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Chapter 6

Lanthanides and Algae

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Additional information is available at the end of the chapter

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Abstract

This chapter discusses the ecological and physiological impacts of lanthanides on algae as primary producers in aquatic environments. Although lanthanides are nonessential elements for living organisms, their bioaccumulation is a common phenomenon. Here, we critically review the ecological effects of increasing levels of lanthanides directly reaching water systems through mining, application of fertilizers, and the production of advanced technologies. We describe interactions between lanthanides and algae, with a particular focus on various applications including fertilizers, tracers, bioindicators, bioremediation, and recycling. We examine the stimulatory effects of low levels of lanthanides versus their toxicity at higher levels and discuss mechanisms by which they may affect the algal cell. This chapter highlights the importance of a better understanding of the biological roles of lanthanides.

Keywords: algae, microalgae, lanthanides, bioaccumulation, environmental pollution, toxicity, fertilizers, metals, recycling, remediation

1. Introduction

Lanthanides play many roles in a number of different fields including chemistry, biology, and medicine [1]. They have also become indispensable in many modern technologies but the growing demand for these metals has also increased their release into the surrounding biosphere. Therefore, it is important to consider and address the impacts of increased lanthanides on the environment. The affinity of algae for these elements can pose a serious environmental threat or be a unique opportunity for the treatment of contaminated areas.

Lanthanides are considered nonessential elements that can induce both positive and negative physiological responses in the living organism. They are not essential for any known

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metabolic process, but under certain conditions, they may have a positive effect [2, 3]. Unlike heavy metals, whose toxicity has been extensively investigated, the effects of lanthanides have been neglected [4], particularly, their impacts on aquatic environments that are associated with the exploitation of lanthanides [5]. Water contamination by metals is a global problem, and metal recovery from wastewaters and industrial wastes is significant not only from an ecological point of view but also because of the sustainable availability of these materials [6].

This review aims to summarize our knowledge of positive and toxic effects of lanthanides on algae in order to better elucidate their biological roles. Various applications and methods of use, including the possibility of remediation and lanthanide recycling, are also summarized.

2. Lanthanides in algae

The presence of lanthanides (Pr, Nd, and Sm) was recorded for the first time in the red alga *Phymatolithon calcareum*, originally *Lithotamnium calcareum*, near the coast of Roscoff in France [7].

Algae contain a diverse spectrum of lanthanides, regardless of size (micro or macroalgae), structural arrangements (unicellular, fibrous, and crustaceous), algal type (e.g., Chlorophyta, Rhodophyta, and Charophyta) as well as Cyanobacteria [8–11]. These analyses show that seaweed lanthanide concentrations may be 10–20 times higher than those in terrestrial plants ([8], see **Table 1**) and more than 100 times higher than in sea water [10, 16].

Total lanthanides can range from 1 to 1.3 μg/g of algal biomass under laboratory conditions, and can be achieved easily, whereas under natural conditions (freshwater and sea water), the total amount of lanthanides ranges between 10^{-3} and 10^{-1} μg/g of algal biomass ([4, 17–19], and links therein).

	Tree[a]	**Tea**[b]	**Moss**[c]	**Potato**[d]	**Red alga**[e]	**Brown alga**[f]	**Green alga**[g]
Sc	nd	0.085	nd	nd	nd	nd	nd
Y	nd	0.360	0.127	0.011	nd	nd	nd
La	0.280	0.600	0.266	0.017	0.362	**3.990**	0.032
Ce	0.370	1.000	0.493	0.038	0.943	**9.080**	0.076
Pr	0.091	0.120	0.056	0.007	0.049	**0.910**	0.008
Nd	0.155	0.440	0.402	0.015	0.191	**4.910**	0.039
Sm	0.031	0.085	0.036	0.008	0.034	**0.900**	0.009
Eu	0.004	0.018	0.009	0.001	0.008	**0.090**	0.028
Gd	0.024	0.093	0.037	0.007	0.044	**1.020**	0.012
Tb	0.017	nd	0.005	0.001	0.006	**0.090**	0.001
Dy	0.021	0.074	0.024	0.002	0.030	**0.710**	0.012
Ho	0.004	0.019	0.004	0.000	0.006	**0.090**	0.002
Er	0.006	—	0.013	0.002	0.015	**0.350**	0.008
Tm	0.001	—	0.001	0.000	0.002	**0.020**	0.001

	Tree[a]	Tea[b]	Moss[c]	Potato[d]	Red alga[e]	Brown alga[f]	Green alga[g]
Yb	0.008	0.044	0.011	0.001	0.008	**0.290**	0.007
Lu	0.019	0.007	0.001	0.000	0.001	**0.020**	0.001
Total	**1.034**	**2.945**	**1.489**	**0.117**	**1.704**	**22.460**	**0.239**

The data correspond to mean values established in μg/g dry weight. In bold, the highest values of the series are highlighted.

[a]Samples of *Pinus silvestris* (pine needles), Germany [12].

[b]Certified reference material GBW07605 tea leaves, China [13].

[c]*Hylocomium splendens*, Sweden [14].

[d]*Solanum* sp. from a food market, China [15].

[e]Red alga *Grateloupia filicina*, Japan [10].

[f]Brown alga *Padina* sp., Malaysia [11].

[g]Green alga *Codium fragile*, Japan [9].

Table 1. Examples of lanthanides and their concentrations in different plants and locations (according to Goecke et al. [3]).

Organism	Yao et al. [20]	Shi et al. [21]
Crustacea	0.15	0.15–0.81
Fish	0.07-0.23	nd
Macroalgae	**1.30–1.40**	**0.78–49.10**
Mollusks	3.32	0.37–21.60
Zooplankton	0.17	nd

Macroalgae in bold and values in μg/g dry weight [20, 21].

Table 2. Lanthanide content in coexisting environmental samples from two studies in China.

There are only a few studies comparing lanthanides in different coexisting organisms, including algae. These studies indicate the relevance of lanthanides, particularly in microorganisms, and clear differences between coexisting groups of organisms (**Table 2**). Such a wide range of biotic concentrations of lanthanides can be generated by: (i) relative concentrations of elements in water; (ii) physical and metabolic processes specific to each type of algae (cell wall components, enzymes, proteins, etc.); and (iii) environmental factors specific to each area, e.g., temperature, light, pH, and nitrogen availability that can affect the two previous factors [22–24].

The concentration of lanthanides in the environment increases with changes in climatic conditions, groundwater action, and volcanic activity [25], but there are also significant anthropogenic sources of lanthanides in phosphoric mineral fertilizers, industrial waste waters, and mine extractions [4, 18, 26–29]. Algae can serve as bioindicators because they can accumulate these elements in their cells (**Table 1**).

3. Beneficial effects of lanthanides

The probable biological effect of lanthanides is related to similarities between their ionic radii and coordination numbers with elements such as Ca, Mn, Mg, Fe, or Zn. Another aspect is

their ability to form stable complexes with organic molecules [30]. Substitution of essential metal ions involves, for example, changes in enzyme activity, protein conformation, or polymerization. Also, changes in the use or allocation of ion channels affects specific membrane permeability and the cellular ion ratio.

Although lanthanides have been used for decades, particularly in China, as fertilizer in agriculture, their specific effects on plants and less so on algae, are not understood. Beneficial effects of lanthanides on growth and quality have been studied, mostly on crops [14, 31, 32] and domestic animals [14, 33–35]. Absorption, transmission, and metabolic conversion of nutrients were stimulated; metal deficiencies were overcome; and increases in metabolism via enzymatic activities were observed. Likewise, effects of lanthanides on photosynthesis or resistance to stress caused by drought, acid rain, and/or toxic metals (reviewed by [14, 32, 36, 37]) have been described. However, a specific cellular or molecular model for these observations has not been proposed and therefore mechanisms of action of lanthanide in plants or algae remain unclear [38].

One of the positive effects of lanthanides is connected with their ability to alleviate calcium deficiency because of Ln^{2+} and Ca^{2+} ions with high chemical similarities. These similarities, as well as the fact that lanthanides have higher valence values compared to calcium, resulted in Ln

Algae	Lanthanide	Positive effect	Negative effect	Reference
Arthrospira platensis (B)	La^{3+}	38.53–53	>53.94	[43]
**Arthrospira platensis* (B)	$LaCl_3$	30–40	>40	[44]
Chlamydomonas reinhardtii (C)	Ce^{3}	5–20	—	[45]
	La^{3+}	5–20	—	[45]
Chlorella vulgaris (C)	Ce^{3+}	1.8	2.1	[46]
**Ch. vulgaris* v. *autotrophica* (C)	12 different Ln	—	29.14	[47]
**Desmodesmus quadricauda* (C)	La^{3+}	<7.2	>72	[48]
Euglena gracilis (E)	Dy^{3+}	50–100	180–1000	[49]
Isochrysis galbana (H)	La	7.28–87.4	—	[50, 51]
	Gd	6.36–57.23	—	[50, 51]
	Yb	5.78–17.34	—	[50, 51]
Microcystis aeruginosa (B)	La^{3+}	<7.2	>72	[48]
Skeletonema costatum (O)	13 different Ln	—	28–30	[52]
	Sc	—	21.88	[52]
	Y	—	43.21	[52]

Algal divisions are characterized as Chlorophyta (C), Haptophyta (H), and Ochrophyta (O); Cyanobacteria (B) and Euglenophyta (E). If the algal species has a new name, it is referred to using the actual name and an asterisk (*); for names according to Algaebase, see Guiry et al. [53].

