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Review

Advances in the Fate of Rare Earth Elements, REE, in Transitional Environments: Coasts and Estuaries

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Abstract: The production of rare earth elements, REE, has significantly increased over the past years, in parallel with the latest advances in nanotechnologies and representing a new group of emerging contaminants. They find application in construction, transport, agriculture, electronics, catalysis, and biomedicine. Their extraordinary intrinsic characteristics are fundamental for overcoming current technological challenges. The accumulation of REE is consistent in near-shore waters being affected by runoff, wastewater discharge, and proximity to built-up areas. Bioavailability in water, sediments, and accumulation in marine biota as well their endocrine disruptor effect is mostly unknown. There is a significant gap of knowledge on the ecotoxicological behaviour of REE in marine areas. The existing investigations have been performed inside well-mixed estuarine systems, due to complex hydrodynamics and multiple sediment transport situations. This hampers the definition of regulatory thresholds for REE concentrations and emissions. The review summarizes the existing information on REE geochemistry and physicochemical conditions influencing dissolution, surface complexation reactions, and distribution at the continent–ocean interface, as well as their speciation, bioavailability, and detrimental effects on living organisms. Strategies for reducing REE usage and inputs are also discussed.

Keywords: rare earth elements; estuaries; coastal environment; distribution; speciation; environmental tracers; bioaccumulation; ecotoxicity; fluxes controlling strategies

1. Introduction

REE are less than 20% of all elements naturally occurring in the environment [1]. They are defined as a group of 17 elements comprising scandium (Sc), yttrium (Y), and lanthanum (La) elements of group 3B of Periodic Table, and the 14 elements of the lanthanides series, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Lanthanides have a very similar electronic configuration, with two external s electrons, an internal d electron, and 1 to 14 more internal f electrons, giving rise to a group of very similar elements. Therefore, REE have substantially similar physicochemical properties due to their electronic structure [2]. They have +3 oxidation state, are quite stable, and show contraction, with gradual decline in the ionic radius with increasing atomic number [3]. REE are highly reactive due to their electronic configuration [4]. They have low solubility and easily precipitate or form complexes with hydroxide, carbonate, fluoride, phosphates, or humic and fulvic acids [5–7].

All these elements tend to be found together in the same ores [8,9]. Two further groups are identified: light rare earth elements, LREE from La to Eu, and heavy rare earth elements, HREE, from Gd to Lu and Y [8]. Y, because of its low atomic weight, should be among the LREE, but it is classified with the HREE due to the similarity of its properties, due to its cation Y^{3+}, and radius between Dy and Ho, and deposits with those of this second group [10]. Sc represents the lightest REE, but it is not classified in any of these REE

groups because of its absence in the same deposits [10] and because of the difference of its properties with respect to both LREE and HREE [11].

Another classification of the Australian Industry Commission [12], primarily used in mineral extraction terminology, divides REE in three groups: light REE, La, Ce, Pr, Nd, and Pm; medium REE, Sm, Eu, and Gd; heavy REE, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y. A mention also deserves the classification of the U.S. Geological Survey (USGS) [13], which is like that of IUPAC [14], considering La, Ce, Pr, Nd, Pr, Sm, Eu, and Gd as LRE, and Tb, Dy, Ho, Er, Tm, Yb, and Lu as HREE.

REE have similar chemical characteristics [15], i.e., most of them exist in the trivalent oxidation state, and their atomic, physical, and chemical properties vary gradually along the series [16]. In the environment, LREE tend to have higher affinities for particles, while HREE are more readily complexed by dissolved ligands [17]. Ce and Eu are atypical and have additional oxidation states, i.e., Ce (VI) and Eu (II) [3].

REE are classified as critical resource materials for high technology industrial applications [18]. REE represent nowadays extremely important ingredients in all high-technology gadgets, and for this reason, they are defined as the vitamins of modern industry [19].

Thus, even though REE in the environment come mainly from geogenic sources, their provenance from high tech devices, agriculture, and medicine is growing steadily. REE have in fact many applications as catalytic converters, Ce; permanent magnets, Pr, Nd, Dy, Ho; batteries, La, Ce, Nd; or magnetic resonance imaging, MRI, agent, Gd; and some REE are also used in the development of drugs for cancer treatment [20–22]. They are applied in military defence systems, lighters, flints, fluorescent lamps, high-tech, high-temperature superconductors, information storage, and agricultural products [23–25]. They are indispensable in emerging clean energy [26], and hence they are fundamental for the current transition from traditional energy sources to clean energy technologies, wind turbines, electric vehicles, and energy-efficient lighting [27]. The demand for REE from green technologies will reach 51.9 kilotonnes, as rare earth ores in 2030, especially of Nd and Dy [26].

They are in use in agriculture, forestry, animal husbandry, and aquaculture [28] and to increase meat digestibility and quality in diet supplemented with REE-enriched yeast [29]. In China, REE find application as fertilizer supplements to increase yields and crop quality [30]. Lanthanides in the surface soil layer of China reached 100–200 mg/kg [31], with bioaccumulation consequences [32,33]. Asia—namely, in China—shows the most critical risk of REE pollution level, followed by Europe, Africa, USA, and Australia [34].

Due to such large use, the world consumption of REE in 2020 was 540 kt and is continuously increasing by 6% each year [10,35].

The two flows of REE, natural and anthropic, may exert cumulative and synergic damaging effects [36], that alter the natural REE distribution [23], especially in natural aquatic systems, disturbing biogeochemical cycles.

REE are recent contaminants, and this limits the knowledge about their environmental fate in terms of bioaccumulation, bioavailability, and toxicity. For this reason, environmental discharge of REE is usually not regulated by governments. Moreover, diffuse REE inputs from the air and water runoff from hard-standing areas hinders the set-up of regulation rules especially in estuaries that receive different input from their catchments [36,37]. The literature displays [37,38] that only wastes and treated water from mining activities are embedded in three European regulations, establishing threshold concentrations of REE, EIA directive/EU1452/; Directive/EU 0621/; Directive/EU 1359/ [38]

Thus, REE in aquatic environments, must be considered as ubiquitous contaminants; the presence has already been measured in waters, suspended particles, and sediments of rivers [39], estuaries [40], and oceans [41,42]. REE have been detected in coastal areas at trace concentrations [43]; however, their harmful ecosystem effects have been only hypothesised [44]. In the marine environment, REE may interact with the resident biota by different pathways. They can bioaccumulate in organisms and be further transferred along the trophic web, resulting in biomagnification or bio-dilution in the upper trophic lev-

els [37]. Environmental concentrations of the fractionated pools of REE, LREE, and HREE, normalized to reference reservoirs, i.e., chondrite, shales, makes it possible to highlight geochemical processes, tracer water masses, and anthropic releases [45–47], as is often the case of Sm and Gd showing positive anomalies in many estuaries of the world [48]. Anthropogenic anomalies of Gd, La, and Sa in aqueous samples are often reported [49]. Following anthropogenic Gd, the anomalies of La, Sa, and Eu are reported [50]. The positive Gd anomalies reported for river waters worldwide are caused by the large use of Gd-based contrast agents used in magnetic resonance imaging (MRI) [50]. Sm finds applications in many different areas, from high-strength permanent magnets to control rods in nuclear reactors, and it is used as a catalyst in assisting the decomposition of plastics and the dechlorination of polychlorinated biphenyls [49]. A survey of the anthropogenic dissolved and colloid/nanoparticle-bound Gd and Sm in the Rhine River suggests that while the anthropogenic Gd is not particle-reactive, and hence exclusively present in the truly dissolved REE pool, the anthropogenic Sm is also present in the colloidal/nanoparticulate REE pool [49].

