

Review

Rare Earth Elements (REE): Origins, Dispersion, and Environmental Implications—A Comprehensive Review

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Abstract: The rare earth elements (REE) comprise a group of 16 chemically very similar elements that occur widespread in rocks, soils, and water bodies, share similar ionic radii to the essential element Ca^{2+} , and consequently also occur in biota. Given that REE form mainly trivalent cations, they also share similarities to Al^{3+} . Compared to their chemical cognate Ca, they have a higher reactivity. Thus, their accumulation in soils may constitute a severe environmental threat. Over the last decades, the increasing use of REE in modern technology and fertilizers raised concerns about the pollution of soils and water bodies, which led to a rapidly increasing number of publications dealing with REE toxicity to plants, animals and humans, the fate of REE in soil–plant systems, REE cycling in ecosystems and impacts of REE pollution on food security. This review aims to give an overview of the current knowledge on the occurrence of REE in the total environment, including relevant environmental processes governing their mobility, chemical speciation and transfer from abiotic compartments into biota. Beginning with an overview of analytical approaches, we summarize the current knowledge on the ecology of REE in the lithosphere, pedosphere, hydrosphere and biosphere, including impacts of soil pollution on food security and public health.

Keywords: biosphere; hydrosphere; lithosphere; pedosphere; availability; soil fractions; complexation; rhizosphere; toxicity



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1. Introduction

The initial technical application of rare earths took place at Althofen in Carinthia, Austria. Today's Treibacher Industrie AG was originally founded in 1898 at the site of a former Fe-smelter by Carl Auer von Welsbach. Auer von Welsbach discovered the rare earth elements Pr, Nd, Yb, and Lu, and had produced REE-based “flints” as essential parts of lighters, which are still produced today, beneath other Zr, V, and Mo-based products and compounds [1]. In recent years, due to the intense mining and processing of rare earths, much has been published about environmental contaminations and interactions with biota, and the environmental effects of REE have become of increasing concern.

The rare earth elements (REE) comprise 16 chemically very similar elements from the group IIIB of the periodic table, including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu), yttrium (Y), and scandium (Sc) [2]. Despite their name, REE are, in fact, not rare but occur widely in minerals, rocks, soils, and biota at concentrations comparable to essential micronutrients. Specifically, in the Earth's crust, the average concentrations of REE vary from 66 mg/kg (Ce) to 0.3 mg/kg (Lu). The sum concentrations of all REE together (150 mg/kg) and even the concentrations of individual elements from this group, such as Ce, are higher than the more studied essential trace metals Ni (75 mg/kg), Cu

(55 mg/kg), and Zn (70 mg/kg) [3,4]. Irrespective of their absolute concentration level in different environmental compartments, which vary considerably, the concentrations typically decrease with increasing atomic number. Moreover, REE with even atomic numbers are more frequent than their neighbors with odd atomic numbers according to the Oddo–Harkins rule. Compared to other elements from the periodic system, no other group with a uniform oxidation state displays such a remarkable similarity as REE [5]. As a unique feature in this group, all 16 REE exhibit ionic radii similar to Ca^{2+} (Ca^{2+} 100 pm, La^{3+} 103.1 pm) [6]; however, under most biogeochemical relevant conditions, all REE form trivalent cations with the exception of Cerium (Ce), which also can exist in the tetravalent state, and Europium (Eu), which also can exist in the divalent state [7,8]. Thus, REE strongly interact with phosphate and negatively charged surfaces [9–11], and their biogeochemical behavior resembles that of other trivalent metals, particularly Al^{3+} [12–14]. Consequently, REE can be used to model the geochemical behavior and speciation of trivalent actinides (Am^{3+} , Cm^{3+} , Cf^{3+}) in natural waters to predict their fate and transport [15].

