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Lanthanides and Algae

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<http://dx.doi.org/10.5772/intechopen.80260>

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

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 $\mu\text{g/g}$ 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} $\mu\text{g/g}$ 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.

^aSamples of *Pinus silvestris* (pine needles), Germany [12].

^bCertified reference material GBW07605 tea leaves, China [13].

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

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

^eRed alga *Grateloupia filicina*, Japan [10].

^fBrown alga *Padina* sp., Malaysia [11].

^gGreen 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
<i>Arthrospira platensis</i> (B)	La^{3+}	38.53–53	>53.94	[43]
* <i>Arthrospira platensis</i> (B)	LaCl_3	30–40	>40	[44]
<i>Chlamydomonas reinhardtii</i> (C)	Ce^3	5–20	–	[45]
	La^{3+}	5–20	–	[45]
<i>Chlorella vulgaris</i> (C)	Ce^{3+}	1.8	2.1	[46]
* <i>Ch. vulgaris</i> v. <i>autotrophica</i> (C)	12 different Ln	–	29.14	[47]
* <i>Desmodesmus quadricauda</i> (C)	La^{3+}	<7.2	>72	[48]
<i>Euglena gracilis</i> (E)	Dy^{3+}	50–100	180–1000	[49]
<i>Isochrysis galbana</i> (H)	La	7.28–87.4	–	[50, 51]
	Gd	6.36–57.23	–	[50, 51]
	Yb	5.78–17.34	–	[50, 51]
<i>Microcystis aeruginosa</i> (B)	La^{3+}	<7.2	>72	[48]
<i>Skeletonema costatum</i> (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 $\mu\text{mol/L}$).

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).

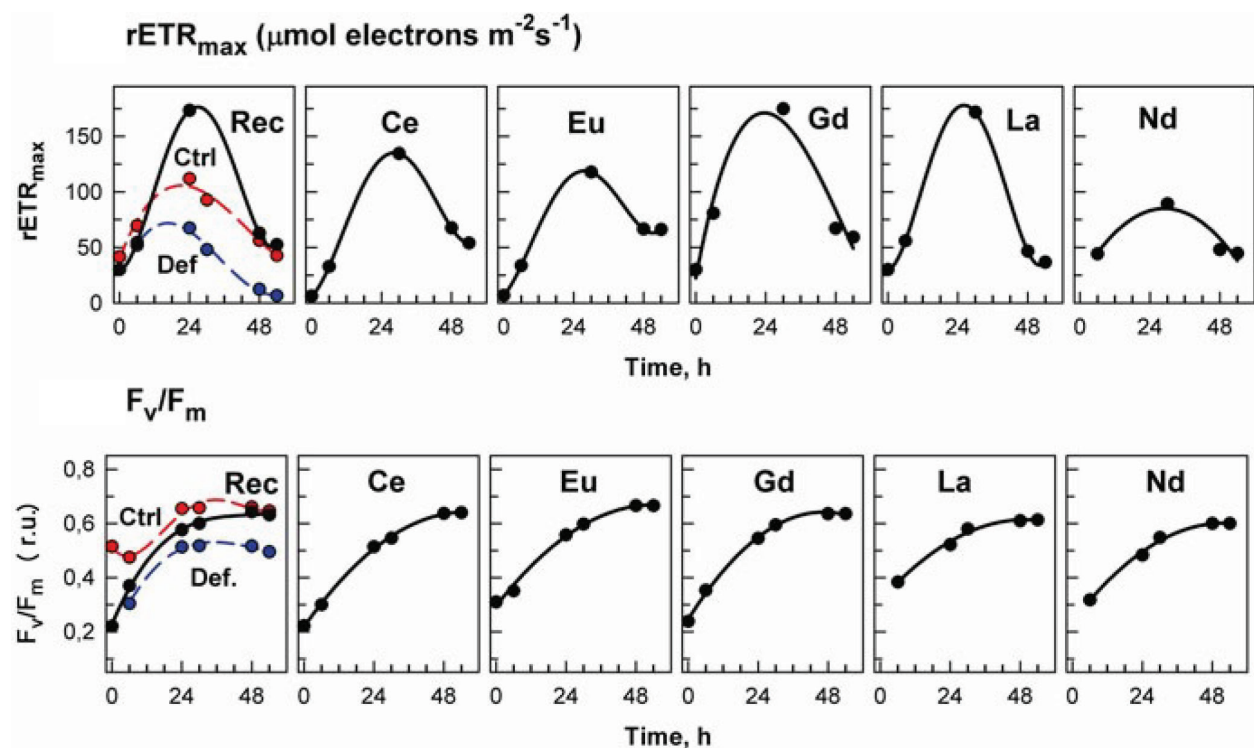


Figure 1. Photosynthetic parameters expressed as maximum relative electron transport rates ($rETR_{max}$), and the maximal quantum yield (F_v/F_m), in cultures of the alga *Desmodesmus quadricauda*, grown either in complete mineral medium (Ctrl, red symbols, dashed curve) or in calcium-deficient mineral 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 pluviialis*, 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].