Sholkovitz [51,52] reports that there is fractionation of REE during the formation of weathering products from parent rocks and that weathered products accumulate REE and tend to be LREE-enriched relative to the parent rock. Fractionation is due, in part, to the formation of more soluble HREE-complexes that are transported away from the weathering zone and to the preferential retention of the LREE by adsorption to or incorporation into secondary minerals. The same author [51,52] states that the solution pool of REE in river waters is strongly HREE-enriched and is fractionated to the same extent as that of surface seawater. This means that the evolved REE composition of sea water is coupled to chemical weathering on the continents and reactions in estuaries. A particular behaviour is shown by Ce and Eu having valency of +2 besides +3, and +4 as well as +3, respectively influencing the solubility and stability of compounds and hence of anomalies in the REE patterns. It is known that most waters show negative Ce and Eu anomalies [16].

The research on the behaviour of REE in marine estuaries and coastal environments is developing. The core of the review is to present the existing information on REE behaviour and on fate processes in estuaries and coastal environments.

1.1. The Natural Abundance

The discovery of REE occurred in 1787, but it was not published by Arrhenius until the following year [53]. Their magnetic, luminescent, and electrochemical value has been estimated only few decades ago [54]. The "rare" definition does not reflect their abundance in the environment, which is higher than those of gold or copper, Figure 1, but the form in which they occur, dispersed in ores instead of in the native form of aggregates or nuggets [55,56].

REE are widely distributed in the Earth's crust in average concentrations ranging from 150 to 220 mg/kg [57], which is significantly higher than other commonly exploited elements and much higher than their respective chondritic abundances [58].

The mean total crustal abundance of REE is 169 mg/kg, and LREE, La to Gd, are 137.8 mg/kg, far higher than HREE, 31.34 mg/kg. The most abundant REE in the Earth crust are Ce and La, 63 mg/kg and 31 mg/kg, a presence richer than those of Cu, 28 mg/kg, and Pb, 17 mg/kg [59]. The rarest ones are Tm and Lu, with levels of 0.30 mg/kg and 0.31 mg/kg, respectively, higher than those of Au, 0.0015 mg/kg, Ag, 0.053 mg/kg, and platinum group elements [59]. According to the Oddo–Harkin rule, the REE abundance is greater for those with an even atomic number compared with those with an odd atomic number, and abundance decreases through the lanthanide series [3].
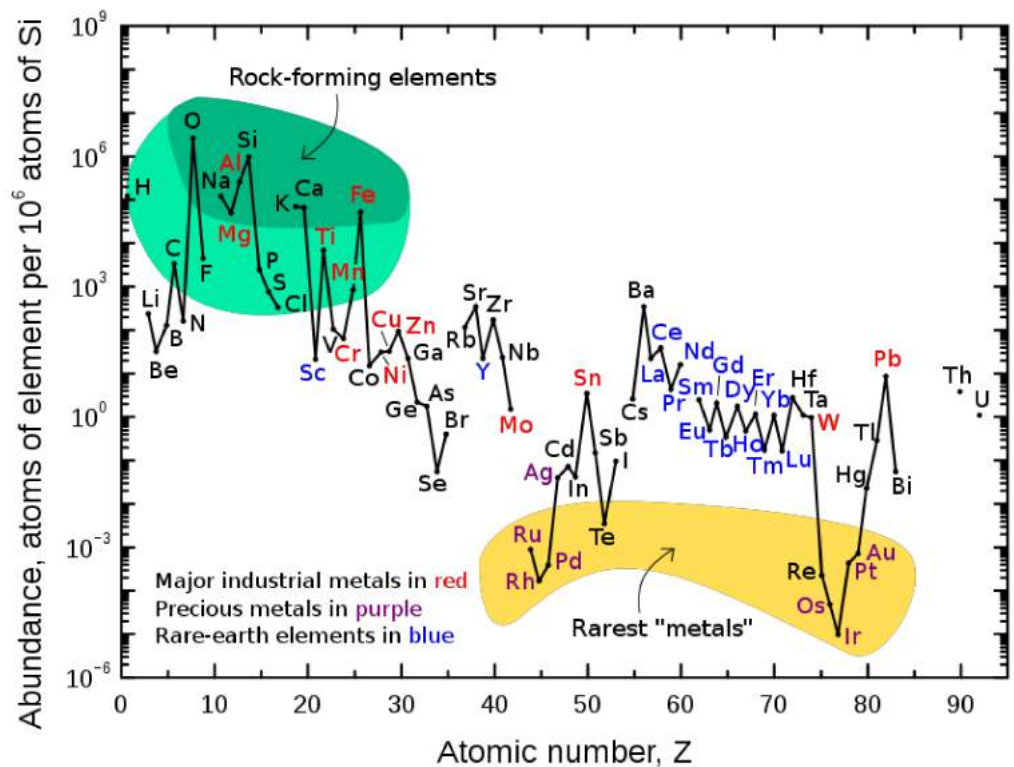
Figure 1. Natural abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. Source [60].

Currently, more than 200 REE-bearing minerals have been identified [56,61]. Typical existence of REE is in granites, pegmatites, carbonatites, and perovskites [58]. They are usually enriched with phosphate-minerals such as apatite, monazite, bastnaesite, and others [58]. REE minerals are monazite, bastnaesite, loparite, and the lateritic ion-adsorption clays with high grades of LREE, La–Eu, or ceritic earths and xenotime which contains higher grades of heavy rare earth elements, HREE, Gd–Lu or ytter earths [58].

Zhou et al. [54] reported that in the world there are 178 deposits with REE totalling 478 megaton, Mt, as rare earth ores. A survey of 2018 estimates that overall world reserve as metal is 140 Mt, of which 55 are in China, 22 in Brazil, 19 in the Commonwealth of Independent States, and 13 Mt in the USA [13]. Thus, China holds 39% of the overall reserve and produces 100 Kt per year of REE, or 90% in 2010 [62]. These resources could sustain global REE production for more than a hundred years [54]. Moreover, China developed leading processing technologies and production facilities for REE exploitation.

