez-Boti et al., 2009; Tranchida et al., 2011; Roussiez et al., 2013; Ayache et al., 2016); conversely, occurrence and distribution of REE in marine biota have scarcely been investigated. To our knowledge, there are only two studies that have analyzed the distribution of REE in plankton from the Mediterranean Sea

(Strady et al., 2015; Battuello et al., 2017); examining REE in marine organisms is of great importance because of their increasing levels in seawater environments and, consequently, in the marine food chain.

Of the marine organisms that can be utilized as bioindicators of trace elements and REE in marine environments, seaweeds have several advantages as they are widespread, easy to collect and have a considerable ability to take-up trace elements in solution and concentrate them. Moreover, as they are at the base of the marine food chain, macro algae are essential in the transfer of trace elements to higher trophic levels.

We determined REE concentrations and distributions in seaweeds from three different sites located in Northwestern Mediterranean coastal areas. These sites have different environmental protection in the Ligurian and Northern Tyrrhenian Sea. The macro algae species collected for this study were the most abundant and widespread in all three sampling sites and were represented by the three phylum Chlorophyta (green algae), Ochrophyta (brown algae) and Rodophyta.

Macro algae species from these three locations were the subject of a previous investigation that focused on essential and nonessential trace elements, in the perspective of identifying the species potentially suitable for human and animal nutrition, as well to identify any potential risks for consumers due to the presence of toxic metals such as lead, cadmium and mercury in seaweeds of Mediterranean origin (Squadrone et al., under review).

In this study, we aimed to measure, for the first time, the concentrations of REE in marine Mediterranean seaweeds, identifying patterns and fractionations of REE, and verifying the potential use of REE as pollution tracers in the studied area.

2. Materials and methods

2.1. Sampling area

All three sampling locations were situated in the northwestern Mediterranean Sea (Figure 1).

The first sampling site was located in Bergeggi (SV), a Marine Protected Area of the Ligurian Sea (44°14'26. 94"N, 8°26'50. 98"E, General Reserve named B zone.) Here, human activities are restricted and regulated by the Italian law. Close to this site is located the industrial and commercial harbor of Vado Ligure (SV), characterized by high shipping traffic.

The second site was in the Island of Elba (Tyrrhenian Sea, 42°42'35. 17"N, 10°24'44. 97"E), five nautical miles off the Tuscan coast. Elba is the most populated island of the Tuscan archipelago, especially in summer.

The third sampling site was located in the little Capraia Island, (43°4'26. 90"N, 9°49'39.63"E, in the National Park of the Tuscan Archipelago, PNAT), another Marine Protected Area of the Ligurian Sea, about 30 nautical miles off Tuscan coast. The island has few inhabitants and no industrial activities.

Seaweed samples were collected in summer 2016. After collection, the macro algae were washed on board with seawater and then stored in refrigerated conditions. The specimens were transported to the laboratory and examined under the stereomicroscope, after being cut into thin sections, in order to identify the macro algae species. Before analyzing the seaweeds for REE content in the chemical laboratory, samples were rinsed with tap water, followed by a rinse with distilled water, then freeze-dried and homogenized to obtain a fine powder. Approximately 1-1.5 g of each sample were utilized for quantitation of REEs.

2.2 Determination of REE

Samples mineralization was performed using a microwave digestion lab station (Ethos 1, Milestone, Shelton, CT, USA), equipped with a 10 positions rotor for high pressures polytetrafluoroethylene (PTFE) digestion tubes.

All digestion tubes were cleaned with concentrated acid, rinsed with ultrapure water and dried at room temperature under a chemical hood. Disposable polypropylene tubes were used to storage mineralized samples. Freeze-dried samples (1.0-1.5 g) were directly weighed into PTFE digestion

106 tubes. 7 mL of HNO_3 (70% v/v) and 1.5 mL of H_2O_2 (30% v/v) were then added before the
107 microwave digestion process, programmed as follows: heating to 130°C in 8 min, hold for 2 min,
108 heating to 200°C in 8 min, hold for 5 min; cooling for 30 min. Digested samples were then
109 quantitatively transferred to 50 mL polypropylene tubes and gravimetrically diluted to a final
110 weight of 50 g with ultrapure water.
111 REE determination was performed by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS
112 Xseries II, Thermo Scientific, Bremen, Germany) equipped with a multi-vial auto sampler (ASX
113 520, CETAC Technologies, Omaha, NE, USA). Instrument was tuned daily before each analytical
114 trial. Certified Reference Materials (REE-1 from the National Institute of Standard and
115 Technology), blank reagents and standard solutions were processed during each analytical session
116 to verify performances of the methods. The limit of quantification (LOQ) was 0.010 mg Kg^{-1}.
117 Results were expressed in mg Kg^{-1} dry weight as the mean for each site with standard deviation; the
118 sum of REE (ΣREE), of light REE (LREE) and of heavy REE (LREE) are also shown (Table 1).
119 *2.3 Statistical analysis*

120 The one-way analysis of variance (ANOVA) was employed to compare the average contents of the
121 sum of REE (ΣREE) in macro algae between the three sampling sites and between the macro algae
122 species in the same site (Table 2). The unpaired t-test was used to compare the average contents of
123 ΣREE in macro algae between sites 2 and 3. Results were considered statistically significant at p
124 values of < 0.05. Graph Pad Statistics Software Version 6.0 (GraphPad Software, Inc., USA) was
125 used for statistical evaluations.

126 **3. Results and Discussion**

127 REE are typical lithophile elements, with scarce presence in biological tissues. Seaweeds
128 mostly develop in marine environments in contact with sediments and suspended particulate from
129 geologic origin is present in their environment. Therefore, fine geological particulate, containing
130 REE, are incorporated in plants tissues in different amounts.