All REE have the same outer electron configuration and show very similar chemical behavior [16]. The ground-state electronic configuration of La is the xenon core plus 5d1 and 6s1. After La, the 4f orbitals are filled, leading to an increasing contraction of the 5s and 5p electron orbits with increasing atomic number (the so-called lanthanide contraction). Thus, the effective ionic radius of the trivalent ions decreases slightly but systematically from La^{3+} (103.1 pm) to Lu^{3+} (86.1 pm) [7]. The radius of Ho (90 pm) is similar to that of Y [5]. Accordingly, REE are sometimes sub-grouped into light rare earth elements (LREE), including those with a lower mean atomic mass than 153 and a larger effective radius than 95 pm (La, Ce, Pr, Nd, Sm, and Eu) and heavy rare earth elements (HREE) including those with a higher mean atomic mass than 153 and a lower effective ion radius than 95 pm (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) [5]. Most of the dissimilarities that do exist among REE in terms of the formation of Ce and Eu anomalies, as well as fractionation patterns, can be attributed to differences in their ionic radii or variations in valences (e.g., Ce^{3+} or Ce^{4+}). In particular, the stability of complexes with electronegative organic and inorganic ligands, as well as sorption on surfaces, increases with decreasing ionic radius. Thus, in environmental compartments, the mobility of HREE often appears higher than that of LREE in the presence of ligands, whereas sorption processes preferentially immobilize HREE rather than LREE. As a result, individual REE can be enriched or depleted relative to other representatives of this group. Fractionation of HREE relative to the LREE has been reported during an array of biogeochemical processes [17–19], justifying the use of REE as tracers (pseudo-isotopes) to investigate petro- and pedogenesis (e.g., [20–23]). In archaeology, the pattern of REE was successfully used to discern between natural and anthropogenic sediment units of paleosols, and REE signatures may help to assign fossils to their proper depositional unit [24]. In other research fields, the group of REE has been paid much less interest compared to the transition metals and metalloids, primarily due to the fact that REE has been neither considered essential nor strongly toxic to most biota. Thus, they were commonly neglected in plant nutrition and environmental sciences. However, in recent years, the number of publications on REE has rapidly increased due to their great importance for modern industry [25], which led to the intensification of mining and raised concerns about their environmental impact [26]. In particular, pollution of soils and water bodies with REE gave cause for concerns about their toxicity to plants, animals and humans, the fate of REE in soil–plant systems, REE cycling in ecosystems, and the impacts of REE pollution on food security [9,27–34]. This review aims to give an overview of the current knowledge on REE ecology with an emphasis on the occurrence of REE in the lithosphere, pedosphere, hydrosphere, biosphere, and anthroposphere, including relevant environmental processes controlling their mobility, chemical speciation and transfer from abiotic compartments into plants and animals.

2. Analytics

Historically, the determination of REE in Europe was rarely ordered and financed in analytical labs because of unknown toxicities and lack of thresholds. Multi-element screening occasionally provided information on a few elements (e.g., Ce, La, Y); however, the data obtained were scarcely reported in the literature and were lost at a later time. Generally, the determination of REE in environmental samples is particularly challenging because of their comparable low concentrations, especially in biological samples, their occurrence in highly stable minerals requiring a total matrix dissolution, and the interferences caused by matrix compounds during the determination process.

In case of solid samples, nuclear techniques overcome the need of dissolution. Neutron activation analysis has been successfully used for the analysis of rocks and coals [35,36] and provides good results for La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, and Sc in REE-enriched soil, plant and fertilizer samples [37,38]. Additional REE data have been obtained in soil analyses [39], as well as studies on bentonite [40], quartz [41], and even zircon [42], but also in moss samples as well [43]. The samples are irradiated with thermal neutrons, and the gamma emission spectrum is recorded at defined time intervals. Dy, Er, Eu, and Pr can be determined via short-lived isotopes after a few minutes irradiation, and the others after some hours of irradiation (Table 1). In case a reactor is not available, an ^{241}Am source can be used for Y and Sc, but with far more insensitive detection limits for REE [44]. However, significant drawbacks arise from interferences and long measuring times [35,36], making this method unsuitable for rapid analytics of environmental samples. In addition, high P contents in green plants produce a strong bremsstrahlung, which requires high-resolution detectors [45].