Table 3. Examples of studies testing the effect of lanthanides on growth, physiology, and survival of microalgae, specifying the concentrations at which positive, neutral, and negative effects were observed (values in μmol/L).

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ions easily replacing Ca^{2+} and being able to bind with a higher affinity to multiple receptors, thus having various effects on metabolism depending on the effect of the replaced metal [31, 39–42].

In the majority of experiments carried out with algae and lanthanides, attention was focused on algal (eventually cyanobacterial) growth properties without any effort to understand mechanism(s) of beneficial effects (**Table 3**). Thus, it is not clear whether the beneficial effects of lanthanides are due to the mitigation of nutrient deficiencies (such as Ca^{2+}, Mg^{2+}, or Mn^{2+}), as previously found in plants [2, 48, 54–56], or to the fact that lanthanides are involved in some physiological reactions such as scavenging of oxygen-free radicals [30, 57, 58] or due to their ability to neutralize inhibitory effects of heavy metals [37].

In a study on the effect of lanthanides in alleviating metal deficiency in algae, Li et al. [59] showed that La^{3+} at low concentrations were able to partly substitute for a Ca^{2+} deficiency in the green macroalga *Chara corallina*, thereby enabling cytoplasmic streaming. Lanthanides can also induce a stimulating effect on the green microalga *Desmodesmus quadricauda* [2]. Five additions of different lanthanides, added at low concentrations, partially compensated the adverse effect of a Ca^{2+} deficiency (probably by substitution), but were not able to alleviate a Mn^{2+} deficiency. To specifically measure physiological stress caused by nutrient limitation, a decline in cellular growth and cell division was followed and a pulse amplitude modulation (PAM) fluorimeter was used to detect changes in photosynthetic parameters (**Figure 1**).

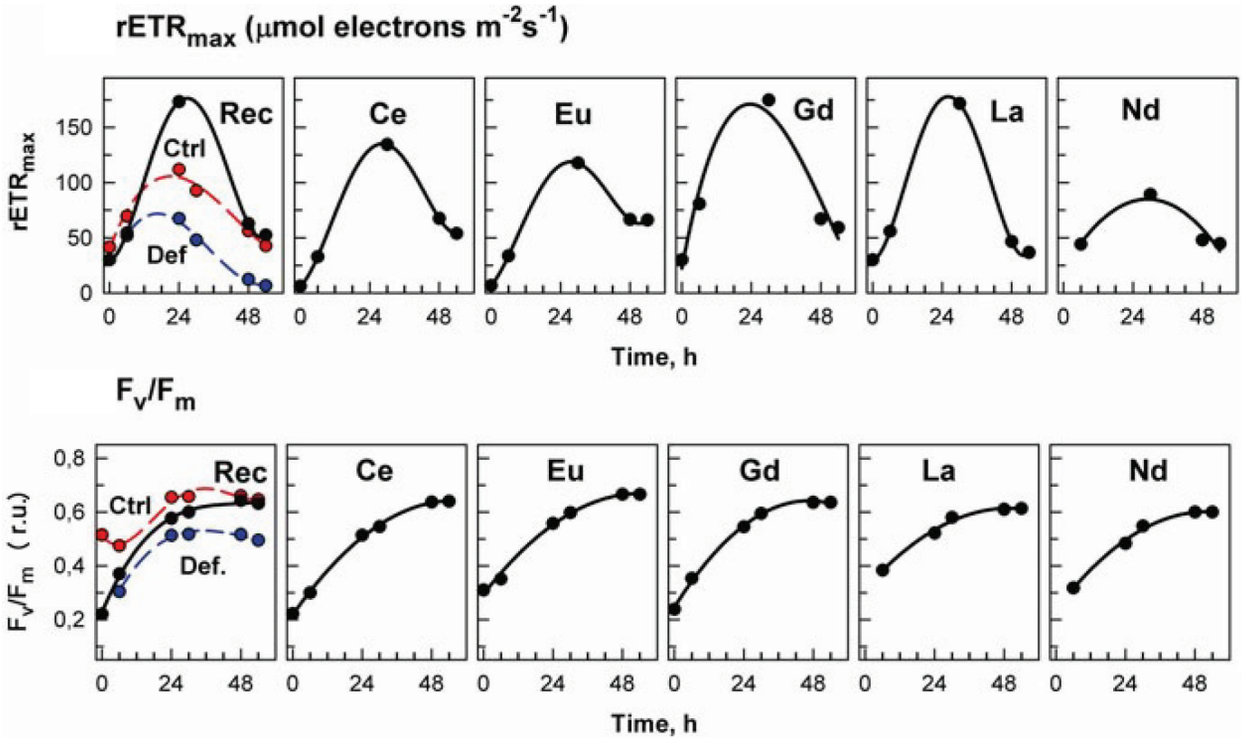


Figure 1. Photosynthetic parameters expressed as maximum relative electron transport rates (rETRmax), and the maximal quantum yield (*Fv/Fm*), in cultures of the alga *Desmodesmus quadricauda,* grown either in complete mineral medium (Ctrl, *red* symbols, *dashed* curve) or in calcium-deficient mineral medium (Def, *blue* symbols, *dashed* curves). To calcium-deficient cultures, either complete mineral medium (Rec, *black* symbols, *solid* line) or different lanthanides (Ce, Eu, Gd, La, Nd) were added, as marked in individual panels. Complete photosynthetic parameters are displayed in the original publication (modified from Goecke et al. [2]).

The effects of single lanthanides and monazite on growth rate, lipid profile, and pigments in two biotechnologically interesting algae (*Parachlorella kessleri* and *Trachydiscus minutus*) were evaluated. The impact of lanthanides depended on the combination of species, element, and light intensity. For example, the presence of Ce, La, and Sc caused the growth rate of *T. minutus* to rapidly rise at low light intensity. The saturated fatty acid content increased at the expense of polyunsaturated fatty acids in both species. The effect on pigments was variable [60].

The use of lanthanides in agriculture and in aquatic cultures is gradually increasing although their impact on the environment has not been sufficiently verified. Lanthanides are not yet commercially available to increase the production of algal biomass despite the fact that their effects on economically interesting pigments and lipids are known. In the alga *Haematococcus pluvialis*, cellular growth and production of astaxanthin increased after the addition of Ce^{3+} at a concentration of 1 mg/L. However, this effect was dose-dependent and growth at higher concentrations of Ce^{3+} was inhibited [61].

4. Toxicity of lanthanides

The toxicity of lanthanides has been reported as low, but is dependent on their chemical form and processing, as reported by Hodge-Sterner's classification system [62]. In soil and water, however, a surplus of lanthanides has a negative to toxic effect on human beings and animals [63]. Human exposure to lanthanides and effects on health are discussed by Pagano et al. [64]. The best studied effects on health are for Ce, La, and Gd, and the rest remain unclear [64]. The toxicity of lanthanides to various organisms is described in several reports [31, 42, 65], but maximum admissible concentrations, thresholds, and toxicity levels are poorly defined [66]. For each organism or species, the toxicity of different lanthanides differs, but the exact effects remain unknown [67, 68] (**Table 3**).

The ability of lanthanides to be involved in the metabolism of several basic elements has been considered as a possible cause of their toxicity [36]. Due to this phenomenon, differences in normal functions of several enzymes have been found, as demonstrated by work describing ATPase and pectate lyase [69, 70], ion channel blocking [71], or mineral transport [42, 72].

Although toxic effects of lanthanides have been reported for various microorganisms (**Table 3**), there is little evidence to generalize their effect on algae. Only a few orders of Charophyta [73], Chlorophyta [46, 48, 74], Dinophyta [75], Euglenophyta [49], Bacillariophyceae [76, 77] and Haptophyta [50], and Cyanobacteria [78, 79] have been studied. Most other algal studies, however, contained little or no data on the bioavailability of lanthanides. The relationship between lanthanide concentrations and stimulatory or inhibitory effects on the same algal species are therefore inconsistent. Moreover, many algal groups or species have not yet been tested for toxicity and no tests for macroalgae have been developed. The database on bioassays for algal toxicity is summarized in Guida et al. [80].

The transfer of lanthanides is expected through the food chain, as algae are primary producers [66, 81]. The toxicity of lanthanide on algae therefore needs to be addressed because any harmful effects may result in the transfer of negative effects to organisms at higher trophic levels [67, 82, 83].

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Recent studies on the toxicity of lanthanides to algae describe the depletion of nutrients rather than toxicity itself [83, 84], see Section 7. In these works, it was suggested that lanthanides could capture some essential nutrients such as phosphates, resulting in an effect on growth (death by hunger). The relationship between lanthanides and phosphate was analyzed in detail in [85]. This important property should be examined in more detail because it could affect the bioavailability of these metals (EC_{50}), changing the evaluation of their impact on the environment.