All REE occur in nature but not in pure metal form. Promethium, the rarest, only occurs in trace quantities in natural materials, as it has no long-lived or stable isotopes [63]. LRE resources are found mainly in monazite minerals in northern China, with the Bayan Obo mine in Inner Mongolia being the world's largest REE mine in operation. HREE resources are enriched in ion adsorption deposits in southern China, where Jiangxi and Guangdong provinces hold almost 70% of the total deposits [64]. Many processing steps are involved in REE manufacturing, making their separation very complex [65].

1.2. The Sources of REE Contamination

There are several REE sources for estuary aquatic environments that can be natural or anthropic. REE can come from rock and soil erosion processes and wind driven transported to open sea [66]. Post-consumer REE products, waste electronic and electrical equipment (WEEE), once reaching the landfills become an incredible source of REE for oceans [67]. Some of these devices, such as computer screens, can contain up to 72% of Eu in a liquid phase [2,68]. Thus, recycling plants for WEEE and other REE-containing wastes such as

fluorescent lamps, which are common in several countries, including China, India, Pakistan, Nigeria, Ghana, and Vietnam, represent a serious threat [69]. One of the main sources of REE for aquatic systems is the discharge of REE-contaminated wastewater [70], thus representing a great threat for coastal environments via runoff and leaching.

Another important source of REE comes from fertilizers and animals' feeds [31,71,72]. Phosphatic rocks with high loads of REE are often used in the manufacture of phosphate fertilizers and thus may pollute estuaries [3].

2. Fate of REE in Riverine and Estuary System

The amount of REE in the fluvial water/sediment system is influenced by the parent materials and organic matter contents, soil texture, paedogenetic processes, and anthropogenic activities [73]. The contraction of the ionic radii of REE leads to systematic changes in the chemical properties along the series with HREE showing a higher propension to form complexes. LREE are preferentially scavenged on particle surfaces, while HREE are retained in dissolved state because of stronger complexation with ligands, CO_3^{2-}, PO_4^{3-}, and organic ligands [17,45,74]. Sholkovitz [75] reports that the concentration and fractionation of REE in river waters are highly pH dependent. With increasing pH fractionation of REE scales occurs in the following order: LREE > MREE > HREE. With decreasing pH REE are released from particle surfaces in the same order. This means that REE composition in fluvial waters depends much more on water chemistry rather than the rock composition.

REE in river waters are fractionated between colloidal and suspended particles, as oxyhydroxides [76], and solution phases, but it is especially the interaction with the former phases that is responsible for REE transport and distribution [51,52]. Within the dissolved REE, Fe-organic colloids are the major carrier of REE, and this also explains the direct relationship between REE and Fe in rivers and estuaries [77].

A model proposed by Moermond et al. [78] addresses, in riverine waters, the complexation of REE mainly with dissolved organic matter, followed by carbonates and bicarbonates, whereas in seawater the preferential sequence of complexation was carbonates, bicarbonates, and then free ions [78]. This appears mainly driven by pH increase from 6 to 9, with a decrease in the free ions and in REE bound to humic ligands, and an increase in REE carbonate and bicarbonate complexes [78]. The abundance of REE in river water, suspended or dissolved, is important to an understanding of their cycling and interaction with seawater as well for knowing their abundances in the continental crust [79,80].

Few studies refer to the distribution of REE in freshwater systems, and most of the existing ones clearly show anthropogenic industrial sources. Emblematic are the cases of 1.5 t of La in the Rhine [81] and the marked increase in Gd by more than 2 orders of magnitude in Berlin, Germany [82], from wastewater treatment plants. In organic-rich rivers, the REE transportation via colloids can cover up to 100% [83,84]. Generally, the REE in rivers decreases from riverine to brackish to sea water. In fact, mixing processes of fresh with saltwater in estuary zones result in coagulation of colloidal and particulate-bound lanthanides and subsequent sedimentation with removal rates in the range of 30% to 90% [51,52,77]. Once rivers enter the estuary, many physicochemical processes, adsorption, flocculation, diagenetic remobilization, and resuspension occur at the fresh water–sea water interface [76]. Estuaries are important dynamic interfaces linking the continents to the oceans via the transfer of materials from processes of chemical weathering, mechanical soil erosion, and products of biological and anthropogenic activities. REE are often used as tracers of geochemical processes [85–88]. In fact, they are used as tracers of the history of sedimentation by natural processes, such as shoreline erosion and weathering products on the seabed [46] and indicators of sediment provenance [89] and anthropogenic activities [90]. The biogeochemical behaviour of REE in estuarine is influenced by complex hydrodynamics and sediment transport pathways [52,87,88,91–101].

Weathering, erosion and riverine transport, and provenance of sediments and sands have been studied in different estuaries [102]. In estuaries, REE are often normalized to suitable standards, chondrite, shales, and the deviations/anomalies in the abundance of

one element from the other REE can be quantitatively assessed and then used as water-mass tracers [45], source trackers for suspended particles and groundwater/river discharge [103], and as proxies for redox reactions. REE estuary sediment distribution can also be useful in discriminating the influence of iron oxyhydroxides [104], hydrothermal alterations [105], and volcanoes [106]. Thus, the study of REE contents and shale normalized patterns together with the above-mentioned features could be useful in providing a better geochemical characterization of estuary systems [76].

2.1. Fractionation

Even though REE are chemically coherent, in estuary waters they fractionate in relation to biogeochemical processes [70]. The gradual decreasing ionic radius with increasing atomic number and increasing covalence due to progressive infilling of their 4f electron shell is responsible for fractionation processes [107]. Thus, it is possible to observe low anomalies for La, Gd, and Lu due to slight differences between the stabilities of their chemical complexes, and greater anomalies for Ce and Eu being more redox-sensitive [108].

2.1.1. Factors Controlling Fractionation of REE

Distribution, fractionation, fluxes, and composition of dissolved REE in estuary is governed by flushing time, water/particle interactions, solution chemistry, flocculation, organic and inorganic complexation, adsorption, and sediment resuspension, [70]. Diffusion depends on the nature and speciation of REE, geochemical conditions as dissolution and surface complexation reactions with inorganic and/or organic ligands [30]. The abundance and fractionation of dissolved REE depend on certain intrinsic characteristics including salinity, pH, redox potential, dissolved organic matter, mineral phases, and type and concentration of chelating agents [109], flow conditions, microorganism activity, and variations in atmospheric precipitation [110]. A more detailed presentation of the factors influencing REE fractionation is reported in the bioaccumulation section and in the case of La, see Section 3.

