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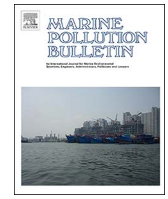

A first report of rare earth elements in northwestern Mediterranean seaweeds

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A R T I C L E I N F O

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A B S T R A C T

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.

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., 1985) 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; Martınez-Botì 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,

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Fig. 1. Sampling sites, study area.

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 (Fig. 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 was 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