5. Bioaccumulation of metals in algae

In recent decades, metal uptake by algal biomass has been studied with great interest. Uptake can be by passive binding, so-called "biosorption," or an active process of "bioaccumulation,"

Algae	Lanthanide	Reference
**Amphidinium carterae* (D)m	Ce	[90]
Aphanothece sacrum (C)m	14 different Ln, Y	[91]
Carteria sp. (C)m	Ce	[90]
Chaetoceros muelleri (O)m	Ce, La	[19]
Chlorella vulgaris (C)m	La	[92]
**Cylindrotheca closterium* (O)m	Ce	[90]
**Diacronema lutheri* (C)m	Ce, La	[19]
Euglena gracilis (E)m	Nd	[93]
Euglena gracilis (E)m	Ce, Nd	[94]
Microcystis aeruginosa (B)m	Ce, La	[90]
Nannochloropsis gaditana (C)m	Ce, La	[90]
Platymonas sp. (C)m	Ce	[90]
**Porphyridium purpureum* (R)m	Ce	[90]
Sargassum polycystum (O)	Eu, La, Yb	[95]
Sargassum polycystum (O)	Eu, La	[96]
Sargassum sp. (O)	Eu, Gd, La, Nd, Pr, Sm	[1, 97]
Tetraselmis chui (C)m	Ce, La	[19]
Thalassiosira sp. (O)m	Ce	[90]
Turbinaria conoides (O)	Ce, Eu, La, Yb	[98]
Ulva lactuca (C)	14 different Ln, Y	[99]

Algal divisions Chlorophyta (C), Ochrophyta (O), and Rhodophyta (R), and Cyanobacteria (B), and the protist classes Dinophyceae (D) and Euglenophyceae (E) are specified. If microalgae were utilized, they are annotated with an (m). If an algal species has a new name, it is referred to with the actual name and an asterisk (*); names are according to Algaebase, see Guiry et al. [53].

Table 4. Studies on algal accumulation, biosorption and/or desorption of lanthanides.

where uptake or removal of elements is metabolically controlled [86, 87]. Some metals belong to the group of essential micronutrients, being important for growth and development of plant cells, and are involved in active metabolism [88]. Bioaccumulation of chemical compounds depends on rates of uptake and metabolism, and on the ability of the organism to degrade or store compounds. In essence, the process of accumulation of elements in algal cells is very complicated and depends on the properties of the species (type, size, form, and state of development), the element (charge, chemical form, and concentration), and the medium (pH, type, and concentration of metal salts or presence of complexing agents) [89]. As can be seen in **Table 4**, accumulation, biosorption, and desorption of lanthanides occurs in micro- and macroalgae, including brown, green, and red algae, algal flagellates, and also cyanobacteria. The potential for biosorption of cerium ions by cyanobacteria *Arthrospira* (*Spirulina*) was also tested [100]. Live and dead algae were shown to efficiently accumulate these metals because

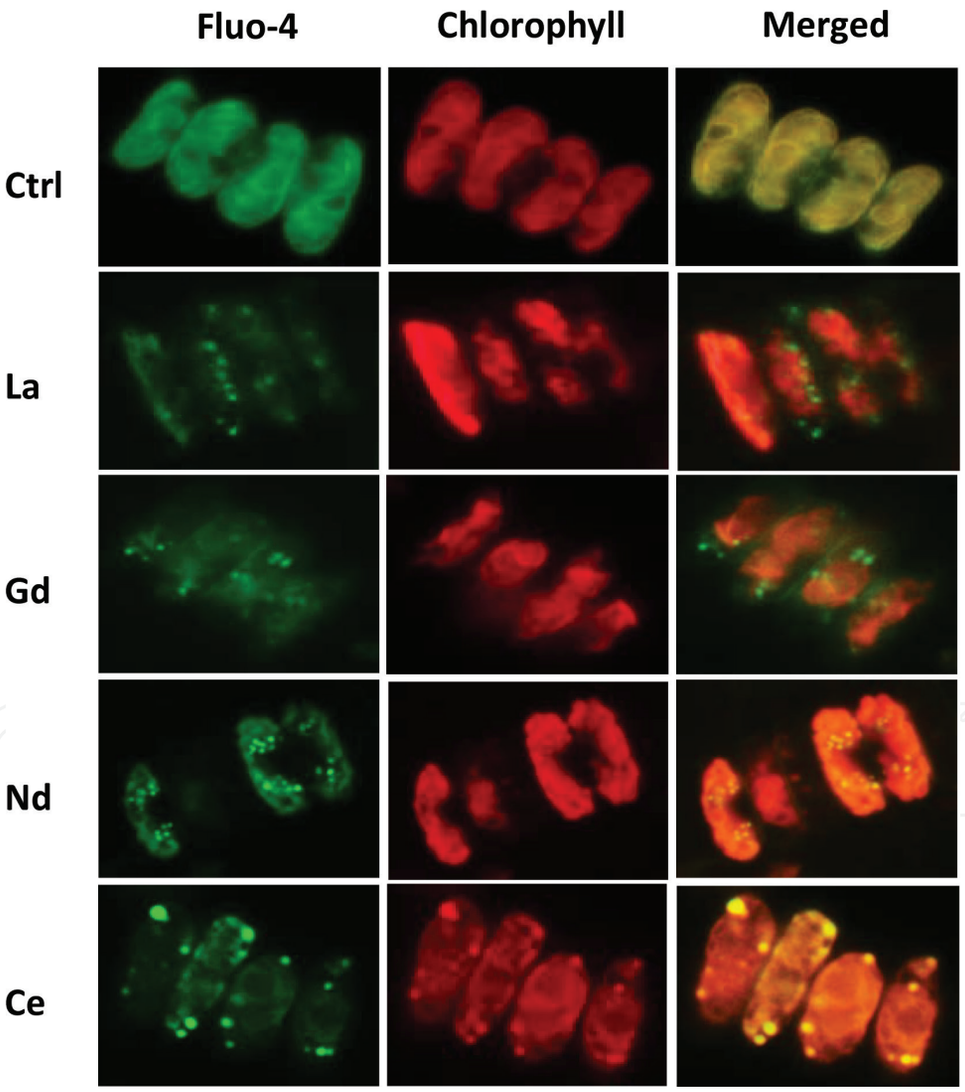


Figure 2. Intracellular localization of different lanthanides in *Desmodesmus quadricauda*. The absorbed lanthanides (horizontal rows) were visualized in cells stained with the fluorescent dye Fluo-4 (left column). Chloroplasts are visualized by autofluorescence of chlorophyll (middle column). In merged photos (right column), the localization of lanthanides seen either inside chloroplasts (Nd, Ce) or in the cytoplasm (La, Gd) (according to Řezanka et al. [109]).

of their ability to create chelated metabolites, e.g., with proteins, sugars, nucleic acids, amino acids, nucleotides, etc. [32]. Moreover, lanthanides in algae also have the ability to bind to pigments, and polysaccharides such as cellulose, alginic acid, carrageenan, fucoidan, etc., which are present in algal cells in great quantities and varieties [91, 95, 101–104]. The bioaccumulation of lanthanum by different organisms, including algae, and its ecotoxicity in the aquatic environment is reviewed in [105]. A recent database of studies evaluating lanthanide bioaccumulation in algae is reviewed by Guida et al. [80].

Precise data about mechanisms of entry for lanthanides into algae and their accumulation are sparse. Even in higher plants, which are much more researched, cell processes responsible for lanthanide intake have only recently been described [38]. Several studies have shown that lanthanides concentrate in chloroplasts [93, 94, 106–108]. It was demonstrated that selective deposition of individual lanthanides in chloroplasts or the cytoplasm occurs in the green alga *Desmodesmus quadricauda* [109]. Nd and Ce were located in the chloroplast while La and Gd were found in the cytoplasm (**Figure 2**). Lanthanides increased the total amount of chlorophyll by up to 21% and changed the chlorophyll *a*/*b* ratio. They also changed the relative incorporation of heavy Mg isotopes into chlorophyll molecules [109].

However, many questions regarding the transfer and accumulation of lanthanides remain unanswered. For example, mechanisms of transport through the complex cell wall of algae or cyanobacteria, and whether they are stored in some specific structures or just loosely in the cytoplasm are unclear. Research into resistant strains or natural hyper-accumulators might bring some answers.

6. Biological applications of lanthanides

In biological systems, lanthanides are applied for different purposes such as growth promoters, fertilizers, water bloom killers, or as detection tools (bioindicators, tracers, and markers). Lanthanides have been proposed as growth stimulators for various animals such as pigs and other livestock [110]. Algae were also used as a feed additive to improve the condition of domestic animals [111]. Lanthanide-rich algae are a potential alternative to food supplements or functional foods. However, only one study on young abalones was performed to demonstrate that lanthanide-enriched algal biomass was an effective growth promoter [82]. Therefore, it would be important to increase the number of studies, to obtain relevant data on the effects of lanthanide transmission and to assess the risk of human exposure through food derived from animals [35].

Many microorganisms, including blue-green algae (e.g., *Microcystis* or *Alexandrium* spp.), cause water blooms with negative impacts on health, ecology, and economics. Water blooms produce harmful toxins (e.g., microcystins and saxitoxins) with detrimental effects on humans and animals [84]. Lanthanides affect algal physiology and their impact on the level of microcystins was demonstrated in *Microcystis aeruginosa* [112, 113]. There was a close relationship between lanthanides, phosphorus content and the growth characteristics of cyanobacteria [113].

New techniques of dephosphatisation of the environment include the use of Ln-modified clays [83, 84]. The advantage of these methods is the low level of side effects on living organisms.