Nowadays, the standard analytical techniques for REE determination are atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectroscopy (ICP-MS). Other analytical techniques, such as the electrochemical determination of REE, often suffer from a lack of sensitivity and selectivity [46]. Also, in AAS or ICP-OES, the detection limits for REE are typically insufficient at ambient levels to obtain data within a multi-element screening, except for total La and Ce in soils and minerals. In this case, their determination requires sample pre-treatment and/or enrichment techniques. Enrichment of REE in biological samples with low initial REE concentrations can be achieved by ashing because REE are hardly volatile. In the ashes, REE can be determined by solid AAS [47] or ICP-OES after sample digestion. Other enrichment techniques deploy cation exchangers [48], solvent extraction (e.g., tri-octylphosphine oxide at pH 2.3 [49] or REE co-precipitation with $\text{Fe}(\text{OH})_3$). Alternatively, REE can be pre-concentrated from sample digests or water samples on Sep-pak C18 cartridges [50]. Prior to the enrichment of environmental water samples, a pre-treatment with H_2O_2 -HCl at pH 2 is recommended to crack Gd-chelate compounds [51]. Separation from matrix elements can be achieved by adsorption on a concentrator column (SeaFAST concentrator column CF-N-0200), elution of most matrix elements with NH_4 -acetate pH 6, and recovery of the REE from the column with 10% HNO_3 [52].

Given that most standard analytical equipment requires liquid samples, solid environmental samples must be chemically dissolved prior to analysis. For the evaluation of mobile, potentially bioavailable element fractions, a variety of leaching procedures have been reported in the literature (see Section 3). However, when total REE concentrations are desired, the sample digestion procedure requires a complete dissolution of the sample matrix, where REE are often associated with highly stable silicate minerals. We emphasize that aqua regia presumably dissolves only 25–30% of rocks and soils, leading to an underestimation of total REE concentrations. Thus, thorough digestions with HF are required to obtain correct total results. This is especially problematic when soil data need to be compared because, in standard soil inventories, laboratories prefer to apply aqua regia extracts.

Table 1. Main nuclear parameters and interferences of the radionuclides used to determine REE by neutron activation (from [42]).

Radionuclide	Half-Life, Days	Energy, keV	Quantum Yield, %	Interferences	Energy, keV	Quantum Yield, %
46Sc	83.8	889.28	99.98	–	–	–
140La	1.68	1596.2	95.4	U(n, f)	–	–
141Ce	32.5	145.44	48.3	U(n, f)	–	–
				175Yb	144.86	0.67
142Pr	19.1 h	1575.6	3.7	–	–	–
147Nd	11.0	91.11	28.1	U(n, f)	–	–
153Sm	1.94	69.67	4.73	–	–	–
152mEu	9.3 h	963.39	11.7	152mEu	961.06	0.12
153Gd	240.4	103.18	21.1	233 Pa(233Th)	103.86	0.854
160 Tb	72.3	298.58	26.1	233 Pa	298.81	0.088
165Dy	2.3 h	361.68	0.904	–	–	–
166Ho	1.12	80.57	6.71	133Xe	81.00	36.9
171Er	7.5 h	308.29	64.0	–	–	–
170Tm	128.6	84.25	2.48	182Ta	84.68	2.65
175Yb	4.18	396.33	13.2	–	–	–
177Lu	6.65	208.37	10.4	176Yb→177Lu	208.37	10.4
233 Pa(233Th)	27.0	311.90	38.5	–	–	–
239Np(239U)	2.36	277.60	14.4	–	–	–