131 The concentrations of REE in marine macro algae from the three collection sites of the
132 Northwestern Mediterranean Sea are shown in Table 1 (mg Kg^{-1} dry weight). REE and ΣREE are
133 also graphically presented for the three sites (Figure 2) and for the analyzed seaweeds (Figures 3
134 and 4), to facilitate comparison.
135 A high variability in REE concentrations between the three sampling sites and between species was
136 recorded; the REE concentrations, however, consistently followed the same trend, and
137 concentrations of LREE were always higher than HREE.
138 *3.1 Inter-site variability*
139 In Figures 2a and 2b, mean REE levels in the three sampling sites are graphically represented. As
140 shown, the specific area of collection greatly affected REE concentrations. In fact, macro algae
141 from site 1 (Bergeggi, SV) had the highest concentrations for all the analyzed REE (Table 1). In site
142 1, the highest REE values were found in the Ocrophyta *Halopteris filicina* (Ce 8.8 mg Kg^{-1}, La 4.3
143 mg Kg^{-1}, Nd 4.1 mg Kg^{-1}, Y 3.4 mg Kg^{-1}, Sc 1.5 mg Kg^{-1}, Pr 1.1 mg Kg^{-1}, Sm and Gd 0.87 mg Kg^{-1}, Dy 0.64 mg Kg^{-1}, Er 0.32 mg Kg^{-1}, Yb 0.27 mg Kg^{-1},Tb and Ho 0.22 mg Kg^{-1}, Eu 0.17 mg Kg^{-1},
145 Tm 0.80 mg Kg^{-1}, Lu 0.78 mg Kg^{-1}) and the lowest concentrations were found in the Rodhopyta
146 *Ganonema farinosum* (Ce 4.8 mg Kg^{-1}, La 2.5 mg Kg^{-1}, Nd 2.2 mg Kg^{-1}, Y 2.0 mg Kg^{-1}, Sc 0.84 mg
147 Kg^{-1}, Pr 0.55 mg Kg^{-1}, Sm and Gd 0.46 mg Kg^{-1}, Dy 0.35 mg Kg^{-1}, Er 0.19 mg Kg^{-1}, Yb 0.15 mg
148 Kg^{-1}, Eu 0.10 mg Kg^{-1}, Tb and Ho 0.080 mg Kg^{-1}, Tm and Lu 0.030 mg Kg^{-1}).
149 Despite being located in a marine protected area, site 1 seems to be greatly affected by being
150 situated close to an important industrial and touristic harbor.
151 In site 2 (Elba Island, LI), we detected the highest levels of all elements in the Clorophyta *Flabellia*
152 *petiolata* (Ce 3.5 mg Kg^{-1}, Y 2.3 mg Kg^{-1}, La 2.2 mg Kg^{-1}, Nd 1.9 mg Kg^{-1}, Sc 0.66 mg Kg^{-1}, Pr
153 0.47 mg Kg^{-1}, Gd 0.45 mg Kg^{-1}, Sm 0.40 mg Kg^{-1}, Dy 0.34 mg Kg^{-1}, Er 0.18 mg Kg^{-1}, Yb 0.15 mg
154 Kg^{-1}, Eu and Ho 0.10 mg Kg^{-1}, Tb 0.091 mg Kg^{-1}, Tm 0.040 and Lu 0.033 mg Kg^{-1}).
155 In site 3 (Capraia Island, LI), the highest REE concentrations were found in the Ocrophyta
156 *Halopteris scoparia* (Ce 6.2 mg Kg^{-1}, La and Nd 2.7 mg Kg^{-1}, Y 1.9 mg Kg^{-1}, Sc 0.87 mg Kg^{-1}, Pr

157 0.65 mg Kg^{-1}, Sm and Gd 0.51 mg Kg^{-1}, Dy 0.34 mg Kg^{-1}, Er 0.17 mg Kg^{-1}, Yb 0.13 mg Kg^{-1}, Eu
158 0.10 mg Kg^{-1}, Ho 0.073 mg Kg^{-1}, Tb 0.070 mg Kg^{-1}, Tm 0.025 mg Kg^{-1}, Lu 0.022 mg Kg^{-1}) and the
159 lowest levels were found in the Rodhopyta *Dudresnaya verticillata.*
160 Sites 2 and 3 seem to be less affected by anthropogenic contamination, and REE mean values were
161 half of those registered in site 1.
162 In Table 2, the comparison between the ΣREE by one-way ANOVA showed a highly significant
163 difference in concentrations between the three locations ($p < 0.0001$). However, the comparison
164 between only sites 2 and 3 using the unpaired t-test resulted in a non-significant difference ($p >$
165 0.05), highlighting that site 1 showed very different levels of REE in seaweeds, while between sites
166 2 and 3, ΣREE values did not differ significantly.
167 *3.2 Interspecies variability*
168 The total levels of REE (ΣREE) are shown for each analyzed species in the three examined
169 locations (Figure 3).
170 In site 1, Bergeggi (SV), the highest values were found overall, especially in green and brown
171 macro algae, while in sites 2 and 3, REE values were lower; however, there was a high interspecies
172 variability in the same sampling site. In fact, in site 1 (Figure 3), the total REE content was in the
173 following decreasing order *Halopteris filicina* (ΣREE 27 mg Kg^{-1} d.w.) > *Flabellia petiolata* >
174 *Padina pavonica* > *Codium bursa* > *Ganonema farinosum* (ΣREE 15 mg Kg^{-1} d.w.); in site 2, the
175 order was *Flabellia petiolata* (ΣREE 15 mg Kg^{-1} dry weight (d.w.) > *Dictyota dichotoma* > *Codium*
176 *bursa = Padina pavonica* > *Peyssonnelia squamaria* > *Laurencia obtusa* > *Caulerpa racemosa* >
177 *Halopteris filicina* (ΣREE 2.1 mg Kg^{-1} d.w.); and finally, in site 3, the order was *Halopteris*
178 *scoparia* (ΣREE 17 mg Kg^{-1} d.w.) > *Padina pavonica* > *Halimeda tuna* > *Peyssonnelia squamaria*
179 > *Cystoseira spp* > *Flabellia petiolata* > *Codium bursa* > *Dudresnaya verticillata* (ΣREE 2.3 mg
180 Kg^{-1} d.w.). A comparison between the three species that were collected in all three locations (*F.*
181 *petiolata, C. bursa, P. pavonica*) is shown in Figure 4. The REE pattern was similar, but

concentrations differed in the same species in the two green macro algae *F. petiolata* and *C. bursa* from the three sites; the brown macro alga *P. pavonica* showed almost the same levels of REE in sites 2 and 3, but a higher value in site 1.