The unique chemical features of lanthanides make them ideal tracers for geochemical processes in nature [9]. They represent alternative, nonradioactive, highly detectable labels. They were used, for example, to confirm the impact of cyanobacterial mats on deep waters outside French Polynesia, providing evidence for an end-ascending flow [114]. They enable scientists to follow oceanic cycles, petrogenesis, the chemical evolution of the Earth [16, 29], or palaeo-environmental conditions [115–118]. Lanthanides can also serve as anthropogenic activity indicators [27]. Because of their particular affinity to algae, the lanthanide profile may be a useful indicator for exploring the ecology of marine environments [10] and can also be used to monitor sources of pollution from natural events such as volcanic activity [25]. In combination with macroalgal sampling, the lanthanide profile may help to characterize coastal water quality and pollution [22, 23, 27].

Lanthanides have been used for their inert nature as detection agents in various experiments, for example, in studies of the rate of passage and digestibility of nutrients in humans and animals [119–121]. Lanthanide oxides have been used as markers in sea cucumber (*Apostichopus japonicus*) grown on a variety of macroalgal diets [121].

In the development of new, sensitive detection methods, active chelates of lanthanides have been obtained and tested. They are used in sensitive immunoassays to suppress the background [122] or as very sensitive fluorescence probes [123]. An example of their use is the labeling of the cyanotoxin microcystin [124, 125].

7. Remediation of lanthanide waste and their recovery

In countries with sufficient sources of lanthanides (mainly China), these elements are used as fertilizers to increase agricultural production. With increasing consumption, waste with varying contents of different lanthanides has increased significantly and rapidly. The most important of these are magnets (neodymium), metal alloys (europium and yttrium), batteries, glass, and catalysts (cerium and lanthanum) [126]. Other important sources of lanthanide waste are phosphate mineral fertilizers, industrial wastewater, sewage sludge, mining processes, or wastes from industrial aluminum production [4, 18, 26–29]. Lanthanides present in ecosystems from agricultural production can thus penetrate into the groundwater and migrate to rivers and lakes [58] or to the sea [127]. Some studies on ecological effects and potential threats due to the bioaccumulation of lanthanides have been described, but they are not long-term enough to draw any general conclusions [128, 129]. Relevant regulations or standards concerning doses and threshold values for the presence of lanthanides in the environment have also not been established [38]. In China, lanthanides are cited as the main source of environmental contamination [130]. They are also considered to be emerging pollutants outside of China, requiring the specification of threshold values for concentrations and emissions of lanthanides in the environment [64, 131]. Removing these lanthanide contaminants is therefore a very important requirement in order to reduce the ever-increasing environmental burden on the aquatic environment.

In addition to this very important requirement for remediation, the need for recycling of lanthanides from any (not only liquid) industrial production waste becomes even more acute.

One reason is the risk of reduced availability of resources (China owns more than 95% of natural sources) or their relatively rapid depletion from other sources. Replacement of lanthanides with alternate substances in industrial applications is currently not possible [132, 133]. Due to their unique chemical and physical properties and their extensive applications in industrial products, the importance and demand for these elements is constantly increasing [131, 134]. The economic impact of an emerging lanthanide shortage increases the urgency for efficiently using renewable energy sources from the ever increasing number of different types of waste products worldwide. At present, research is focused on the progressive and cost-efficient recycling of lanthanides for industrial processes [4, 95, 102, 135, 136], which would reduce risks associated with inaccessibility or depletion of natural resources while minimizing environmental problems associated with their extraction and processing [137].

One of the most widespread lanthanide-containing wastes is electrical and electronic equipment, including lighting equipment, computers, or photovoltaic panels. This waste is a growing threat to the world's environment, and lanthanide recovery is therefore becoming economically attractive. The main sources for recycling are luminophores, powder mixtures obtained from electronic waste and containing high concentrations of lanthanides. Luminophores are obtained from television screens or monitors, as well as energy-saving bulbs and lamps, where they are used to convert cathodic tube radiation or ultraviolet electric discharge into mercury vapor and visible light. These luminophores occur as a powder attached to the inner surfaces of mesh or tubes. The glass parts of these waste networks, monitors, screens, and light bulbs can be easily recycled, but luminophore layers must be removed because the luminescent compounds would reduce the quality of recycled glass. The luminophores as waste represent a toxicity problem but, on the other hand, are a concentrated source of various lanthanides, either in the form of dry powder or wet mud [138].

7.1. Chemical recycling

Lanthanides from waste sources can be recycled by chemical separation from solutions (e.g., chemical precipitation, electrochemically, membrane division, reverse osmosis, etc.). These methods are comparatively costly and, moreover, are often a source of other nonorganic wastes [139]. Methods such as pyrometry and hydrometallurgy for the extraction of lanthanides from ores have significant negative impacts on the environment and involve high costs [126]. The other serious disadvantage is the dependence on a single and limited source and possibly the depletion of other natural resources [126, 140, 141]. These traditional physicochemical processes are expensive or even inefficient for the treatment of sewage containing low concentrations of metal ions [142]. A by-product of conventional methods is the associated large volume of contaminated water, high temperatures and a high consumption of chemical compounds [143, 144]. Researchers are therefore looking for low-cost approaches and at the same time environmentally friendly technologies.

7.2. Biosorption

As a biotechnological approach, biosorption is considered to be a more efficient and cheaper alternative to conventional chemical methods of recycling lanthanides [133, 145, 146]. Various different organic residues of animal or plant origin, including resin, activated charcoal, or

biomass of various organisms (algae, fungi, and bacteria), have been shown to adsorb different lanthanides and have been tested as biosorbents [95, 98, 132, 147]. The development of effective biological methods for lanthanide regeneration from these materials was proven in the aerobic, genetically modified bacterium, *Caulobacter crescentus* [148]. The use of various other biosorbents, including algae, bacteria, fungi, and yeasts, has also been evaluated [149]. Seaweeds, especially brown seaweeds, have been identified as strong biosorbents due to the presence of binding sites for chemical moieties such as carboxyl, amine, and hydroxyl groups [86]. Marine macroalgae are particularly important [150, 151]. For example, Oliveira et al. and Oliveira and Garcia [97, 152] evaluated the potential of *Sargassum* sp. biomass for biosorption of Eu, Gd, La, Nd, Pr, and Sm. They observed the rapid and efficient recovery of these metals, even though they were unable to separate them. The authors suggested that carboxyl groups present in alginates (the main component of the cellular brown algal wall) are the major reactive functional groups. Similar results were obtained with other brown seaweed such as *Sargassum* spp. [16, 96, 102, 135] and *Turbinaria conoides* [98]. Some unicellular algae such as *Chlorella* spp. and *Nannochloropsis* spp. and cyanobacteria *Microcystis* spp. were also shown to be active biosorbents of lanthanides (La^{3+} and Ce^{3+}) [19, 153]. The disadvantage of adsorption methods, including biosorption, is the generation of secondary wastes similar to chemical approaches although at a considerably lower rate, the subsequent processing of which is often financially demanding [154].

7.3. Accumulation in living cells

Methods for the recycling of lanthanides via living cells offer an alternative, which does not have the disadvantages of chemical and adsorption approaches. Accumulation of lanthanides from the environment is cost-effective and does not produce any substantial secondary waste. In addition, it is a great advantage that it can also be effective in water containing very low lanthanide concentrations, which is problematic in other approaches.

Waste solutions containing lanthanides often have high acidity. Thus, the discovery that the sulfothermophilic red alga *Galdieria sulphuraria* can effectively accumulate lanthanides from various waste solutions, in which no other organisms can grow, was of great importance [155]. The unicellular red alga *G. sulphuraria* can grow autotrophically or heterotrophically in a wide range of different sugars or polyols at a pH of about 1.5 and a temperature of 56°C [156–158]. The ability to accumulate lanthanides was demonstrated in aqueous solutions containing a mixture of Nd^{3+}, Dy^{3+}, and La^{3+} at pH 2.5, with an efficiency greater than 90% and at a lanthanide concentration of 0.5 ppm [155]. The efficiency remained unchanged at pH values in the 1.5–2.5 range. The authors also showed that lanthanides accumulated inside the cells not only by adsorption to the cell walls, but also by other mechanisms. Although the alga *G. sulphuraria* is indispensable for the treatment of waste solutions that prohibit the growth of most other living organisms, the species is virtually unusable for remediation of most natural water resources, particularly marine water due to its requirement for growth at a low pH. The marine green alga *Ulva lactuca* has been found to remove toxic metals (Cd, Pb, and Hg), and this approach is cost-effective and more efficient than passive adsorption using nonliving biomass [159–161].

Up to now, only one paper has been published demonstrating the high potential of seaweed (in this case, brown algae *Gracilaria gracilis*) to remediate sea water contaminated with

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lanthanides [162]. *G. gracilis* was able to effectively remove low concentrations (0.5 mg/L) of lanthanides with 70% yield. The ability of *G. gracilis* to remove lanthanides (Y, Ce, Nd, Eu, and La) from such low concentrations in waste water therefore has the potential to overcome one of the greatest difficulties in recycling these elements so far [162]. It seems therefore promising to use live algae for lanthanide accumulation as an alternate technology for simple and efficient recycling from wastewater.