The literature reports large-scale release, modification, distribution, and removal of REE in many estuaries of the world [108]. There is an interesting study of Sholkovitz, dating back 1976 [111], that showed that in the low salinity estuarine mixing zone where freshwater mixes with seawater, seawater cations modify the negative surface charges of particles and colloids and facilitate flocculation, impeding REE river flows to reach seawater. The two main processes regulating REE fluxes are salinity-induced coagulation of colloids and adsorption/desorption from the particulate material [112]. The processes of removal, i.e., flocculation, complexation, adsorption, scavenging, and remineralization, occurring in shallow seawater mandate the normalization of REE to standard reference values. LREE and HREE behave differently. In the presence of organic matter and carbonates, LREE are adsorbed by Mn–Fe oxyhydroxides and clay minerals or precipitate as REE phosphates, whereas HREE are more stable if complexed by these ligands [113]. Loads of REE are especially regulated by the composition of the river discharges and the mixing conditions. When pH is in the acidic range, REE tend to be dissolved, and when pH is alkaline precipitate, REE are adsorbed onto clays and hydroxides [114]. Depletion of LREE relative to HREE, negative Ce anomaly and positive La, and Gd natural anomalies are reported [115–117]. Sholkovitz [52] indicated that the balance between coagulation and release from particles determines the net flux and fractionation during estuarine mixing. The author reports that coagulation and preferential removal order of LREE > MREE > HREE are dominant and that it is difficult to identify and quantify the release of dissolved REE in estuaries from suspended particles and sediments as this is a more spatially diffuse process than is coagulation in the low salinity zone. The same Sholkovitz [52] observed REE removal of 97% in the low salinity mixing zone of the Amazon estuary, whereas under high salinity there is a preferential removal of HREE [118]. A similar removal path was reported by Borrego et al. [114], Andrade et al. [119], and Saha et al. [108], with a fractionation pattern evidencing the enrichment of HLRE and a depletion of HREE relative

to NASC, North American Shale Composite, the most used reference standard. Thus, REE in seawater are of one or two orders of magnitude lower than river water [77]. For example, Elderfield et al. [77] reported La levels in rivers of 20–600 ng/L and of 5–40 ng/L in estuaries and coastal areas. A more recent paper of Merschel [120] disagree with these data, reporting more conservative behaviour of REE. Some authors have identified dominant factors of speciation and fractionation of REE in estuaries [121], considering total organic carbon, TOC, as the most important factor for speciation and bioavailability of REE in estuary sediments. While 50–60% of REE was bound to inert complexes and not bioaccessible, about 20–30% was associated with TOC. In addition, Zhang et al. [122] considered that REE were fractionated as iron and manganese compounds, 8.5–16%, carbonates, 3–6%, and water soluble, 1–11%.

2.1.2. Environmental Application of REE as Tracers of Pollution

The processes of diagenesis, erosion, weathering, and sedimentation contribute to the REE pollution of estuaries [123]. The level and distribution pattern of REE in water/sediment will help to determine their sources of pollution, either natural and/or anthropogenic. Thus, REE may be useful indicators of anthropogenic inputs. For instance, anomalously high Gd concentrations in waters may indicate contamination with treated wastewater containing hospital effluents [82]. In other cases, it is possible to discriminate mining activities as the case reported by Shynu et al. [124] studying REE distribution in sediments of the Mandovy estuary in India. Authors found that the fine-grained Fe–Mn ore particulates that spilled during transport through the estuary and uploading operations in the port region-controlled estuary REE distribution in the estuary.

Hu et al. [125] studied REE in offshore sediments of Western Xiamen Bay in China and potential sources. The patterns of chondrite-normalized REE exhibited a negative slope, as expressed by LREE/HREE ratios, and enrichment factors, indicating that the REE in surface sediments were from the continental crust and anthropogenic activities such as domestic sewage sludge and coal combustion. The same authors used the ratios La/Yb, La/Sm, Gd/Yb to establish some potential sources and reported that REE sediment accumulation in surface sediments might be related to natural sources (parent materials and Pb–Zn deposit) and anthropogenic activities (coal combustion and domestic sewage originating from the Marabasco river estuary in the pacific coast of Mexico). This tropical coastal system is rich in iron oxy-hydroxides [126]. Authors found that REE concentrations in the estuary sediments show a strong correlation with Al and Fe, with LREE having a greater affinity for Fe and HREE for Al. The presence of magnetite and the iron oxy-hydroxide enrichment enhanced this antagonism.

3. The Bioaccumulation and Bioavailability of REE

REE can be detected in most of the biota, and the accumulation pattern follows generally the Oddo–Harkin rule [127], with La usually being the second most common lanthanide after cerium (Ce) [77,127].

In estuary aquatic environments, bioaccumulation and bioavailability of REE are strictly linked together. Generally, the more available pool is water soluble and exchangeable [128]. REE bioavailability depends on the REE speciation, which is influenced by physicochemical parameters, pH, alkalinity, and ionic strength and by the presence of different organic and inorganic complexing agents [78]. Although the literature displays some studies on REE distribution and fractionation in estuarine systems, little is known about bioavailability [96].

REE accumulation has been observed in plankton in the Mediterranean Sea [129], algae in China [129], bivalves in Japan and Germany [41], fish in the United States and China [130], and turtles in Sicily [131]. Mayfield and Fairbrother [132] surveyed 10 North American fish species, reporting that REE in freshwater fish muscle ranged from 0.014 to more than 3 mg/kg dry weight, dw. Another study conducted in China [133] on four species

of freshwater fish and six species of marine ones highlighted REE means of 35.8 mg/kg dw in freshwater fish and 21.0 mg/kg dw in marine fish.

The specific characteristics of organisms and aqueous phase play a paramount role for bioaccumulation. LREE have been found to accumulate in higher amounts in fish, daphnia, duckweed, and shellfish, as well as in phytoplankton [134].

Specific cases of bioaccumulation was found with regard to La as in the whole soft parts of scallop *Chlamys varia* [135], 0.12–2.96 μg/g dry wt basis; the amphipod *Paramoera walker*, 0.10–0.17 μg/g dry wt basis [136]; blue mussels *Mytilus edulis*, 1.141 μg/g dry wt basis [137]; the snails (*Potamopyrgus antipodarum*; *Lymnaea stagnalis*; *Radix ovata*; *Physella acuta*; *Planorbarius corneus*; *Planorbis planorbis*); and bivalves (*Dreissena polymorpha*; *Corbicula fluminae*) [127]. In another recent report, Nørregaard et al. [138] showed a REE accumulation in liver, gill, and muscles of *Salvelinus alpinu*, typical of arctic and subarctic coastal waters, after exposure to Ce, La, and Y.