As shown in Table 2, the one-way interspecies comparison revealed highly significant differences between the different macro algae species for each site. This finding is in line with the scarce literature regarding REE in macro algae. In fact, other authors have underlined the interspecies variability in REE levels. Fu and coauthors (2000) suggested that REE patterns are division-dependent; while Sakamoto and coauthors (2008) indicated that the mechanism of uptake could be different and related to seaweed morphology, even if the accumulation of REE in seaweed is still not elucidated.

3.3 Chondrite-normalized REE pattern (Leedey Oklahoma chondrite)

To define a normalized REE pattern (Figure 5), we utilized the normalized values reported by Masuda (1975) for the Leedey chondrite, which is considered the most primitive chondrite (Sakamoto et al., 2008). Chondrite meteorites are, in fact, used as a reference for the normalization of REE, as they are thought to be similar to the original composition of the Earth's crust (Masuda et al., 1973). Moreover, during this meteorite formation, lanthanide fractionation did not occur (Song et al., 2006; Antonina et al., 2013), therefore, if fractionation between REE in seaweeds occurred, the comparison with the chondrite pattern could disclose this phenomenon.

In our study, the REE patterns were comparable in the three sites (Figure 5), even if, as previously indicated, site 1 (Bergeggi, SV) showed higher overall REE concentrations than the other two locations. The REE Ce and Eu have additional valences compared to the other lanthanides, and when Ce and/or Eu concentrations are enriched or depleted compared to the levels recorded in chondrite, this phenomenon is defined as a Ce or Eu (positive or negative) anomaly. In seaweeds from the three sites, a Eu negative anomaly was observed (Figure 5), while the REE ratios (Ce/La, Gd/Yb, La/Yb) were almost the same in the three different stations (mean values 1.8, 3.3 and 17, respectively).

208 The Eu anomaly is thought to be strictly dependent on lithology (Moller et al., 2004) and
209 enrichment or depletion was explained by the Eu capacity to be mostly incorporated into
210 plagioclase minerals.
211 Despite the very different sites of origin, the chondrite-normalized pattern profile of Mediterranean
212 seaweeds appeared to be very similar to the pattern found by Mashitah and co-authors (2012) in
213 brown seaweeds from Malaysian coasts.
214 The REE patterns normalized by chondrite (Figure 5) are typical of geological materials
215 such as sediments, confirming that REE measurements are compatible with a geological material
216 incorporated in macro algae tissues in different amounts. Moreover, the patterns are similar among
217 sampling sites suggesting that correspond to sediments of similar origin.
218 *3.4 Comparison with REE in biota*
219 In a previous study, we analyzed Ce and La concentrations in marine zooplankton from the
220 Northwestern Mediterranean Sea (Battuello et al., 2017). We observed that concentrations for both
221 these elements decreased from herbivorous to carnivorous copepods, and were in the average range
222 of 0.50 - 1.86 mg Kg^{-1} for Ce and 0.28 - 0.88 mg Kg^{-1} d.w. for La (lowest values in carnivores).
223 In this investigation, Ce and La in seaweeds were in the medium range of 7.2 - 2.5 mg Kg^{-1} and 3.7
224 - 1.3 mg Kg^{-1} d.w., respectively, showing the higher ability of REE to accumulate in seaweeds
225 compared to zooplankton. As for as we know, we cannot compare these results with other seaweeds
226 from the Mediterranean Sea, but a few studies have been performed in other parts of the world. For
227 example, Hou and Yan (1998) analyzed La levels in Chinese coast seaweeds, finding the highest
228 values reported in seaweeds to date, 10.14 mg Kg^{-1} d.w. in green macro algae and 6.73 mg Kg^{-1} d.w.
229 in red macro algae, while the highest value we found for lanthanum was 4.3 mg Kg^{-1} in *H. filicina*
230 and *P. pavonica* from site 1.
231 Masitah (2012) analyzed REE concentrations in *P. pavonica* (Malaysian coast), and found ΣREE
232 values ranging from 62 to 8.4 mg Kg^{-1}, higher concentrations than in the Mediterranean area, where

233 the range we registered was 22 - 7.9 mg Kg^{-1} (Table 1, Figure 2). REE in *Padina sp*. from the
234 Malaysia areas decreased in the following order:
235 Ce>Nd>La>Pr>Gd>Sm>Dy>Er>Yb>Eu=Tb>Ho>Tm>Lu.

236 In our study, in site 1 (Bergeggi, SV), the order of REE was:
237 Ce>La>Nd>Y>Pr>Gd=Sm>Sc>Dy>Er>Yb>Eu>Tb>Ho>Tm>Lu, while in sites 2 and 3, the order
238 was the same, namely Ce>Y>La>Nd>Sc>Pr>Gd>Sm>Dy>Er>Yb>Eu>Ho>Tb>Tm>Lu,
239 demonstrating that *P. pavonica* samples in these two sites have the same geological "fingerprint".
240 Moreover, it was evident that these findings reflected a different pattern of REE in seaweeds, not
241 only between the two different marine areas (Malaysia and Mediterranean), but also between the
242 Mediterranean stations that we investigated. Sakamoto and co-authors (2008) investigated REE
243 patterns in seaweed species collected in the Pacific Ocean (Japan). They found that seaweeds
244 accumulated REE at levels 10^3 times higher than concentrations detected in seawater, and that the
245 accumulation factor was higher for the heavy REE.

246 In order to estimate the bio concentration factor (BCF), which is defined as the accumulation of a
247 chemical from water in an organism (Landis et al., 2011), we used the REE concentrations
248 measured in surface waters of the Mediterranean Sea (Censi et al., 2004), ranging from 0.00013 μg
249 L^{-1} (Yb) to 0.0029 μg L^{-1} (La). In fact, as REE partitioning is controlled by complexation and
250 binding constants on an ocean-wide basis (Sholkovitz et al., 1994; Strady et al., 2015), we decided
251 to apply them on a regional basin-wide basis, with the approach already utilized in the study by
252 Strady and co-authors (2015).