8. Conclusions

Algae are very important organisms in terms of ecology, being at the very beginning of the food chain. Their relationships with metals therefore affects other living organisms. Their ability to accumulate lanthanides may have an impact on the surrounding environment, representing both a threat and an opportunity, with the potential for further study and use. As bioaccumulation abilities and beneficial or toxic effects of lanthanides differ in individual algal strains, it is difficult to predict specific ecological hazards. Algae in combination with lanthanides offer a wide variety of applications. They can be used as bioindicators, fertilizers, toxin detectors, or for phytoremediation and recycling. Therefore, understanding the relationships between algae and lanthanides is very important. Once we understand the molecular mechanisms of their effects, we will have greater opportunities for their use.

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References

[1] Oliveira RC, Guibal E, Garcia O. Biosorption and desorption of lanthanum(III) and neodymium(III) in fixed-bed columns with *Sargassum* sp.: Perspectives for separation of rare earth metals. Biotechnology Progress. 2012;**28**:715-722

[2] Goecke F, Jerez C, Zachleder V, Figueroa FL, Bišová K, Řezanka T, Vítová M. Use of lanthanides to alleviate the effects of metal ion-deficiency in *Desmodesmus quadricauda* (Sphaeropleales, Chlorophyta). Frontiers of Microbiology. 2015;**6**:2

[3] Goecke F, Zachleder V, Vítová M. Rare earth elements and algae: Physiological effects, biorefinery and recycling. In: Prokop A, Bajpai RK, Zappi ME, editors. Algal biorefineries. Switzerland Cham, Heidelberg, New York, Dordrecht, London: Springer International Publishing; 2015. pp. 339-364

[4] Liang T, Li K, Wang L. State of rare earth elements in different environmental components in mining areas of China. Environment Monitory Assess. 2014;**186**:1499-1513

[5] EPA. Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues. United States Environmental Protection Agency EPA 600/R-12/572/December 2012

[6] Kanchana S, Jeyanthi J, Kathiravan R, Suganya K. Biosorption of heavy metals using algae: A review. International Journal of Pharmacological Medical and Biological Science. 2014;**3**:1-9

[7] Servigne M, Tchakirian A. Sur la présence d'éléments des terres rares dans les Algues calcaires (*Lithotamnium calcareum*). Comptes Rendus de l'Académie des Sciences. 1939; **209**:570-572

[8] Hou X, Yan X. Study on the concentration and seasonal variation of inorganic elements in 35 species of marine algae. Science of Total Environment. 1998;**222**:141-156

[9] Fu F, Akagi T, Yabuki S, Iwaki M, Ogura N. Distribution of rare earth elements in seaweed: Implication of two different sources of rare earth elements and silicon in seaweed. Journal of Phycology. 2000;**70**:62-70

[10] Kano N, Aoyagi Y, Imaizumi H. Determination of rare earth elements in some seaweed samples on the coast in Niigata prefecture by inductively coupled plasma mass spectrometry. Journal of Environmental Chemistry. 2001;**11**:221-231

[11] Mashitah SM, Shazili NAM, Rashid MKA. Elemental concentrations in brown seaweed *Padina* sp. along the east coast of Peninsular Malaysia. Aquatic Ecosystem Health & Management. 2012;**15**:267-278

[12] Markert B. The pattern of distribution of lanthanide elements in soils and plants. Phytochemistry. 1987;**26**:3167-3170

[13] Zhang N, Huang C, Hu B. ICP-AES determination of trace rare earth elements in environmental and food samples by on-line separation and preconcentration with acetylacetone-modified silica gel using microcolumn. Analytical Sciences. 2007;**23**:997-1002

[14] Tyler G. Rare earth elements in soil and plant systems—A review. Plant Soil. 2004; **1-2**:191-206

[15] Li Y, Yang JL, Jiang Y. Trace rare earth element detection in food and agricultural products based on flow injection walnut shell packed microcolumn preconcentration

coupled with inductively coupled plasma mass spectrometry. Journal of Agricultural Food Chemistry. 2012;**60**:3033-3041

[16] Sakamoto N, Kano N, Imaizumi H. Determination of rare earth elements, thorium and uranium in seaweed samples on the coast in Niigata Prefecture by inductively coupled plasma mass spectrometry. Applied Geochemistry. 2008;**23**:2955-2960

[17] Ogata T, Terakado Y. Rare earth element abundances in some seawaters and related river waters from the Osaka Bay area, Japan: Significance of anthropogenic Gd. Geochemical Journal. 2006;**40**:463-474

[18] Sahoo PK, Tripathy S, Equeenuddin SM, Panigrahi MK. Geochemical characteristics of coal mine discharge vis-à-vis behavior of rare earth elements at Jaintia Hills coalfield, north-eastern India. Journal of Geochemical Exploration. 2012;**112**:235-243

[19] Richards RG, Mullins BJ. Using microalgae for combined lipid production and heavy metal removal from leachate. Ecological Modelling. 2013;**249**:59-67

[20] Yao J-M, Gong Z-B, Li Y-C, Wen Y-Y, Li J, Wang T. Determination of rare earth elements in marine organims by inductively coupled plasma-mass spectrometry with microwave digestion. Journal of Instrumental Analysis. 2007;**26**:473-477

[21] Shi Q, Shi Q, Guo W-D, Hu M-H, Yang Y-P, Wu Y-M, Gong Z-B. The content of rare earth elements in benthic organisms from the Xiamen Bay and their distribution and environmental implications (in Chinese). Acta Oceanologica Sinica. 2004;**26**:87-94

[22] Jayasekera R, Rossbach M. Use of seaweeds for monitoring trace elements in coastal waters. Environmental Geochemistry and Health. 1996;**18**:63-68

[23] Vasquez J, Guerra N. The use of seaweeds as bioindicators of natural and anthropogenic contaminants in northern Chile. Hydrobiologia. 1996;**326-327**:327-333

[24] Sánchez-Rodríguez I, Ma H-D, Choumiline E, Holguăn-Quiones O, Zertuche-Gonzălez J. Elemental concentrations in different species of seaweeds from Loreto Bay, Baja California Sur, Mexico: Implications for the geochemical control of metals in algal tissue. Environmental Pollution. 2001;**114**:145-160

[25] Schacht U, Wallmann K, Kutterolf S. The influence of volcanic ash alteration on the REE composition of marine pore waters. Journal of Geochemical Exploration. 2010;**106**:176-187

[26] Volokh AA, Gorbunov AV, Gundorina SF, Revich BA, Frontasyeva MV, Pal CS. Phosphorus fertilizer production as a source of rare earth elements pollution of the environment. Science of Total Environment. 1990;**95**:141-148

[27] Olmez I, Sholkovitz ER, Hermann D, Eganhouse RP. Rare earth elements in sediments off Southern California: A new anthropogenic indicator. 25. Environmental Science Technology. 1991;**25**:310-316

[28] Elbaz-Poulichet F, Dupuy C. Behaviour of rare earth elements at the freshwater-seawater interface of two acid mine rivers: The Tinto and Odiel (Andalucia, Spain). Applied Geochemistry. 1999;**14**:1063-1072

[29] Zhu ZZ, Wang ZL, Li J, Li Y, Zhang ZG, Zhang P. Distribution of rare earth elements in sewage-irrigated soil profiles in Tianjin, China. Journal of Rare Earths. 2012;**30**:609-613

[30] Valcheva-Traykova M, Saso L, Kostova I. Involvement of lanthanides in the free radicals homeostasis. Current Topics in Medicinal Chemistry. 2014;**14**:2508-2519

[31] Brown PH, Rathjen AH, Graham RD, Tribe DE. Rare earth elements in biological systems. In: Geschneidner KAJ, LeRoy E, editors. Handbook on the Physics and Chemistry of Rare Earths. 1990. pp. 423-452

[32] Hu ZH, Richter H, Sparovek G, Schnug E. Physiological and biochemical effects of rare earth elements on plants and their agricultural significance: A review. Journal of Plant Nutrition. 2004;**27**:183-220

[33] von Tucher S, Schmidhalter U. Lanthanum uptake from soil and nutrient solution and its effects on plant growth. Journal of Plant Nutrition and Soil Science. 2005;**168**:574-580

[34] Zhang L, Yang T, Liu Y, Xu S, Zeng F, An L. Effect of lanthanum ions (La^{3+}) on ferritin-regulated antioxidant process under PEG stress. Biological Trace Elements Research. 2006;**113**:193-208

[35] Schwabe A, Meyer U, Grun M, Voigt KD, Flachowsky G, Danicke S. Effect of rare earth elements (REE) supplementation to diets on the carry-over into different organs and tissues of fattening bulls. Livestock Science. 2012;**143**:5-14

[36] Pang X, Li D, Peng A. Application of rare earth elements in the agriculture of China and its environmental behavior in soil. Environmental Science Pollution Research International. 2002;**9**:143-148

[37] Volland S, Bayer E, Baumgartner V, Andosch A, Lutz C, Sima E, Lutz-Meindl U. Rescue of heavy metal effects on cell physiology of the algal model system *Micrasterias* by divalent ions. Journal of Plant Physiology. 2014;**171**:154-163

[38] Wang L, Li J, Zhou Q, Yang G, Ding XL, Li X, Cai CX, Zhang Z, Wei HW, Lu TH, Deng XW, Huang XH. Rare earth elements activate endocytosis in plant cells. Proceedings of National Academy of Science, USA. 2014;**111**:12936-12941

[39] Jegerschold C, Rutherford AW, Mattioli TA, Crimi M, Bassi R. Calcium binding to the photosystem II subunit CP29. Journal of Biological Chemistry. 2000;**275**:12781-12788