Ma et al. [139] studied REE in the Pearl River Delta of China and found enhanced accumulation of LREE in oyster from suspended particles, due to recycling and different industrialized activities. Jiao et al. [140] assayed the levels of REE in the mantis shrimp *Oratosquilla oratoria* collected from Shandong Province, China. The calculation of estimated daily intake (EDI), target hazard quotient (THQ), and total target hazard quotient (TTHQ) showed that REE were below harmful limits.

Many bioaccumulation trials fail to reproduce real conditions found in the field, matrices, and concentrations. An alternative procedure for studying REE exposure of aquatic organisms is the use of the diffusive gradient in thin-films, DGT, which provides reliable and sensitive in situ measurements of DGT-labile metal species [141]. However, the effectiveness of the DGT approach is often questioned for measuring REE in estuarine waters. This is the case of the study of Cánovas et al. [142] reporting on the REE availability in the estuarine waters of the Ría of Huelva, SW Spain, strongly affected by mining activities. Authors considered the ability of REE to cross the biological membranes and related metal lability to the concentration of REE in the water column. The ineffectiveness of the DGT to measure bioavailability was attributed to the instability of complexes in contact with the DGT membranes and the inability of metals to form thermodynamically stable complexes of the absorption with colloids.

3.1. Fish Species as Bioindicator of REE Pollution

Some authors [130] evaluated the possibility of using European eels, *Anguilla anguilla*, as an indicator of estuary REE. Bioaccumulation of REE in this fish is rather significant, being a benthic species living in contact with the sediment and at the top of the trophic chain of estuarine [143,144]. Later, Lortholarie et al. [37] studied REE bioaccumulation in the yellow and silver European eel, *Anguilla*, in the Loire estuary, characterized by a large anthropogenic pressure. The results showed that males accumulated more REE than females and that silver eels accumulated more REE than yellow ones. Authors observed an increase in the temporal REE accumulation for silver eel muscles related to the increase in REE uses. More recently, the same authors, [145] studied REE organotropism in the same species and estuary. They observed differences were between life stages and genders, with most accumulating organs being gills and liver. REE distribution was also different between genders. The gonads of female silver eels showed a specific profile with greater presence of Gd, up to 74.2% of REE with respect to male. Other example of tropism is reported by Pernice et al. [146] who determined preferential accumulation of La in digestive glands of two nautilus species with similar physiology but from different geographic areas. Purpleback flying squid *Sthenoteuthis oualaniensis* collected in the Indo-Pacific Ocean demonstrated age-dependent differences in accumulation in certain tissues, such as liver [147]. The liver of adult squids possessed significantly lower La concentrations than that of juveniles. The same pattern occurred for other lanthanides and some essential elements. Squids represent a high trophic level in the marine food web; thus, in addition to seawater, diet may contribute to accumulation. Therefore, it was assumed, that changing

food sources during the life span of *S. oualaniensis* was responsible for the variations between stages. However, the same authors found higher La in the stomach content of adults. Chassard-Bouchard and Hallegot [148] also studied the fate of La after uptake by molluscs and found that the element, adsorbed via the gills or the digestive gland, undergoes detoxification through adsorption to insoluble fractions within the cells of the digestive gland, accumulating as insoluble lanthanum-phosphate in organelles. Bustamante and Miramand [135] studied the tissue concentration and partitioning of La, Nd, and Ce among in variegated scallop *Chlamys varia* from an unpolluted and a polluted location in the Atlantic Ocean near the French coast. Authors found that animal tissues from the polluted site showed higher concentrations of lanthanides. Digestive glands followed by gonads and gills showed the highest uptake of REE. Lowest La concentrations occurred in muscle. High lanthanide concentration in gills was related to direct seawater exposure, compared with gonads, where transport from the intestine via food particles occurred.

Sometimes the length of the shell is an indicator of REE accumulation, as shown by Riget et al. [137] who related elemental concentration and length of the shell of the blue mussels, *Mytilus edulis,* from four unpolluted sites in the West Greenland fjord. Authors found a lanthanum level increase of about 100%, while shell length was doubled.

Another bioindicator of REE is reported to be the fiddler crab, *Leptuca leptodactyla* [149]. The authors used the crab to verify the presence of REE in two mangrove areas of the Ubatuba, northern littoral of São Paulo state, Brazil, and revealed the presence of REE, especially La and Ce, with a correlation with city sewage anthropic flows. Fiddler crabs have direct relation with the mangrove sediments being deposit feeders, and bioturbators [150]. Another high-REE-accumulating marine species is the mantis shrimp *Oratosquilla oratoria*, widely distributed in the coastal waters of China. Ng et al. [151] found LREE accumulation in this shrimp to be 10 times higher compared with HREE. Authors such as Bonnail et al. [152] consider using the high REE accumulation capacity of bivalves to survey acid mine drainage pollution, similar to the approaches used by metal pollution monitoring programs [153].

3.2. Mechanisms of Bioavailability

Here we report the case of the free ion, La^{3+}, the most bioavailable lanthanum species, followed by hydroxides [78]. Molecular or ionic mimicry have been suggested as processes that enable uptake of non-essential, cationic metal species across membranes [154]. La^{3+}, for example, resembles calcium ions for ionic binding capacity and dimension. The high charge to volume ratio of La^{3+} increases its chances to bind on protein sites, where it can replace Ca^{2+}, Mg^{2+}, Fe^{3+}, and Mn^{2+} [155]. The open question is whether La^{3+} can cross cellular membranes. Some authors [155] report that the La^{3+} displacing Ca^{2+} from the cell membrane hampers Ca-dependent functions. However later studies of Wang et al. [156,157] demonstrated La^{3+} uptake into the cell. A former study of Palasz and Czekaj [158] speculated that the REE could be internalized through a Ca channel. Due to the existing research gap, bioaccumulation in marine primary producers occurs according to paths borrowed from those of terrestrial plants: bioaccumulation occurs in parallel with the increased activity of the enzyme glutamic oxaloacetic transaminase, GOT [134].

3.3. Factors Influencing Bioavailability

The bioavailability of La depends on many different factors, such as the water hardness, Ca^{2+}, Mg^{2+}, alkalinity, HCO_3^-, CO_3^{2-}, pH, and dissolved organic carbon, DOC. All these features modify the activity of the bioavailable species and ultimately modify the interaction with the organism membranes. As already stated before, the richness of HCO_3^- and CO_3^{2-} decreases the bioavailability of REE [78,159,160]. This could be attributed to increased competition for Ca-binding sites on the proteins of the membrane or to formation of biologically unavailable La-carbonates causing a decrease in the potential bioavailable forms, La^{3+} and $LaOH^{2+}$ [78]. This might implicate the modulation of the environmental quality criteria with the water hardness, like that already elaborated for cadmium [161].