253 BCF was usually expressed as the ratio of the concentration of the chemical in the organism and in
254 water; our findings are shown in Figure 6.
255 The BCFs were expressed in the following decreasing order:
256 Ce>Yb>Pr>La>Nd>Sm>Eu>Tb>Gd>Dt>Ho>Tm>Lu>Er, and with the exception of Yb, the bio
257 concentration factors were higher in LREEs than in HREEs.

In a previous investigation in the studied area (Squadrone et al., under review), we found that different macro algae accumulated trace elements from seawater to different extents, and that brown and green macro algae had higher values than red macro algae. In fact, in seaweeds from site 1, important concentrations of iron, aluminum, manganese, copper, nickel and chromium were registered.

In this study, the same site (Bergeggi, SV) showed the highest levels of REE.

We suggest that REE concentrations in macro algae from sites 2 and 3, being non-contaminated areas, could constitute a baseline record for these elements in Mediterranean seaweeds, due to their characteristic elemental profile. In the presence of anthropogenic sources, such as in site 1, this unique profile was altered, and we can, therefore, suggest the use of REEs as pollution tracers.

4. Conclusions

REE, due to their unique chemical properties have become crucially important in many industrial applications, and the global demand is still increasing. Following the consequent release of REE in terrestrial and aquatic environments, due to the extraction process and production of several industrial components, REE can be considered new emerging inorganic contaminants, for which the potential risks for human health and ecosystems have still not been investigated. Seaweeds have been shown to constitute a useful tool for biomonitoring REE, as they can concentrate REE at higher levels than in seawater. This study constitutes the first investigation of REE in seaweeds from the Northwestern Mediterranean Sea, providing the first record, which can be utilized for future comparisons.