With regard to total REE analysis, the most commonly applied digestion procedures use closed vessel microwave digestion or open vessel digestion with a combination of HClO₄ and concentrated HF [53], HNO₃ with H₂O₂ and HBF₄ [54] or HNO₃ and diluted HF (4.8%) [55]. Instead of glass vessels, PTFE-pressure bombs are recommended because of unwanted interactions with vessel walls. In unknown samples, the use of HBF₄ instead of HF is recommended because excess HF which is not readily consumed, may lead to the precipitation of insoluble REE fluorides and might damage the glassware of nebulizer and/or spray chamber of ICP-OES and ICP-MS devices [56]. When the use of HF is not possible, a fusion of ground rock and soil samples with mixtures of borates or carbonates represents a suitable alternative [57,58].

Currently, most data on REE in environmental samples have been obtained by ICP-MS because of its superior sensitivity and selectivity. REE can be directly determined in water samples utilizing an ICP-MS equipped with a concentric nebulizer. Interferences on Eu must be corrected for BaO⁺, and ⁴⁵Sc is severely interfered by ²⁹Si¹⁶O, ²⁸Si¹⁶O¹H, ¹²C¹⁶O₂¹H, and ¹³C¹⁶O₂, and requires the determination in collision/reaction mode [8,59,60]. In ICP-MS, lower oxide formation can be achieved by higher forward power applied to the torch and a lower nebulizer rate compared with default values [61]. To assess possible interferences of BaO⁺ on Eu⁺ mass, the calibration can be performed with expectable Ba-concentrations over Eu [62]. Similarly, ¹⁴⁷Sm⁺ may be overestimated from ¹³⁰Ba¹⁶O⁺ and ¹⁵¹Eu from ¹³⁴Ba¹⁶OH⁺, whereas interferences of chlorides upon the rare earth masses are typically negligible [61]. As for any other elements, the determination of REE by ICP-MS requires the addition of an internal standard to the liquid samples. Given that the internal standard must be absent in the samples and should resemble the atomic masses of the desired analyte, rhodium, rhenium and indium are the most frequently used for the quantification of REE in environmental samples [52,56]. Due to the advantages of mass spectrometry, the method is often coupled with other analytical techniques, enabling the direct determination

of low analyte quantities in solids (laser ablation ICP-MS) [52]. Finally, coupling ICP-MS with liquid chromatography (LC-ICP-MS) and electrospray ionization-MS-MS allow the chemical speciation of REE in environmental samples [63]. Other modern techniques targeting solid samples, such as energy-dispersive X-ray fluorescence (EDXRF), often suffer from overlapping characteristics of L X-ray lines of the lanthanides with Ti, V, Cr, Mn, and Fe, which necessitates a complex and time-consuming separation and enrichment [64].

Whereas the detection limits of ICP-OES of about 0.1 mg/kg are sufficient for most total digests of soils and sediments, in case of mobile fractions and biological matrices (author's experience), an ICP-MS is needed to come down to almost 0.0001 mg/kg (depends on blanks and dilution due to digestion method). Detection limits for neutron activation of an about 100 mg sample range within 0.01–0.2 mg/kg for most REE [44].