Bioavailability of La in aqueous systems is influenced by complexation with the dissolved organic matter, the presence of competitive cations, and pH [83]. Mechanistic studies based on mean DOC concentration of world fluvial waters of 5 mg/L reported La^{3+} complexed with sulfate at pH 5.4 and carbonate at pH 7.9 [83]. At neutral pH, La^{3+} complexes with soluble organic matter even though the authors do not exclude the competing role of Fe, Al, and of carbonate ions, especially for light molecular weight DOC at neutral to alkaline pH [162].

Zhao and Wilkinson [163] studied the bioavailability of seven REE for the freshwater alga *Chlamydomonas reinhardtii* in the presence of organic ligands. On the base of the biotic ligand model, BLM, the authors initially hypothesized that complexation would reduce bioaccumulation in direct proportion to the concentration of the free ion. The results of the study evidenced that the uptake of REE was much higher than that predicted by the BLM. In the case of Thulium, Tm, the enhanced uptake was attributed to the formation of a ternary complex among the ligand, Tm, and the metal transport site on the cell membrane. As organic ligands are ubiquitous in natural waters, it is likely that REE will be in complexed form and that simple models will underestimate REE bioavailability. Thus, it is crucial to have a deep knowledge of REE speciation to predict their bioavailability, especially in natural waters where the stability constants of REE with the organic matter are poorly known [163].

In general, the literature reports that the bioaccumulation of REE in the marine environment has a limited chance for biomagnification and often undergoes trophic dilution [36,152,164]. However, a contrasting result is reported by Reindl and Falkowska [165], who found the dominant presence of HREE in the muscles of key clupeid from Gdansk Bay, South Baltic Sea, and Iberian Peninsula, Northeast Atlantic. REE also accumulate in the ova and seminal fluid, highlighting intergenerational transfer, meaning the accumulation and biomagnification potential of REE in the trophic chain [165]. Souza et al. [37] studied the trophic transfer in a neotropical mangrove ecosystem food web. The authors discovered significant evidence of biomagnification along the levels, plankton, oyster, shrimp, crabs, and fish for some REE and for others a bio-dilution, depending likely to different pollution degrees, according to Souza et al. [37]. The study also found that Ce, La, and Y inputs were linked to solid waste from steel factories and that Nb was linked to atmospheric particulate.

4. The Toxicity of REE

In general, the eco-toxicological behaviour of REE resembles that of non-essential metals, with lower effects at low concentrations, whereas at higher concentration, toxicity increases [166]. There are reports highlighting the toxicity of La because of its bioaccumulation in the brain and nervous system of marine organisms [167]. Knowledge on the toxicological mechanisms of REE in marine systems is deficient and most of the literature refers to LREE, mainly La and Ce [71,72]. Among marine taxa, crustaceans (invertebrates) are the taxonomic group with the largest number of studies and show the highest sensitivity towards La. Studies on *Daphnia carinata* [159] in three media of different composition and water hardness reported a strong relation between La toxicity and water hardness and total Ca content, as well as medium composition. Water hardness modifies the toxicity, as La^{3+} competes with Ca^{2+} for binding sites in biological systems [155] and leads to increasing mortality with decreasing water hardness. Mechanisms of toxicity can be borrowed from plants. Carpenter et al. [168] report how REE may interfere with the uptake of Ca in plants having similar ionic radii, inhibiting root growth, cell wall integrity, photosynthesis, and flowering. Elevated levels of La, Ce, and Pr, >50 mg/L, may inhibit photosynthesis [169]. REE may interfere with biogeochemical cycling and macrofaunal diversity [170]. Thus, La and Ce are often chosen as REE models in toxicity determinations because of their wide use and high abundancy with respect to other REE in the environment [171]. For these reasons La and Ce are more investigated, and more thermodynamic data are available for chemical speciation calculations [172]. Impairments in sea urchins' larval development, morphological changes in tentacles of cnidarians, physiological changes and oxidative

stress in mussels, loss of growth and reproduction in microcrustacean water flea, and physiological impairment in the European eel are reported [130,173–177].

REE influence main biological processes, embryogenesis, fertilization, cytogenetic, and redox endpoints. Cytotoxic inhibition of mitotic activity, mitotic aberration, and micronuclei introduction were observed in *Paracentrotus lividus* and *Arbacia lixula* sea urchins [71,72]. They can alter the functions of calcium due to similarity in size and affinity for phosphate groups of macromolecules [176]. Redox imbalance leading to oxidative stress, OS, lipid peroxidation, and modulation of antioxidant activities are reported for La and Ce [178–180]. Hongyan et al. [181] reported induced changes in enzymatic activities after exposure of the Cyprinid *Carassius auratus* to REE. Oral et al. [182] detected excess of mitotic aberrations in sea urchin embryos and gametes. González et al. [183], in a survey with different species, bacteria, algae, crustaceans, rotifer, and cnidarians, concluded that the REE toxicity is dependent on organisms and increases with the atomic number. In a study on rare minnow, *Gobiocypris rarus*, Hua et al. [184] evidenced that La severely caused gills desquamation and necrosis and liver histopathological changes. Significant variations in gill dimensions and metabolic disturbance were observed. The toxicity of La and Y on the developing embryos and juveniles of marine mussel *Mytilus galloprovincialis* was studied by Mestre et al. [185]. Authors reported a greater toxicological effect onto developing embryos and larvae than juveniles. The study also set up the predicted no effect concentration, PNEC, as a first step toward deriving environmental quality criteria and for assessing the environmental risk. PNEC defines the maximum concentration allowed at which the ecosystem is protected [186].

Consideration of metal speciation during exposure is essential for improving our understanding of metal toxicity to aquatic organisms [187]. Studies of Aharchaou et al. [188] related the toxicity of La and Ce to metal speciation in solution and demonstrated that the calculated free ion concentration was a good indicator of toxicity. Increasing the ambient calcium concentration protected the test algae by reducing the amount of lanthanide internalized into the cells. The results suggested that, at constant pH 5.5, REE accumulation and toxicity are linked to the free ion concentration and ambient calcium concentration, as predicted by the biotic ligand model.

The assessment of REE toxicity is also hampered by the chemical nature of REE, which are almost insoluble at neutral pH, of phosphates, which are ubiquitous in algal growth media, and carbonates at high pH [189]. REE precipitation has been seen in many artificial laboratory studies and test media [159,190,191]. El-Akl et al. [189] bypassed the issue using an alga such as *Chlorella fusca*, which is capable of growing with low phosphate medium. Another major problem for toxicity assessment comes from the scant demonstrated capacity of the biotic ligand model, BLM, normally used for bivalent metals [192] to explain trivalent REE bioavailability in the presence of different organic ligands [183]. In light of these considerations, González et al. [183] hypothesized that the toxicity and risk of REE in the absence of phosphates would be significantly higher than that shown in the literature [183]. Other authors consider that La and Ce might have similar toxicity features due to the similarity of their physicochemical properties [193]. This wide limitation of data leads some authors to base their REE prediction of toxicity on free cation concentrations, attributing a protective role to Ca [194,195].