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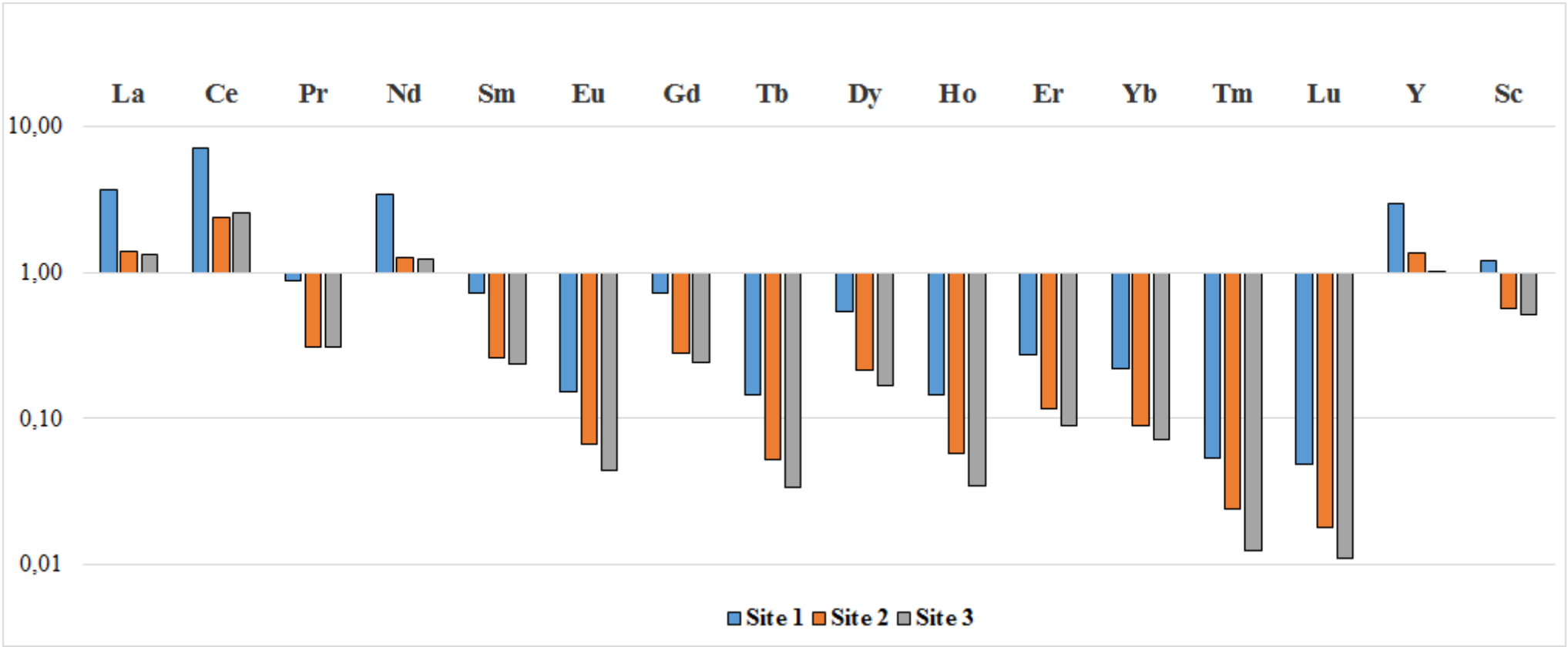
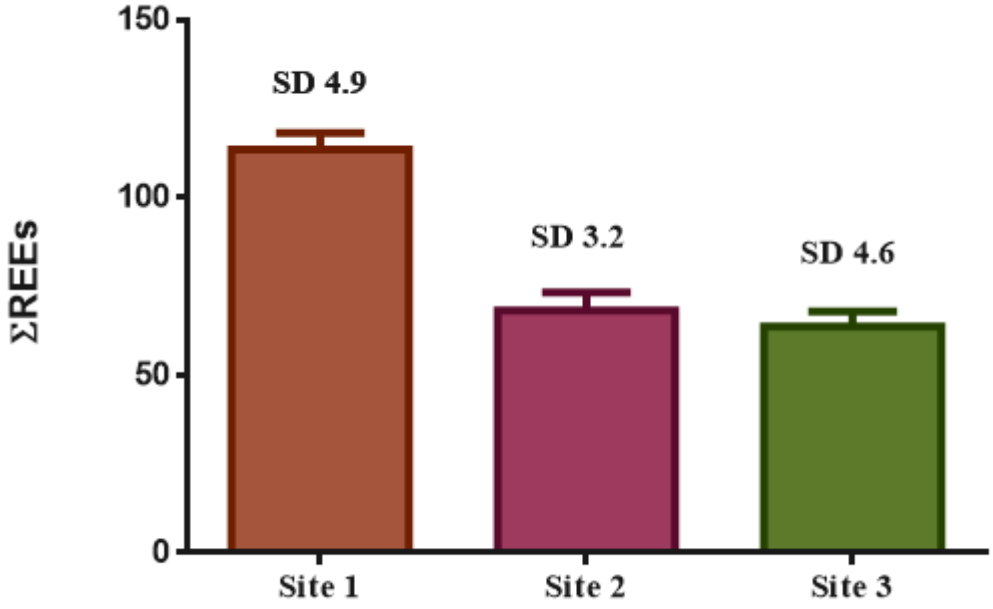
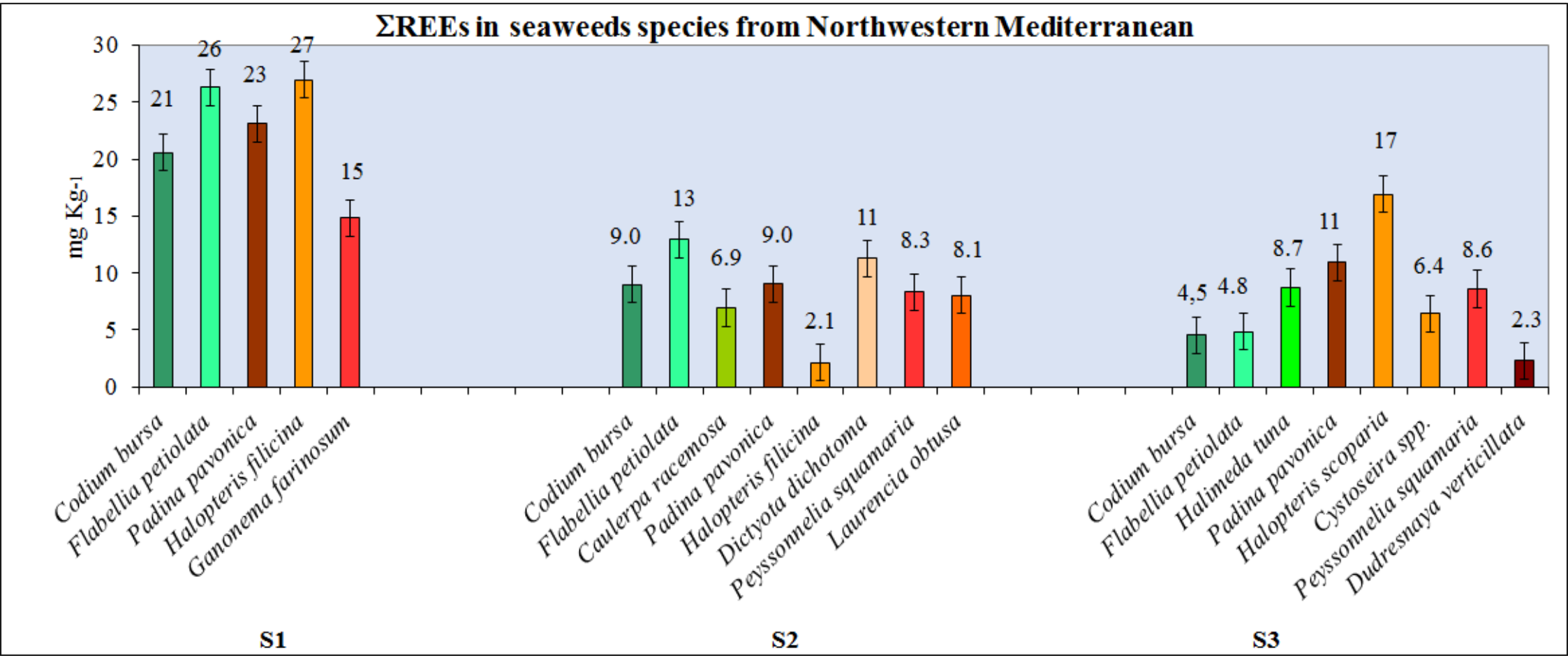
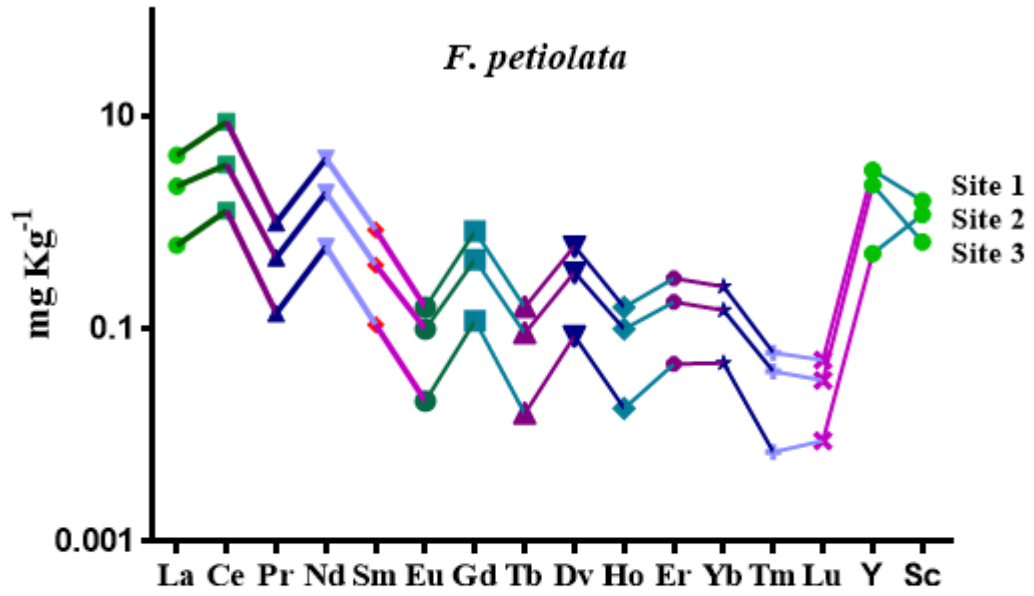
360