[40] Ono T. Effects of lanthanide substitution at Ca^{2+}-site on the properties of the oxygen evolving center of photosystem II. Journal of Inorganic Biochemistry. 2000;**82**:85-91

[41] Wei Y-Z, Zhou X-B. Effect of neodynium on physiological activities in oilseed rape during calcium starvation. Journal of Rare Earths. 2000;**18**:57-61

[42] Wang XP, Shan XQ, Zhang SZ, Wen B. Distribution of rare earth elements among chloroplast components of hyperaccumulator *Dicranopteris dichotoma*. Analytical and Bioanalytical Chemistry. 2003;**376**:913-917

[43] Gong D, Li G, Zhang S, Chen T. Effect of external rare earth La^{3+} on growth and physiological property of *Athrospira* in alkaline lake of Erdos plateau. Journal of the Chinese Society of Rare Earths. 2011;**29**:504-507

[44] Liu A. Effects of La on growth and the chlorophyll contents of *Chlorella* in heterotrophic culture. Chinese Rare Earths. 1999;**20**:38-40

[45] Liu Y-F, Tang R-H, Zhang Q-X, Shi J-Y, Li X-M, Liu Z-Q, Zhao W. Stimulation of cell growth of *Tetrahymena pyriformis* and *Chlamydomonas reinhardtii* by trace elements. Biological Trace Element Research. 1986;**9**:89-99

[46] Evseeva T, Geras'kin S, Majstrenko T, Brown J, Belykh E. Comparative estimation of 232Th and stable Ce (III) toxicity and detoxification pathways in freshwater alga *Chlorella vulgaris*. Chemosphere. 2010;**81**:1320-1327

[47] Su D, Tai P, Li P, Ke X. Toxic effects of lanthanides on *Chlorella autrophica*. Chinese Journal of Ecology. 2005;**24**:382-384

[48] Jin X, Chu Z, Yan F, Zeng Q. Effects of lanthanum(III) and EDTA on the growth and competition of *Microcystis aeruginosa* and *Scenedesmus quadricauda*. Limnologica. 2009;**39**:86-93

[49] Fuma S, Takeda H, Takaku Y, Hisamatsu S, Kawabata Z. Effects of dysprosium on the species-defined microbial microcosm. Bulletin of Environmental Contamination and Toxicology. 2005;**74**:263-272

[50] Qu K-M, Yuan Y-X, Xin F-Y. Effects of rare earth on growth of *Isochrysis galbana*. Oceanologia et Limnologia Sinica. 1998;**29**:552-557

[51] Qu K-M, Yuan Y-X, Xin F-Y. Enhancement of 3 rare earth elements to *Isochrysis galbana*. Journal of Fishery Sciences of China. 1998;**5**:42-47

[52] Tai P, Zhao Q, Su D, Li P, Stagnitti F. Biological toxicity of lanthanide elements on algae. Chemosphere. 2010;**80**:1031-1035

[53] Guiry MD, Guiry GM, Morrison L, Rindi F, Valenzuela Miranda S, Mathieson AC, Parker BC, Langangen A, John DM, Barbara I, Carter CF, Kuipers P, Garbary DJ. AlgaeBase: An on-line resource for algae. Cryptogamie Algologie. 2014;**35**:105-115

[54] Wei Y-Z, Zhou X-B. Effect of neodymium on physiological activities in oilseed rape during calcium starvation. Journal of Rare Earths. 2000;**18**:57-61

[55] Huang H, Liu X, Qu C, Liu C, Chen L, Hong F. Influences of calcium deficiency and cerium on the conversion efficiency of light energy of spinach. Biometals. 2008;**21**:553-561

[56] Gong X, Hong M, Wang Y, Zhou M, Cai J, Liu C, Gong S, Hong F. Cerium relieves the inhibition of photosynthesis of maize caused by manganese deficiency. Biological Trace Elements Research. 2011;**141**:305-316

[57] Peng A, Pang X. The free radical mechanism of rare earth elements in anti-adversity for plants. Environmental Chemistry. 2002;**21**:313-317

[58] Ippolito MP, Fasciano C, d'Aquino L, Morgana M, Tommasi F. Responses of antioxidant systems after exposition to rare earths and their role in chilling stress in common duckweed (*Lemna minor* L.): A defensive weapon or a boomerang? Archives of Environment Contamination Toxicology. 2010;**58**:42-52

[59] Li ZJ, Zhang ZY, Yu M, Zhou YL, Zhao YL. Effects of lanthanum on calcium and magnesium contents and cytoplasmic streaming of internodal cells of *Chara corallina*. Biological Trace Element Research. 2011;**143**:555-561

[60] Goecke F, Vítová M, Lukavský J, Nedbalová L, Řezanka T, Zachleder V. Effects of rare earth elements on growth rate, lipids, fatty acids and pigments in microalgae. Phycological Research. 2017;**65**:226-234

[61] Li Z, Cai MG, Huang SY, Shi RG, Lu XX, Qi AX, Wu R. Effects of cerium on cell growth and astaxanthin production of *Haematococcus pluvialis*. Marine Sciences. 2008;**32**:37-41

[62] Hodge HC, Sterner JH. Tabulation of toxicity classes. American Industry Hygiene Association. 1949;**10**:93-96

[63] Abramczuk JW. The effects of lanthanum chloride on pregnancy in mice and on preimplantation mouse embryos invitro. Toxicology. 1985;**34**:315-320

[64] Pagano G, Guida M, Siciliano A, Oral R, Kocbas F, Palumbo A, Castellano I, Migliaccio O, Thomas PJ, Trifuoggi M. Comparative toxicities of selected rareearth elements: Sea urchin embryogenesis and fertilization damage withredox and cytogenetic effects. Environment Research. 2016;**147**:453-460

[65] Bulman RA. Metabolism and toxicity of the lanthanides. In: Sigel A, Sigel H, editors. Metal Ions in Biological Systems. The Lanthanides and their Interrelations with Biosystems. New York: Marcel Dekker; 2003. pp. 39-67

[66] Thomas PJ, Carpenter D, Boutin C, Allison JE. Rare earth elements (REEs): Effects on germination and growth of selected crop and native plant species. Chemosphere. 2014; **96**:57-66

[67] Barry MJ, Meehan BJ. The acute and chronic toxicity of lanthanum to *Daphnia carinata*. Chemosphere. 2000;**41**:1669-1674

[68] Maheswaran J, Meehan B, Reddy N, Peverill K, Buckingham S. Impact of rare earth elements on plant physiology and productivity. A Report for The Rural Industries Research and Development Corporation. Rural Industries Research and Development Corporation; 2001. pp. 1-40

[69] Yoder MD, Jurnak F. The refined 3-dimensional structure of pectate lyase-C from *Erwinia-Chrysanthemi* at 2.2-angstrom resolution—Implications for an enzymatic mechanism. Plant Physiology. 1995;**107**:349-364

[70] Squier TC, Bigelow DJ, Fernandezbelda FJ, Demeis L, Inesi G. Calcium and lanthanide binding in the sarcoplasmic-reticulum atpase. Journal of Biological Chemistry. 1990; **265**:13713-13720

[71] Palasz A, Czekaj P. Toxicological and cytophysiological aspects of lanthanides action. Acta Biochimica Polonica. 2000;**47**:1107-1114

[72] Kastori R, Maksimovic I, Zeremski-Skoric T, Putnik-Delic M. Rare earth elements: Yttrium and higher plants. Zbornik Matice Srpske za Prirodne Nauke. 2010;**118**:87-98

[73] Reid RJ, Rengel Z, Smith FA. Membrane fluxes and comparative toxicities of aluminium, scandium and gallium. Journal of Experimental Botany. 1996;**47**:1881-1888

[74] Hu Q-H, Zheng S-P, Tang S-M, Guan L-H. Effects of Sm and Y on growth of *Chlorella ellipsoidea*. Agro-Environmental Protection. 2001;**20**:398-400

[75] Yang G, Kong Q. Effect of La^{3+} and Nd^{3+} on growth, DHA yield and nitrogenase activity of *Crypthecodinium cohni*. Journal Chinese Rare Earth Society. 2002;**20**:168-171

[76] Xin F-Y, Yuan Y, Qu K-M. Influence of lanthanum amino acid complexes on *Chaetoceros mulleri*. Chinese Journal of Applied Ecology. 1998;**8**:206-208

[77] Tai P, Zhao Q, Su D, Li P, Stagnitti F. Biological toxicity of lanthanide elements on algae. Chemosphere. 2010;**80**:1031-1035

[78] Singh RN, Subbaramaiah K. Effects of chemicals on *Fischerella muscicola* (Thaset) Gom. Journal of Microbiology. 1970;**16**:193-199

[79] Wang YJ, Li J, Lu Y, Jin HB, Deng SH, Zeng YM. Effects of cerium on growth and physiological characteristics of *Anabaena flos aquae*. Journal of Rare Earths. 2012;**30**:1287-1292

[80] Guida M, Siciliano A, Pagano G. Rare earth element toxicity to marine and freshwater algae. In: Pagano G, editor. Rare Earth Elements in Human and Environmental Health at the Crossroads between Toxicity and Safety. Singapore: Pan Stanford Publishing Pte. Ltd.; 2017. pp. 143-153

[81] Wang X, Tu Q, Hua Z. Uptake of rare earth elements by algae (*Chlorella pyrenoidosa*) in aquatic system. Environment Chemistry. 1993;**12**:219-224