3. Sequential Leaching Methods to Evaluate the Mobility and Plant Availability of REE

Total REE concentrations in soil do not necessarily reflect REE mobility and availability to plants [65–67]. Hence, many different chemical procedures have been proposed in the literature that aim to predict the chemical speciation, mobility, and plant availability of REE in soils [65,66,68–70]. Most of these methods use extractants that simulate soil physicochemical processes in the root zone of plants and are designed as sequential extractions to identify and quantify plant-available element pools, assuming that plants access certain element fractions through changes in rhizosphere chemistry. Although the approach suffers from a limited selectivity of extractants, the method represents a cheap and easily applicable approach to gaining insights into the chemical bonding form, bonding strength, and accessibility of elements for plants by adjusting the composition of the extraction solution to the chemical features of the target elements and/or the natural occurring chemical compounds in the soil–plant system. It was demonstrated [66] that mobile REE fractions, such as water-soluble, exchangeable, and organically bound element fractions in soils, correlated with the REE concentrations in alfalfa. In contrast, a correlation was found [68] between the contents of a few elements in wheat and rice and the soluble and exchangeable fraction, but not with an organic fraction, which can be attributed to the higher ability to release of carboxylates and exoenzymes such as phosphatases by alfalfa [71] that may also liberate REE bound into soil organic matter [72]. This highlights the need to adjust extraction protocols according to the main compounds released by plant roots during element acquisition, enabling the plant to influence the root zone chemically and mobilize REE from sparingly soluble forms [73,74]. Thus, recent extraction protocols use diluted organic acids [65,70,75]. It was demonstrated [76] that a mixture of malic and citric acid gave the best prediction of REE available to wheat. Organic acids increase the mobility of REE in soil by forming soluble chelates. The ability to desorb REE from soil particles decreased in the order citric acid > malic acid > tartaric acid > acetic acid. This is consistent with the order of the stability of complexes of REE [77]. However, it has to be noted that there is no single method universally applicable for the prediction of plant availability because many factors control REE mobility, speciation, uptake, and internal translocation of the plants (see Section 7.1). To the contrary, a significant correlation between wheat root and shoot REE contents and elements extracted with 0.1 M HCl was found [69]. This can be explained by the ability of wheat to acidify the rhizosphere but the lack of the ability of wheat to release carboxylates [78].

In sequential procedures, one fraction after the other is removed from the sample, thus allowing the reagents' selectivity to decrease toward the end of the sequence [79,80]. Reabsorption of already desorbed species, desorption of traces and differences in chemical properties of the element investigated can lead to uncertainties about the real meaning of the fraction involved; therefore, the leached fractions are somehow operationally defined [79,80]. As there are much more speciation possibilities in the solid phase compared to the limited leaching solutions available in a sequential sequence (in practical work, about 6 at maximum), the resulting leaching pattern always depends on the applied sequence, and only data from the same procedures and fractions with equal grain sizes should be

compared. Sequential leaching procedures can characterize the remobilization properties of a given sample much better than a single leaching step because additional information about amorphous phases (hydroxides) and clay minerals, like amount and current load, is achieved [80,81].

Nevertheless, the leaching patterns achieved give additional information about the respective mobility under changing environmental conditions and the time scale of availability to biota. Given that REE form cations with relatively high-charge density and high affinity to phosphate, most sequential leaching procedures described in the literature focus on various fractions. These include the mobile fraction (water extractable), exchangeable fraction (salts), acid-soluble fraction (dilute acids), fractions bound into amorphous oxides/oxyhydroxides, crystallized Fe-oxides, REE bound into organics, and residual fractions like apatite [65,66,72,82,83]. Considering many different soil samples, REE concentrations are typically the highest in relatively stable crystalline primary and secondary minerals and decrease in the order residual > crystalline oxides > amorphous oxides > organics > exchangeable, acid-soluble > mobile [66,68,72,83,84], with abnormally high and organically bound REE in areas of restricted mineralization and some accumulation [66,72]. Within a simplified sequential extraction to discriminate acid-mobile and Fe-Mn-Al-oxide-bound REE fractions, substantial immobilities of REE at ambient levels are shown in Table 2. Digesting the sample with an almost saturated KClO₃ solution, acidified with HNO₃, is analogous to using aqua regia. This method allows for the determination of B, Si, Ge, and iodine in addition (refer to Table 2).

Table 2. Median concentrations of REE (mg/kg) in mobile soil fractions from apple orchards in Austria (according to [85,86]).

Element	0.16 M Hac	0.1 M-Ox	KClO ₃ -HNO ₃	HClO ₄ /HNO ₃ /HF
Sc	<0.01	0.36	3.47	5.88
Y	0.033	0.37	9.19	10.8
La	0.041	0.13	15.9	21.8
Ce	0.15	0.30	40.0	46.6

Hac = acetic acid, Ox = oxalate buffer pH 3, KClO₃-HNO₃ = digestion with 10% KClO₃ + 4.3 M HNO₃.