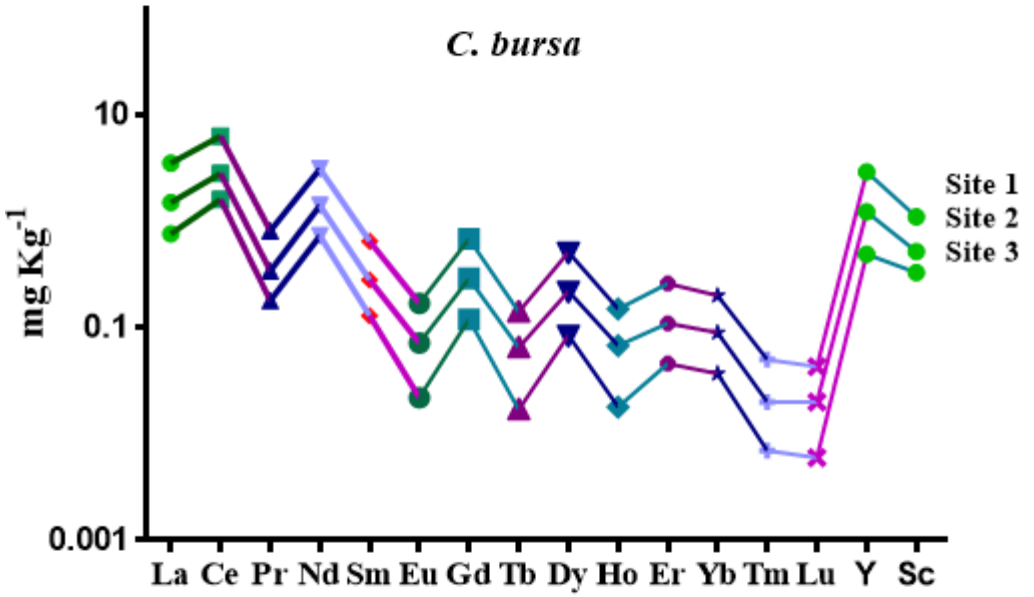

Bergeggi
Site 1
FRANCE
Ligurian Sea
ITALY
Capraia Is.
Site 3
Elba Is.
Site 2
Corse Is.
Tyrrhenian Sea
0
50
100 km

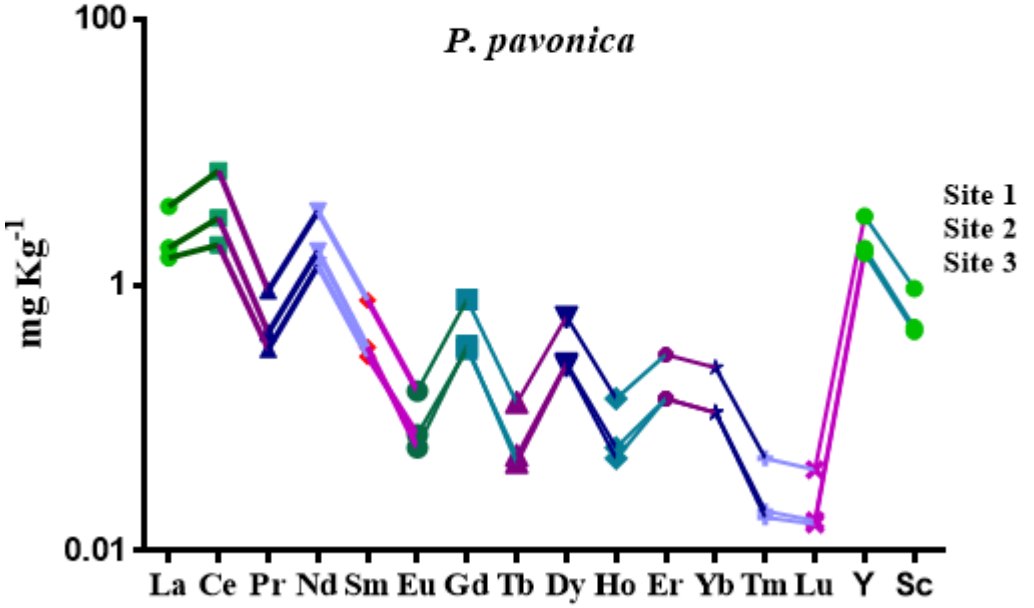

La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Yb
Tm
Lu
Y
Sc
10,00
1,00
0,10
0,01
Site 1
Site 2
Site 3