As stated above, the limited amount of data in the literature means that it is very difficult to establish threshold limits of REE for water and sediments. Herrmann et al. [171] studied the aquatic ecotoxicity of La, considered as the major lanthanides in industrial effluents, to draw such quality criteria. The only quality criteria for the freshwater community were defined due to poor availability of tests with marine organisms.

Nd is an element largely applied in high-tech processes [196], with a high potential to be released into coastal areas from e-waste disposal (50 million tons in 2018) and mining activities, the main source of REE into waters [34]. Its mean concentration in groundwater, depending on climate, geology, vegetation, and oxidation state, is in the range 3.1–146.2 mg/L, at various sites worldwide [34]. In sea water, Nd concentrations

are significantly lower: 2.8 ng/L [197] due to higher pH and sediment accumulation by dissolution and surface complexation reactions with inorganic and organic ligands [9]. However, some areas, such as coastal areas of Hawaii, Kona, and Australia, Labrador beach, revealed concentrations of Nd in seawater of 24–32 mg/L [34]. The increasing presence of Nd in oceans and potential bioaccumulation is supported by a very limited toxicological literature. Only recently, Freitas et al. [177] demonstrated the accumulation of Nd and the biochemical alterations in the mussel *Mytilus galloprovincialis*. The authors exposed the mussel to five different concentrations, 2.5–40 µg/L for 28 days. A metabolic capacity increase and glycogen content (GLY) expenditure were recorded with insufficient elimination of ROS, highlighting cellular damage and compromission on mussel's survival, growth, and reproduction [177]. These data come from laboratory assays and do not faithfully reproduce real field conditions in terms of concentration and duration of exposure. Another growing ecotoxicological concern regards Tb, used in newly developed electronic devices. Mean concentration for Tb of 1.16 mg/kg up to a maximum value of 2.6 mg/kg was measured in downstream Lubumbashi River in the Democratic Republic of the Congo sediments [198]. A recent contribution comes from Lompré et al. [199], who reported metabolic impairment, loss of redox balance, and neurotoxicity in clams, either native *Ruditapes decussatus* or invasive *Ruditapes philippinarum* species, exposed to Tb. Tb, was reported to have effects on physiological features, affecting reproduction and growth capacities. Authors in their exposure experiments adopted a level of Tb of 50 µg/L.

Gadolinium has been found very often in freshwater environments, with levels of 0.347 to 80 µg/L, with more significant anomalies nearby industrialized areas and bioaccumulation range of 0.006 to 0.223 µg/g with variability due to the Gd complexes' chemical speciation [62]. As the free ion Gd^{3+} is toxic, contrast agents correspond to inert chemical complex—for example, Gd-DTPA (Gd chelates of the open-chain diethylenetriaminepentaacetic acid). Its high stability allows a complete excretion by the human organism only a few hours after the examination [62]. These Gd complexes are released into the hydrosphere through the effluent of sewage plants. Gadolinium is a very threating pollutant for aquatic systems, behaving conservatively since it is rarely removed in wastewater treatment plants [200]. A study of Möller et al. [201] reports that Gd complexes are stable and pass through wastewater systems almost unchanged, showing that it is neither adsorbed not co-precipitated, nor does it undergo ion exchange with organic or inorganic particulate sewage matter. Other studies report on the conservative behaviour of anthropogenic complexes of Gd [202]. Some authors as Telgmann et al. [203] report on the trans-metallation with endogenous ions of Fe^{3+}, Zn^{2+}, and Cu^{2+} as being responsible for the release of toxic Gd^{3+} ions. Anomalous levels of Gd in the aquatic environment, mostly freshwater, are reported: [204–207]. In the water column of low salinity zones of estuaries, Gd associates with organic and mineral colloidal ligands and scantly fluxes to pelagic waters [206,208]. Thus, in the estuarine mixing area, anthropogenic Gd is not particle reactive since anionic Gd complexes have a long environmental half-life [209] partitioning from the truly dissolved REE pool [209]. Consequently, anthropogenic Gd may be decoupled from the natural REE and may serve as a conservative tracer of soluble wastewater-derived substances to estuarine and coastal waters [207,210].

The toxicity of Gd and its long-term lability are still poorly known [211,212], and its levels have shown a significant increase over short periods of time in some locations [207]. The effects of Gd in invertebrate marine species include alterations of gene expression, cellular homeostasis, shell formation, metabolic capacity, and antioxidant mechanisms [62]. Specifically, for sea-urchin species, *Paracentrotus lividus and Heliocidaris tuberculate*, inhibition on skeleton growth, changes in the biomineralization process, and induction of autophagy have been shown [213,214]. With respect to Gd, whose levels in sea water are difficult to detect due to its high reactivity, natural La is highly variable and in the range of 20–600, 5–200, and 5–40 ng/L in rivers, estuaries, and coastal areas, respectively [77]. Some authors observed anthropic La release from fluid catalytic cracking catalysts [215,216] or acid mine drainage [216,217] that produce significant enrichment up to 0.04 mg/L, as in a

Spanish aquifer contaminated by acid mine drainage [217] or even higher 0.9 mg/L in streams flowing near acid sulphate soils [218]. Although La^{3+} is a very small fraction of the lanthanum compounds in water and sediment, in this soluble ionic form it has great biological effects [219].

The La cytotoxicity is attributed to the chemical similarity relative to alkaline earth elements through the competition for binding sites with Ca [219]. La acts by damaging Ca-channels of membranes, altering membrane enzyme activities, and influencing tissues components [219]. Gills and liver necrosis were reported by Hua et al. [184] in the freshwater Cyprinidae *Gobiocypris rarus* exposed to La. Early studies of Das et al. [218] report several cases of La^{3+} toxicity to marine fishes, particularly on nervous systems, excretory organs, and smooth muscles. Pinto et al. [220] reported oxidative stress and neurotoxicity and histopathological impacts in gonads, gills, and digestive glands of *Mytilus galloprovincialis* exposed to La. Neurotoxicity, marked increase in acetylcholinesterase, AChE, activity, was also reported by Figueiredo et al. [130] in a La exposure experiment of glass eels; neurotoxicity was attributed to inhibition of AChE binding [138]. A similar effect was also described years back by Tomlinson et al. [221] in electric eel, *Electrophorus electricus*, with La affecting the kinetics of acetylcholinesterase.