Land et al. [82] explored the evolution of REE in operationally defined soil fractions with soil depth in spodosol profiles of Northern Sweden. They found a maximum of organically bound REE at 15–20 cm, increased concentrations in REE bound to stable soil minerals (apatite, crystallized Fe-oxides) with increasing depth and generally a higher portion of REE bound to crystalline oxides than in amorphous oxides. Also, the distribution of REE in soils of a post-mining landscape in Germany was explored [58,83], and it was found that more than 60% of REE were bound to stable crystalline Fe/Mn-oxides and primary and secondary silicates, 20% were present in oxidizable compounds, and 10% in amorphous oxides, whereas the sum of exchangeable (NH₄-acetate, pH 7) and acid soluble (NH₄-acetate, pH 5) was only 3.3%. This suggests that substantial amounts of REE were bound to soil organic matter, and Fe/Mn-oxyhydroxides might have represented significant labile fractions of REE in those soils. In sequential leaching on soil samples collected from sites with different bedrock, the highest rare earth levels in soils were found at sites developed from granite, such as lateritic red soil (523 mg/kg), whereas the concentrations in Solonchaks were very low (85 mg/kg) [18]. Samples from eight soils collected all over China were extracted using a Tessier-like sequence using water, MgCl₂, diluted HCl, H₂O₂ oxidation, hydroxylamine, and HF [66]. Despite relatively high levels of total REE, 60–90% appeared in the residual fraction, and the REE contents in oxidizable compounds formed the second most important REE pool in 6 out of 8 samples. Using citrate–dithionite–bicarbonate as an extractant, it was possible to elucidate variations in REE bound to Fe-oxyhydroxides across different pedons in highly weathered tropical soils [67].

4. REE in the Lithosphere

4.1. Crustal Abundance and Geology

As lithophilic elements with a ubiquitous distribution in Earth's crust, the mineral distribution of REE tends to be controlled by silicate minerals, which are associated with 43% of all REE, followed by carbonates (23% of all REE), oxides (14%), and phosphates (14%) [87]. The average abundance of REE in the Earth's crust is typically higher for LREE than for HREE and varies from 66 mg/kg in Ce to 40 mg/kg in Nd and 35 mg/kg in La to 0.5 mg/kg [3,4]. LREE are primarily concentrated in late-stage felsic differentiates of the magma. In contrast, HREE are concentrated in the early-formed mafic products. Since the continental crust is composed mainly of granitic rocks, the crust is strongly enriched in LREE, together with K, Rb, Cs, Sr, Ba, Zr, Hf, Nb, Ta, W, Th, and U [88]. Igneous intrusions, notably carbonatic alkaline or peralkaline intrusions and pegmatites, contain significant concentrations of REE that occur as oxides, halides, carbonates, phosphates, and silicates but not as sulfides [89]. Of the 250 REE-containing minerals, only the REE phosphates bastnaesite (Ce, La, Nd, Y)(F, OH)CO₃, monazite (La, Ce, Nd)PO₄, and xenotime (Y, Yb)PO₄ are located worldwide with usually large deposits, but they are present only in a few countries [90]. Apatites Ca₅(PO₄)₃(F, Cl, OH) may also contain considerable amounts of REE [82,91]. Within the group of silicates, REE are particularly contained in minerals from the epidote group [92] and zircon [93,94] but have low concentrations in quartz. Large ionic radii and a high oxidation number make the REE incompatible with the crystal lattices of common minerals forming igneous rocks except Eu²⁺, which easily replaces Ca²⁺ in the structure of plagioclase. Following their distribution in rock-forming minerals, pegmatites, rhyolites, granites, and their metamorphic equivalents typically contain higher REE concentrations than basalts and peridotites (Table 3). Clays and shales typically have higher REE concentrations than limestones and sandstones [22]. However, some tholeiitic basalts within the Tertiary newer volcanic province of Victoria (South Australia) show anomalously high REE concentrations, which has been attributed to incipient alteration of the mineral composition of trace metal concentrations at the earliest stages of weathering [95].