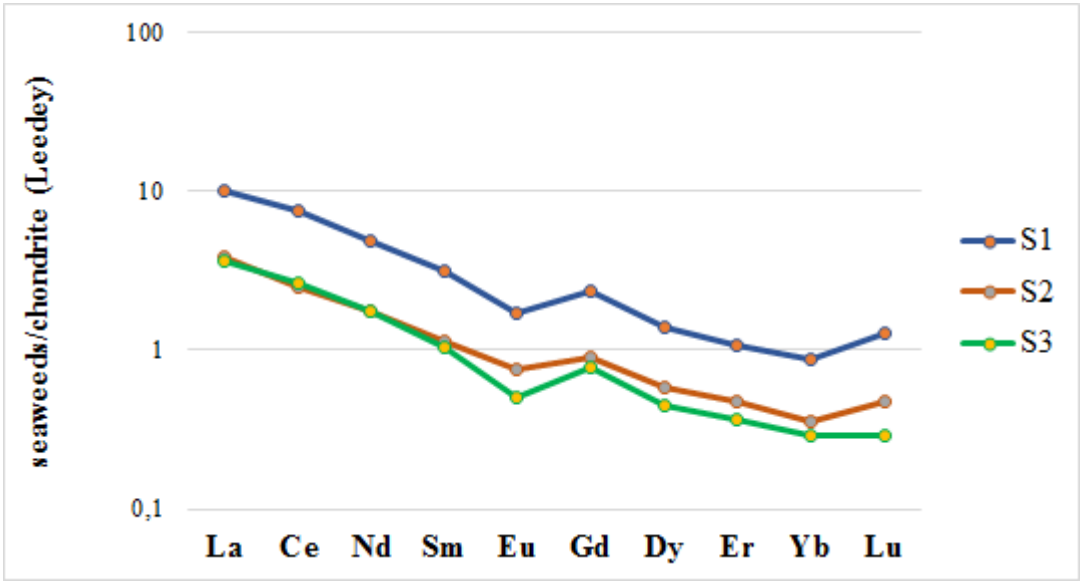

150
100
50
0
ΣREEs
SD 4.9
SD 3.2
SD 4.6
Site 1
Site 2
Site 3

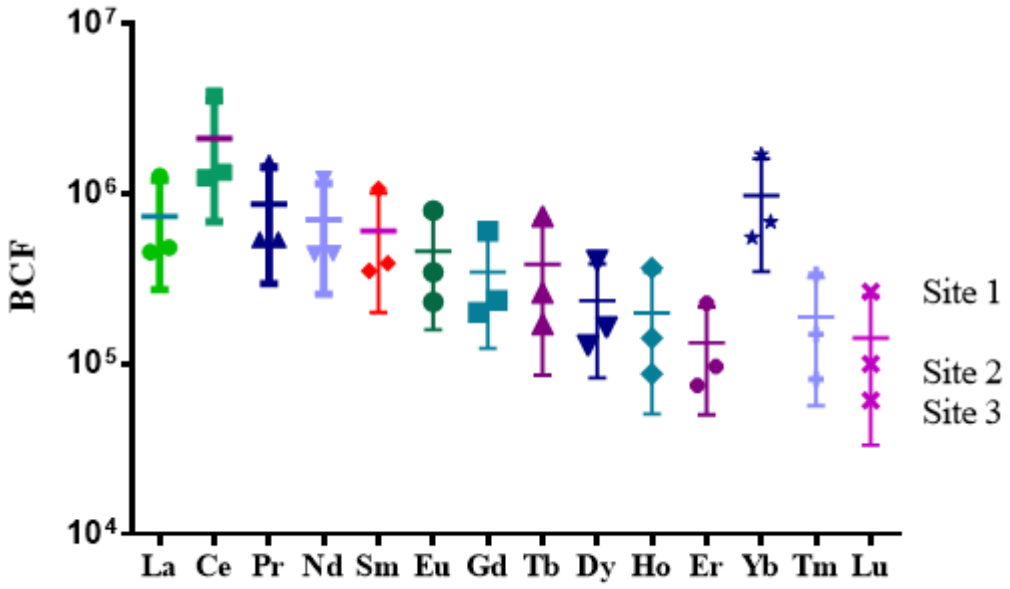

ΣREEs in seaweeds species from Northwestern Mediterranean
mg Kg-1
30
25
20
15
10
5
0
21
26
23
27
15
9.0
13
6.9
9.0
2.1
11
8.3
8.1
4,5
4.8
8.7
11
17
6.4
8.6
2.3
Codium bursa
Flabellia petiolata
Padina pavonica
Halopteris filicina
Ganonema farinosum
Codium bursa
Flabellia petiolata
Caulerpa racemosa
Padina pavonica
Halopteris filicina
Dictyota dichotoma
Peyssonnelia squamaria
Laurencia obtusa
Codium bursa
Flabellia petiolata
Halimeda tuna
Padina pavonica
Halopteris scoparia
Cystoseira spp.
Peyssonnelia squamaria
Dudresnaya verticillata
S1
S2
S3


F. petiolata
10
0.1
0.001
mg Kg-1
La Ce Pr Nd Sm Eu Gd Tb Dv Ho Er Yb Tm Lu Y Sc
Site 1
Site 2
Site 3


C. bursa
10
0.1
0.001
mg Kg-1
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Yb Tm Lu Y Sc
Site 1
Site 2
Site 3


P. pavonica
100
1
0.01
mg Kg-1
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Yb Tm Lu Y Sc
Site 1
Site 2
Site 3


100
10
1
0,1
seaweeds/chondrite (Leedey)
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu
S1
S2
S3


BCF
10^7
10^6
10^5
10^4
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Yb
Tm
Lu
Site 1
Site 2
Site 3

Concentrations of REE in macro algae from Mediterranean Sea (mg Kg^{-1} d.w.)