[82] Bao J, Yongmin C, Shaohong W, Changhal W, Jian L. The effect of several rare earths on *Spirulina platensis*. Marine Science Bulletin. 2000;**19**:92-96

[83] Yuan X-Z, Pan G, Chen H, Tian B-H. Phosphorus fixation in lake sediments using $LaCl_3$-modified clays. Ecological Engineering. 2009;**35**:1599-1602

[84] Lurling M, van Oosterhout F. Case study on the efficacy of a lanthanum-enriched clay (Phoslock (R)) in controlling eutrophication in Lake Het Groene Eiland (The Netherlands). Hydrobiologia. 2013;**710**:253-263

[85] Goecke F, Goecke H. Rare earth elements as phosphate binders: From kidney to lakes. In: Pagano G, editor. Rare Earth Elements in Human and Environmental Health. Danvers, MA, USA: Pan Stanford Publishing Pte. Ltd.; 2017

[86] Davis TA, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. Water Research. 2003;**37**:4311-4330

[87] Kumar D, Pandey LK, Gaur JP. Metal sorption by algal biomass: From batch to continuous system. Algal Research. 2016;**18**:95-109

[88] Andresen E, Peiter E, Kupper H. Trace metal metabolism in plants. Journal of Experimental Botany. 2018;**69**:909-954

[89] Stary J, Kratzer K, Prasilova J. Systematic study of the cumulation of elements on alga. Toxicological and Environmental Chemistry. 1983;**7**:47-60

[90] Rice TR, Willis VM. Uptake, accumulation and loss of radioactive cerium-144 by marine planktonic algae. Limnology and Oceanography. 1959;**4**:277-290

[91] Okajima MK, Higashi T, Asakawa R, Mitsumata T, Kaneko D, Kaneko T, Ogawa T, Kurata H, Isoda S. Gelation behavior by the lanthanoid adsorption of the cyanobacterial extracellular polysaccharide. Biomacromolecules. 2010;**11**:3172-3177

[92] Wang X, Sun H, Xu Z, Dai L, Li Z, Chen Y. The effects and bioconcentration of REE La and its EDTA complex on the growth of algae *Chlorella vulgaris* Beijerinck (in Chinese). Journal of Nanjing University. 1996;**32**:460-475

[93] Kang L, Shen Z, Jin C. Neodymium cations Nd^{3+} were transported to the interior of *Euglena gracilis* 277. Chinese Science Bulletin. 2000;**45**:585-592

[94] Shen H, Ren QG, Mi Y, Shi XF, Yao HY, Jin CZ, Huang YY, He W, Zhang J, Liu B. Investigation of metal ion accumulation in *Euglena gracilis* by fluorescence methods. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 2002;**189**:506-510

[95] Diniz V, Volesky B. Biosorption of La, Eu and Yb using *Sargassum* biomass. Water Research. 2005;**39**:239-247

[96] Diniz V, Weber ME, Volesky B, Naja G. Column biosorption of lanthanum and europium by *Sargassum*. Water Research. 2008;**42**:363-371

[97] Oliveira RC, Palmieri MC, Garcia O Jr. Biosorption of metals: State of the art, general features, and potential applications for environmental and technological processes. In: Shaukat S, editor. Progress in Biomass and Bioenergy Production. London, UK: IntechOpen Ltd.; 2011. pp. 151-177

[98] Vijayaraghavan K, Sathishkumar M, Balasubramanian R. Interaction of rare earth elements with a brown marine alga in multi-component solutions. Desalination. 2011; **265**:54-59

[99] Zoll AM, Schijf J. A surface complexation model of YREE sorption on *Ulva lactuca* in 0.05-5.0M NaCl solutions. Geochimica et Cosmochimica Acta. 2012;**97**:183-199

[100] Sadovsky D, Brenner A, Astrachan B, Asaf B, Gonen R. Biosorption potential of cerium ions using Spirulina biomass. Journal of Rare Earths. 2016;**34**:644-652

[101] Lunde G, Smidsrod O, Haug A. Selectivity of polyuronates for lanthanide ions. Acta Chemica Scandinavica. 1972;**26**:3421-3426

[102] Diniz V, Volesky B. Effect of counterions on lanthanum biosorption by Sargassum polycystum. Water Research. 2005;**39**:2229-2236

[103] Gok C, Aytas S. Biosorption of uranium(VI) from aqueous solution using calcium alginate beads. Journal of Hazardous Materials. 2009;**168**:369-375

[104] Okajima MK, Nakamura M, Mitsumata T, Kaneko T. Cyanobacterial polysaccharide gels with eficient rare-earth-metal sorption. Biomacromolecules. 2010;**11**:1773-1778

[105] Herrmann H, Nolde J, Berger S, Heise S. Aquatic ecotoxicity of lanthanum—A review and an attempt to derive water and sediment quality criteria. Ecotoxicological and Environmental Safety. 2016;**124**:213-238

[106] Guo A, Wang J, Li X, Zhu J, Reinert T, Heitmann J, Spemann D, Vogt J, Flagmeyer RH, Butz T. Study of metal bioaccumulation by nuclear microscope analysis of algae fossils and living algae cells. Nuclear Instruments and Methods in Physics Research Section B. 2000:**161**:801-807

[107] Shen CD, Xu JR, Yu JF. Effect of the rare earth element of Eu on the growth and chlorophyll content of *Chlorella vulgaris*. Freshwater Fishery. 2003;**33**:23-26

[108] Ren QG, Hua Y, Shen H, Zhong L, Jin CZ, Mi Y, Yao HY, Xie YN, Wei SQ, Zhou LW. Cytochemical behavior of rare earth ions in *Euglena gracilis* studied by XAFS. Journal of Radioanalytical Nuclear Chemistry. 2007;**272**:359-362

[109] Řezanka T, Kaineder K, Mezricky D, Řezanka M, Bišová K, Zachleder V, Vítová M. The effect of lanthanides on photosynthesis, growth, and chlorophyll profile of the green alga *Desmodesmus quadricauda*. Photosynthesis Research. 2016;**130**:335-340

[110] He ML, Rambeck WA. Rare earth elements—A new generation of growth promoters for pigs? Archives of Animal Nutrition. 2000;**53**:323-334

[111] Chapman VJ, Chapman DJ. Seaweed as animal fodder, manure and for energy. In: Chapman VJ, Chapman DJ, editors. Seaweed and Their Uses. London and New York: Chapman & Hal; 1980. pp. 30-61

[112] Shen F, Wang L, Zhou Q, Huang X. Effects of lanthanum on *Microcystis aeruginosa*: Attention to the changes in composition and content of cellular microcystins. Aquatic Toxicology. 2018;**196**:9-16

[113] Wang Y, Li Y, Luo X, Ya R, Eg G, Gao H. Effects of yttrium and phosphorus on growth and physiological characteristics of *Microcystis aeruginosa*. Journal of Rare Earths. 2018;**36**:781-788

[114] Jehl C, Barsczus G. Origin of rare earth elements in cyanobacterial mats (kopara) from Tikehau atoll (Tuamotu, French Polynesia). CR Academy of Sciences, Paris. 1995; **322**:205-212

[115] Allwood AC, Kamber BS, Walter MR, Burch IW, Kanik I. Trace elements record depositional history of an Early Archean stromatolitic carbonate platform. Chemical Geology. 2010;**270**:148-163

[116] Oliveri E, Neri R, Bellanca A, Riding R. Carbonate stromatolites from a Messinian hypersaline setting in the Caltanissetta Basin, Sicily: Petrographic evidence of microbial activity and related stable isotope and rare earth element signatures. Sedimentology. 2010;**57**:142-161

[117] Corkeron M, Webb GE, Moulds J, Grey K. Discriminating stromatolite formation modes using rare earth element geochemistry: Trapping and binding versus in situ

precipitation of stromatolites from the Neoproterozoic Bitter Springs Formation, Northern Territory, Australia. Precambrian Research. 2012;**212-213**:194-206

[118] Censi P, Cangemi M, Brusca L, Madonia P, Saiano F, Zuddas P. The behavior of rare-earth elements, Zr and Hf during biologically-mediated deposition of silica-stromatolites and carbonate-rich microbial mats. Gondwana Research. 2015;**27**:209-215

[119] Sheng XY, Hambidge KM, Krebs NF, Lei S, Westcott JE, Miller LV. Dysprosium as a nonabsorbable fecal marker in studies of zinc homeostasis. American Journal of Clinical Nutrition. 2005;**82**:1017-1023

[120] Garatun-Tjeldsto O, Ottera H, Julshamn K, Austreng E. Food ingestion in juvenile cod estimated by inert lanthanide markers—Effects of food particle size. Ices Journal of Marine Science. 2006;**63**:311-319

[121] Xia SD, Zhao P, Chen K, Li Y, Liu SL, Zhang LB, Yang HS. Feeding preferences of the sea cucumber *Apostichopus japonicus* (Selenka) on various seaweed diets. Aquaculture. 2012;**344**:205-209

[122] Hagan AK, Zuchner T. Lanthanide-based time-resolved luminescence immunoassays. Analytical and Bioanalytical Chemistry. 2011;**400**:2847-2864

[123] Niu W, He E, Wu Q, Zhou W, Zhang Y, Huang B, Zhao X. Use of fluorescent europium chelates as labels for detection of microcystin-LR in Taihu Lake, China. Journal of Rare Earths. 2012;**30**:941-946