Some other studies refer to the beneficial effects of La^{3+} in relation to toxicity of heavy metals: Hong et al. [222] reported the La^{3+} mitigation of destruction of intestinal DNA caused by Hg^{2+} and decrease in gill Cd uptake in epithelial cells from *Oncorhynchus mykiss* [223]. Results were often contrasting, depending on organism sensitivities, with early life stages being the most sensitive, according to Block and Pärt [224].

4.1. The Hormetic Effect and the Weight of pH

Many contrasts come out when assaying the ecological risk assessment of REE [172]. A biphasic hormetic effect is described for REE in freshwater or marine environment. Wang et al. [225] evaluated the effect of Nd on the growth and biochemical changes in the freshwater cyanobacteria *Microcystis aeruginosa*. A stimulating effect was observed at levels ≤ 1 mg/L and an inhibitory one at higher concentrations of 5.00–10.00 mg/L. Hormetic REE effects were also reported by Wang et al. [226] and Jenkins et al. [227], but the literature is so limited that it does not help to clarify the weight of hormesis [71,72].

Another unknown role on the REE health effect is pH dependent REE speciation and hence toxicity. Estuaries can receive industrial effluents from mining areas with a combination of the REE by products and acidity pollution. From the limited available literature, it seems that the acidification of the estuaries enhances REE toxicity [71,72].

4.2. REE Detoxification Routes

One possible route of REE detoxification is represented by the already described REE bioaccumulation, see previous section on the trophodynamics, of a large reserve of REE in the digestive glands of fish species, such as scallops, on a subcellular level in organelles, membranes, or granules of the digestive system, as insoluble fractions. Another route could be represented by the REE bio-dilution process along the food web, as outlined by studies of Campbell et al. [228] on trophodynamics of metals in the Artic marine food web. The authors found that La concentrated at high levels in algae and zooplankton with respect to accumulation in fish, seals, and birds. Authors concluded that these elements could be easily bioconcentrated from seawater by pelagic plankton, with limited trophic transference [228].

5. Reducing REE Fluxes

Different solutions can be proposed to reduce the input of REE in the environment and specifically in estuary systems, but most of them are not feasible in the medium term [229], and they are expensive, difficult, and complex [230]. Practical examples regard production of items, such as magnet and power generators requiring low levels of REE or of devices with a longer life as is the case and of wind turbines living more than 10 years [231]. Other

options are the optimization of ore extraction technologies [62], the promotion of e-waste recycling, from spent magnets, catalysts, and cellular phones, Figure 2 [2,232]. Often recovery rates are very low, <0.1% as for phones [233]. Often, e-waste recycling is limited to the laboratory level [2], and standard methods for REE recycling are missing [234]. Another option is trans materialization; as for example, the substitution of Dy in Nd, Dy–Fe–B magnets with Ga-doped sintered Nd–Fe–B magnets [235]. Another example is to use iron borides for hydrogen generation as alternative catalysts [236]. Our thought is that the proposed solutions represent only a weak example of an attempt to contain the increasing release of REE in the environment as with other emerging contaminants. Some of these solutions appear rather impractical since reducing REE load in high tech devices seems unrealistic but perhaps other ideas such as trans materialization and e-waste recycling seem more feasible.
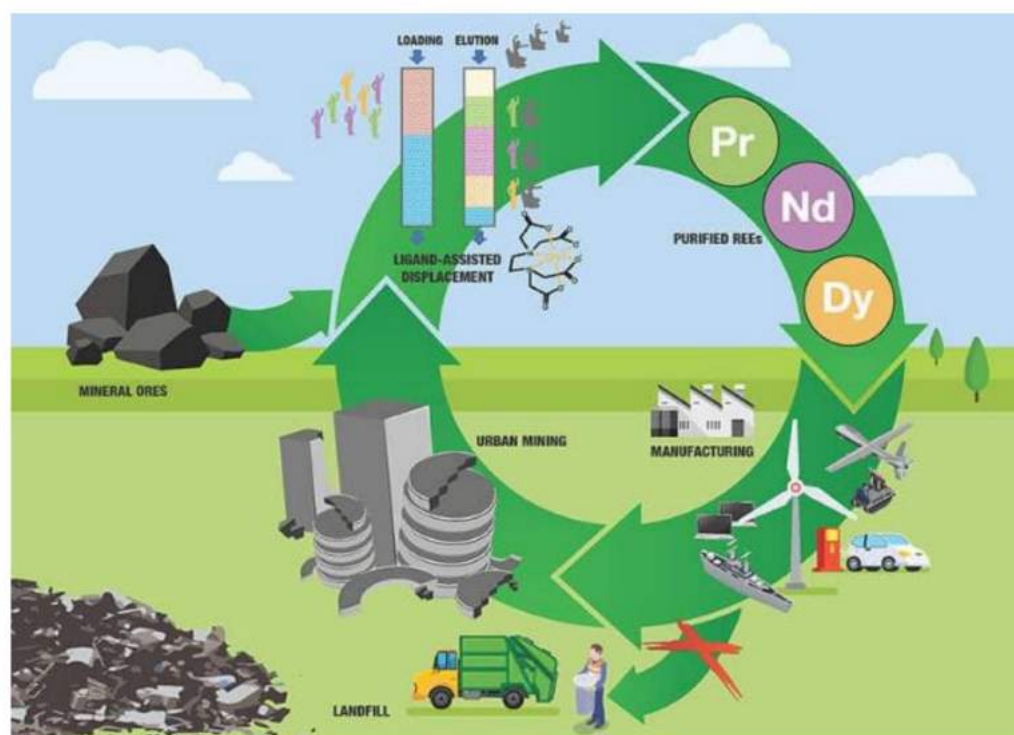

Figure 2. Example of strategic recycling pathway of REE. Source: Source [236].

6. Conclusions

The extensive utilization of REE in day-to-day life urges a deep knowledge of the environmental behaviour of these elements in estuarine and coastal mixing zones to strengthen our understanding of REE geochemistry at the continent–ocean interface. These transition environments are complex systems, comprising different biological systems, plants, fish, zooplankton, and algae that interact with REE in different ways and where REE behaviour and fate is in its infancy state and many knowledge gaps exist. Limited is knowledge of the process of ion exchange, sorption–desorption, and precipitation, as well as knowledge of the persistence, transport, and phase partitioning and interactions of REE with sediment and suspended matter.

There is need for further studies on REE mechanisms of biological uptake, bioaccumulation, and toxicity by aquatic organisms. Most studies focused on the prevalence and concentration of Gd, La, and Ce, and hence, the environmental monitoring and characterization studies must be extended to other REE. New ecotoxicological assays must be performed on different species spanning different ecological levels, from the molecular level to the population level to the ecosystem level and even on to ecosystem services. This

will be fundamental for determining acute and chronic ecotoxicity and for performing accurate risk assessment analyses of REE in estuary and coastal environments.

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