Site	Species	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Tm	Lu	Y	Sc	ΣREE	LREE	HREE
S1	*Codium bursa*	3.5	6.3	0.81	3.1	0.65	0.17	0.68	0.14	0.51	0.15	0.26	0.20	0.050	0.043	2.9	1.1	21	14	5.1
	Flabellia petiolata	4.3	8.8	1.0	4.0	0.85	0.16	0.83	0.16	0.60	0.16	0.30	0.25	0.060	0.051	3.1	1.6	26	19	5.6
	Padina pavonica	3.9	7.2	0.91	3.6	0.77	0.16	0.78	0.13	0.58	0.14	0.30	0.24	0.050	0.041	3.3	0.94	23	16	5.8
	Halopteris filicina	4.3	8.8	1.1	4.1	0.87	0.17	0.87	0.22	0.64	0.22	0.32	0.27	0.080	0.078	3.4	1.53	27	19	6.3
	Ganonema farinosum	2.5	4.8	0.55	2.2	0.46	0.10	0.47	0.08	0.35	0.08	0.19	0.15	0.030	0.030	2.0	0.84	15	10	35
	mean	**3.7**	**7.2**	**0.87**	**3.4**	**0.72**	**0.15**	**0.73**	**0.15**	**0.53**	**0.15**	**0.27**	**0.22**	**0.054**	**0.048**	**2.9**	**1.2**	**22**	**16**	**6.5**
	SD	0.77	1.72	0.21	0.77	0.17	0.03	0.16	0.051	0.11	0.049	0.051	0.048	0.018	0.018	0.55	0.36	4.9	3.6	1.1
S2		**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Tm**	**Lu**	**Y**	**Sc**	**ΣREE**	**LREE**	**HREE**
	Codium bursa	1.5	2.8	0.34	1.4	0.28	0.072	0.29	0.065	0.22	0.068	0.11	0.090	0.020	0.020	1.22	0.52	9.0	6.3	2.2
	Flabellia petiolata	2.2	3.5	0.47	1.9	0.40	0.10	0.45	0.091	0.34	0.10	0.18	0.15	0.040	0.033	2.26	0.66	13	8.5	3.8
	Caulerpa racemosa	1.1	1.8	0.24	1.0	0.22	0.050	0.24	0.040	0.20	0.050	0.11	0.080	0.020	0.020	1.30	0.50	6.9	4.3	2.1
	Padina pavonica	1.6	2.0	0.33	1.4	0.29	0.075	0.33	0.052	0.26	0.060	0.14	0.11	0.020	0.017	1.88	0.48	9.0	5.6	2.9
	Halopteris filicina	0.29	0.64	0.07	0.31	0.070	0.010	0.070	0.010	0.050	0.010	0.030	0.020	0.031	0.003	0.23	0.25	2.1	1.4	0.5
	Dictyota dichotoma	1.8	3.3	0.41	1.6	0.34	0.090	0.36	0.060	0.27	0.070	0.15	0.11	0.020	0.020	1.61	1.13	11	7.4	2.8
	Peyssonnelia squamaria	1.6	2.6	0.32	1.3	0.25	0.070	0.26	0.050	0.18	0.050	0.090	0.070	0.020	0.010	1.02	0.45	8.3	6.0	1.8
	Laurencia obtusa	1.3	2.3	0.28	1.2	0.25	0.060	0.27	0.050	0.21	0.050	0.11	0.080	0.020	0.020	1.33	0.61	8.1	5.2	2.2
	mean	**1.4**	**2.4**	**0.31**	**1.3**	**0.26**	**0.066**	**0.28**	**0.052**	**0.22**	**0.057**	**0.12**	**0.089**	**0.024**	**0.018**	**1.4**	**0.58**	**8.5**	**5.6**	**2.9**
	SD	0.56	0.91	0.12	0.47	0.10	0.028	0.11	0.023	0.084	0.025	0.046	0.038	0.008	0.009	0.60	0.26	3.2	2.1	1.0
S3		**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Tm**	**Lu**	**Y**	**Sc**	**ΣREE**	**LREE**	**HREE**
	Codium bursa	0.76	1.6	0.18	0.73	0.13	0.022	0.12	0.017	0.085	0.018	0.046	0.037	0.0070	0.006	0.49	0.33	4.5	3.4	0.9
	Flabellia petiolata	0.61	1.3	0.14	0.59	0.11	0.021	0.12	0.016	0.086	0.018	0.047	0.048	0.0070	0.0089	0.51	1.19	4.8	2.7	0.9
	Halimeda tuna	1.51	3.0	0.37	1.4	0.26	0.040	0.25	0.030	0.17	0.030	0.090	0.071	0.012	0.0090	1.04	0.42	8.7	6.5	1.7
	Padina pavonica	1.9	3.2	0.44	1.8	0.34	0.060	0.35	0.046	0.25	0.050	0.14	0.11	0.018	0.016	1.74	0.45	11	7.7	2.8
	Halopteris scoparia	2.73	6.2	0.65	2.7	0.51	0.10	0.51	0.070	0.34	0.073	0.17	0.13	0.025	0.022	1.87	0.871	17	13	3.3
	Cystoseira spp.	1.00	1.5	0.23	0.99	0.22	0.050	0.25	0.040	0.20	0.040	0.12	0.096	0.016	0.015	1.38	0.32	6.4	3.9	2.2
	Peyssonnelia squamaria	1.52	2.9	0.35	1.4	0.26	0.050	0.26	0.040	0.18	0.040	0.090	0.070	0.013	0.011	1.01	0.40	8.6	6.4	1.8
	Dudresnaya verticillata	0.52	0.80	0.090	0.35	0.060	0.010	0.070	0.010	0.040	0.010	0.020	0.013	0.0020	0.0020	0.20	0.10	2.3	1.8	0.4
	mean	**1.32**	**2.5**	**0.31**	**1.2**	**0.24**	**0.044**	**0.24**	**0.034**	**0.17**	**0.035**	**0.090**	**0.072**	**0.013**	**0.011**	**1.0**	**0.51**	**7.9**	**5.7**	**2.3**
	SD	0.75	1.7	0.18	0.75	0.14	0.03	0.14	0.020	0.10	0.021	0.051	0.039	0.007	0.0062	0.61	0.35	4.6	3.5	1.0

Table 2 Statistical evaluation

	P value	P value
One-way ANOVA (3 SITES, ΣREE COMPARISON)	P < 0.0001	****
Unpaired t test (SITE 2 AND SITE 3 ΣREE COMPARISON)	P = 0.0811 (P > 0.05)	NS
One-way ANOVA (Site 1, ΣREE interspecies COMPARISON)	P < 0.0001	****
One-way ANOVA (Site 2, ΣREE interspecies COMPARISON)	P < 0.0001	****
One-way ANOVA (Site 3, ΣREE interspecies COMPARISON)	P < 0.0001	****

**** Significant at the 0.01 probability level
NS not statistically significant

Figure 1

Sampling sites, study area.

Figure 2a

Rare earth elements in macro algae from three Northwestern Mediterranean locations (mg Kg^{-1} dry weight, log scale).

Figure 2b

Box-plot diagrams of ΣREE (mean ± SD) in the three sampling locations (mg Kg^{-1} dry weight).

Figure 3

Box-plot diagrams of ΣREE (mean ± SEM) in the macro algae species (mg Kg^{-1} dry weight) from the three examined locations.

Figure 4

REE distribution (mg Kg^{-1} dry weight) in *Flabellia petiolata*, *Codium bursa* and *Padina pavonica* in the three sampling sites.

Figure 5

Chondrite (Leedey, Oklahoma) normalized patterns of REE in Northwestern Mediterranean macro algae (log scale).

Figure 6

Bioconcentration factors in macro algae from the Northwestern Mediterranean Sea.