Table 3. Occurrence of REE in different rocks (mg/kg). The median of 19 representative rocks from the Monchegorsk massif [96], grey granite from South Africa [97], and Cappadocia/Turkey [98].

Element	Monchegorsk	Granite	Limestone	Calcrete	Diatomite	Ignimbrite
Y	3.43	n.a.	2.9	15.2	20.2	14.7
La	2.81	22.2	3.5	19.8	30.8	32.1
Ce	6.48	55.7	4.9	31.5	52.8	52.7
Pr	0.80	6.5	0.6	3.9	6.73	4.43
Nd	3.46	25.2	3.1	14.5	25.5	14.5
Sm	0.67	5.6	0.5	2.4	4.23	2.41
Eu	0.30	0.7	0.1	0.6	0.93	0.43
Gd	0.68	4.7	0.6	2.3	3.77	2.02
Tb	0.11	0.7	0.1	0.4	0.61	n.a.
Dy	0.68	3.8	0.6	2.3	3.36	2.05
Ho	0.14	0.7	0.2	0.5	0.67	0.50
Er	0.36	1.7	0.4	1.5	2.03	1.53
Tm	0.05	0.2	0.1	0.2	0.28	0.40
Yb	0.33	1.4	0.4	1.6	2.12	1.74
Lu	0.05	0.2	0.1	0.2	0.32	0.28

n.a. = not available.

For the interpretation of geochemical and biological processes, REE concentrations found in rocks, soils, and even biological samples are often interpreted relative to concentrations in chondrites, like the chondrite Allende CV3 [99], the chondritic meteorite Leedy [100], or the post-Archean Australian shale [101]. Moreover, normalization approaches are frequently used to distinguish anthropogenic and background contributions,

as seen in [102]. Normalization of REE concentrations compares the analyzed contents of single elements with a standard natural reference system, which facilitates the interpretations of rare element contents concerning fractionation, grouping, anomalies, and anthropogenic components. Chondrite has been used as a representative of the initial REE concentrations at formation time of the Earth's crust and shale as a representative of the post-Archean upper continental crust and reflects sedimentation geochemical processes [102]. The Post-Archean Australian Shale has been based on a set of nine Australian shale samples. The North American Shale Composite relies on 40 shale samples, of which 20 come from the US. The European Shale dates back to a Phanerozoic shale composite prepared in 1935. Mud from Queensland is based on unconsolidated fine-grained sediments [103]. Possibly, the different continents have different scales of original unweathered composition [97,104], but the datasets are relatively close, as shale and its fine-grained precursor sediment are relatively homogenous erosion products, integrating a large area of the upper crustal material (Table 4). Versus chondrite, the standard shale shows equal proportions for elements from Eu to Lu throughout, but enrichments for $\text{La} > \text{Ce} > \text{Pr} > \text{Nd} > \text{Sm}$. Despite slightly different values, normalization versus different reference datasets does not alter interpretations and conclusions of given analytical data [103]. Whereas the shale datasets are similar, representing the continental crust, the reference for the mid-ocean ridge basalt is lower for LREE (La to Sm). Anomalies for specific elements can be quantified by linear extrapolation, interpolations using neighboring elements, or by geometric extrapolation using logarithmic modeling [102]. Cerium negative anomalies are characteristic for seawater because, under oxic conditions, Ce can be easily oxidized to the tetravalent state on the surface of Mn-oxides and thus co-precipitated. For calculation of this anomaly, interpolation from La and Pr or La and Nd and extrapolations from Pr and Nd have been used [102]. The calculation of Eu anomalies by interpolation from Sm and Gd can be interfered by Gd pollution from Gd inputs, which is used as a contrast agent in magnetic resonance imaging for medical purposes; thus, interpolation from Sm and Tb can be used instead.