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

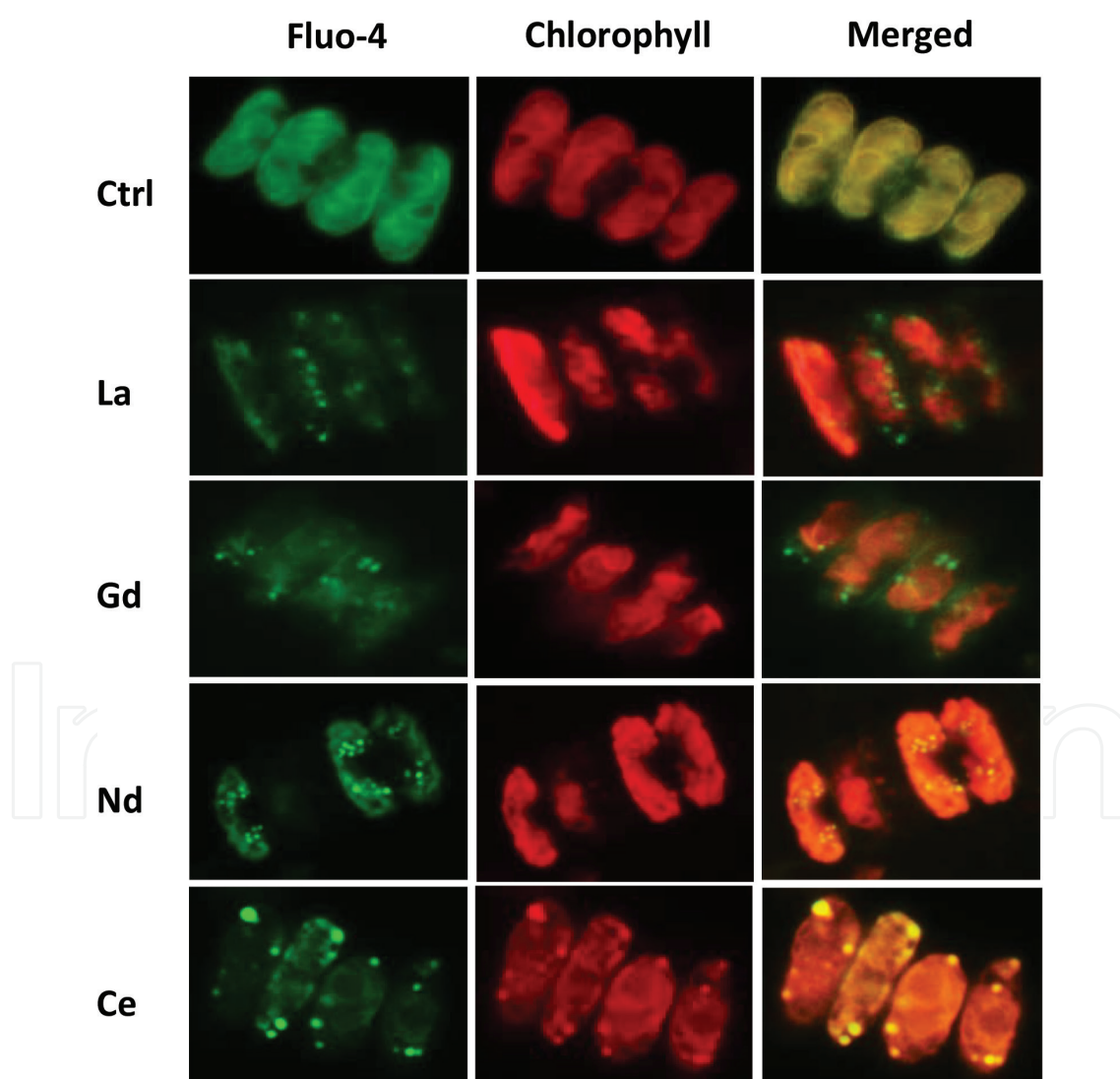


Figure 2. Intracellular localization of different lanthanides in *Desmodesmus quadricauda*. The absorbed lanthanides (horizontal rows) were visualized in cells stained with the fluorescent dye Fluo-4 (left column). Chloroplasts are visualized by autofluorescence of chlorophyll (middle column). In merged 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

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.

Acknowledgements

We thank Prof. John Brooker for critical reading and language corrections of the manuscript. This work was supported by the National Program of Sustainability I, ID: LO1416.

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