[124] Oliveira EJA, Nova SPV, Alves-Jr S, Santa-Cruz P, Molica RJR, Teixeira A, Malageno E, Filho JLL. A fluorescent-labeled microcystin-LR terbium cryptate. Journal of the Brazilian Chemical Society. 2006;**17**:243-250

[125] Santos JG, Dutra JDL, Alves Junior S, da Costa Junior NB, de Sá GF, Freire RC. Theoretical spectroscopic study of the conjugate microcystin-lr-europium cryptate. Journal of Brazilian Chemistry Society. 2012;**00**:1-5

[126] Borges de Lima I. Rare earths industry and eco-management: A critical review of recycling and substitutes. In: Borges de Lima I, Fiklho WL, editors. Rare Earths Industry. Amsterdam, Netherlands: Elsevier Inc.; 2015. pp. 293-304

[127] Goecke F, Aránguiz-Acuña A, Palacios M, Muñoz-Muga P, Rucki M, Vítová M. Latitudinal distribution of lanthanides contained in macroalgae in Chile: An inductively coupled plasma-mass spectrometric (ICP-MS) determination. Journal of Applied Phycology. 2017;**29**:2117-2128

[128] Li G, Jiang J, Chen J, Zou Y, Zhang X. Effects of rare earth elements on soil fauna community structure and their ecotoxicity to *Holotrichia parallela* (in Chinese). Chinese Journal of Applied Ecology. 2006;**17**:159-162

[129] Li JX, Yin XQ, Hong M, Liu JL. Effects of the accumulation of the rare earth elements on soil macrofauna community. Journal of Rare Earths. 2010;**28**:957-964

[130] Wei Z, Hong F, Yin J, Li H, Hu F, Zhao G, Woonchung WJ. Subcellular and molecular localization of rare earth elements and structural characterization of yttrium bound chlorophyll a in naturally grown fern *Dicranopteris dichotoma*. Microchemistry Journal. 2005;**80**:1-8

[131] de Boer MA, Lammertsma K. Scarcity of rare earth elements. ChemSusChem. 2013; **6**:2045-2055

[132] Kim J, Dodbiba G, Tanimura Y, Mitsuhashi K, Fukuda N, Okaya K, Matsuo S, Fujita T. Leaching of rare-earth elements and their adsorption by using blue-green algae. Material Transaction. 2011;**52**:1799-1806

[133] Hennebel T, Boon N, Maes S, Lenz M. Biotechnologies for critical raw material recovery from primary and secondary sources: R&D priorities and future perspectives. New Biotechnology. 2015;**32**:121-127

[134] Massari S, Ruberti M. Rare earth elements as critical raw materials: Focus on international markets and future strategies. Resources of Polonium. 2013;**38**:36-43

[135] Diniz V, Volesky B. Desorption of lanthanum, europium and ytterbium from *Sargassum*. Separation and Purification Technology. 2006;**50**:71-76

[136] Oliveira RC, Garcia JO. Study of biosorption of rare earth metals (La, Nd, Eu, Gd) by *Sargassum* sp. biomass in batch systems: Physicochemical evaluation of kinetics and adsorption models. Advanced Materials Research. 2009;**71-73**:605-608

[137] Du X, Graedel TE. Global in-use stocks of the rare earth elements: A first estimate. Environmental Science Technology. 2011;**49**:4096-4101

[138] Chu KWM, Suan LM. Rare earth minerals: Occurrence, distribution and applications in emerging high-tech industries. Journal of Science Technology in the Tropics. 2012;**6**:61-80

[139] Barmettler F, Castelberg C, Fabbri C, Brandl H. Microbial mobilization of rare earth elements (REE) from mineral solids—A mini review. AIMS Microbiology. 2016;**2**:190-204

[140] Innocenzi V, Vegliò F. Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitations. Journal of Power Sources. 2012;**211**:184-191

[141] Innocenzi V, De Michelis I, Ferella F, Veglio F. Recovery of yttrium from cathode ray tubes and lamps' fluorescent powders: Experimental results and economic simulation. Waste Management. 2013;**33**:2390-2396

[142] Bhat SV, Melo JS, Chaugule BB, Souza SFD. Biosorption characteristics of uranium (VI) from aqueous medium onto *Catenella repens*, a red alga. Journal of Hazard Material. 2008;**158**:628-635

[143] Ponou T, Wang LP, Dodbiba G, Okaya K, Fujita T, Mitsuhashi K, Atarashi T, Satoh G, Noda M. Recovery of rare earth elements from aqueous solution obtained from

Vietnamese clay minerals using ried and carbonized parachlorella. Journal of Environmental Chemical Engineering. 2014;**2**:1070-1081

[144] Chen AM, Ouyang YS, Shi QS, Feng J, Chen YB, Tan SZ. Dissociation of outer membrane for *Escherichia coli* cell caused by cerium nitrate. Journal of Rare Earths. 2010;**28**:312-315

[145] Horiike T, Yamashita M. A new fungal isolate *Penidiella* sp. strain T9, accumulates the rare earth element dysprosium. Applied Environmental Microbiology. 2015;**81**:3062-3068

[146] Volesky B. Biosorbents for metal recovery. Trends in Biotechnology. 1987;**5**:96-101

[147] Anastopoulos I, Bhatnagar A, Lima EC. Adsorption of rare earth metals: A review of recent literature. Journal of Molecular Liquids. 2016;**221**:954-962

[148] Park DM, Reed DW, Yung MC, Eslamimanesh A, Lencka MM, Anderko A, Fujita Y, Riman RE, Navrotsky A, Jiao Y. Bioadsorption of rare earth elements through cell surface display of lanthanide binding tags. Environmental Science Technology. 2016; **50**:2735-2742

[149] Das N, Das D. Recovery of rare earth metals through biosorption: An overview. Journal of Rare Earths. 2013;**31**:933-943

[150] Romera E, Gonzalez F, Ballester A, Blazquez ML, Munoz JA. Comparative study of biosorption of heavy metals using different types of algae. Bioresource Technology. 2007; **98**:3344-3353

[151] Figueira P, Henriques B, Teixeira A, Lopes CB, Reis AT, Monteiro RJR, Duarte AC, Pardal MA, Pereira E. Comparative study on metal biosorption by two macroalgae in saline waters: Single and ternary systems. Environmental Science of Pollution Research. 2016;**23**:11985-11997

[152] Oliveira RC, Garcia OJ. Study of biosorption of rare earth metals (La, Nd, Eu, Gd) by *Sargassum* sp. biomass in batch systems: Physicochemical evaulation of kinetics and adsorption models. Advanced Material Research. 2009;**71-73**:605-608

[153] Zhou P, Lin J, Shen H, Li T, Song L, Shen Y, Liu Y. Kinetic studies on the combined effects of lanthanum and cerium on the growth of *Microcystis aeruginosa* and their accumulation by *M. aeruginosa*. Environmental Contamination and Toxicology. 2004;**72**:711-716

[154] Lee HS, Volesky B. Interference of aluminum in copper biosorption by an algal biosorbent. Water Quality Research Journal of Canada. 1999;**34**:519-531

[155] Minoda A, Sawada H, Suzuki S, Miyashita S, Inagaki K, Yamamoto T, Tsuzuki M. Recovery of rare earth elements from the sulfothermophilic red alga *Galdieria sulphuraria* using aqueous acid. Applied Microbiology Biotechnology. 2015;**99**:1513-1519

[156] Gorss W, Schnarrenberger C. Heterotrophic growth of two strains of acido-thermophilic red alga, *Galdieria sulphuraria*. Plant Cell Physiology. 1995;**36**:633-638

[157] Graverholt OS, Eriksen NT. Heterotrophic high-cell-density fed-batch and continuous-flow cultures of *Galdieria sulphuraria* and production of phycocyanin. Applied Microbiology and Biotechnology. 2007;**77**:69-75

[158] Oesterhelt C, Schmälzlin E, Schmitt JM, Lokstein H. Regulation of photosynthesis in the unicellular acidophilic red alga *Galdieria sulphuraria*. The Plant Journal. 2007;**51**:500-511

[159] Henriques B, Rocha LS, Lopes CB, Figueira P, Monteiro RJR, Duarte AC, Pardal MA, Pereira E. Study on bioaccumulation and biosorption of mercury by living marine macroalgae: Prospecting for a new remediation biotechnology applied to saline waters. Chemical Engineering Journal. 2015;**281**:759-770

[160] Henriques B, Lopes CB, Figueira P, Rocha LS, Duarte AC, Vale C, Pardal MA, Pereira E. Bioaccumulation of Hg, Cd and Pb by *Fucus vesiculosus* insingle and multi-metal contamination scenarios and its effect on growth rate. Chemosphere. 2017;**171**:208-222

[161] Henriques B, Rocha LS, Lopes CB, Figueira P, Duarte AC, Vale C, Pardal MA, Pereira E. A macroalgae-based biotechnology for water remediation: Simultaneous removal of Cd, Pb and Hg by living *Ulva lactuca*. Journal of Environment Management. 2017; **191**:275-289

[162] Jacinto J, Henriques B, Duarte AC, Vale C, Pereira E. Removal and recovery of critical rare elements from contaminated waters by living *Gracilaria gracilis*. Journal of Hazardeous Material. 2018;**344**:533-538

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