Table 4. Normalization concentrations (mg/kg dw) [103] and mean crustal abundance [105].

Element (mg/kg)	Post-Archean Australian Shale	North American Shale Composite	Mud from Queensland	European Shale	Upper Crust	Lower Crust
Y	27.3	27	31.8	31.9	20.7	27.2
La	44.6	32	32.5	44.3	32.3	26.8
Ce	88.2	73	71.1	88.5	65.7	53.1
Pr	10.1	7.9	8.5	10.6	6.3	7.4
Nd	37.3	33	32.9	39.5	25.9	28.9
Sm	6.88	5.7	6.88	7.30	4.7	6.0
Eu	1.21	1.24	1.57	1.48	0.95	1.6
Gd	6.04	5.2	6.36	6.34	2.8	5.4
Tb	0.89	0.85	0.99	0.94	0.50	0.81
Dy	5.32	5.8	5.89	5.86	2.9	4.7
Ho	1.05	1.04	1.22	1.17	0.62	0.99
Er	3.07	3.4	3.37	3.43	n.a.	n.a.
Tm	0.45	0.5	0.51	0.49	n.a.	n.a.
Yb	3.01	3.1	3.25	3.26	1.5	2.5
Lu	0.44	0.48	0.49	0.49	0.27	0.43

n.a. = not available.

In the Monchegorsk ultramafic complex in the Kola region (Russia), some ultramafic rocks follow a nearly chondritic REE pattern, whereas others have a strong LREE enrichment (Table 3). Here, the main factor responsible for the REE distribution is their content in plagioclase [96]. In the region around Lake Baikal (Siberia, Russia), gneisses and mafic granulites show flat, normalized rare earth element patterns and moderate depletion of LREE, which are also reflected in the drainage waters. On the contrary, Paleoproterozoic volcanic rocks, which are felsic and rich in alkalis, have slight LREE enrichment and a

prominent negative Eu anomaly [106]. Very detailed data on various lithofacies of Capadocia (Turkey) has been given in [98], of which the most characteristic is summarized in Table 3.

In Austria [107] and Slovakia [108], geochemical inventories had been made and mapped based on grid-sampling of stream sediments of one sampling point per km². In Austria, median total Ce was 100 mg/kg and La 50 mg/kg; elevated levels were only found in the old crystalline of the Bohemian Massif. For Slovakia, details are given in Table 5.

Table 5. Results of geochemical inventories in Slovakia (mg/kg), median, and range.

	Ce		La	
	Median	Range	Median	Range
Andesites	50	20–88	28	11–61
Basic metavolcanites	24	5–60	15	2–39
Acid metavolcanites	60	14–123	34	9–89
Metapelites	70	29–126	41	10–71
Granites	62	10–147	33	1–83
Carbonates paleozoic	<10	<10–40	3	1–17
Carbonates mesozoic	20	<10–60	20	2–60
Clays	55	17–93	37	18–48
Sandstones	36	5–71	25	8–44

4.2. Sediments

4.2.1. Stream Sediments

The strong partition of REE into the particulate phase, their coherent behavior during weathering, erosion and fluvial transportation, and their high resistance to mobilization make REE in sediments a provenance indicator in geochemical studies. In sediment profiles, REE do not show enhanced fluxes from the bottom to the top [24]. Thus, sediments represent the temporally integrated state of a water body and depend on geological setting, weathering intensity, and erosion, and can be used as screens for pollution. The local concentration depends both on the local lithological composition and the transportation and sedimentation, as REE are enriched in minerals of high specific weight, in the fraction of the smallest grain size sieved, and deposited preferably close to barriers downstream.

The catchment of the Rhine covers possible REE inputs for a long time (Table 6). When REE concentrations in sediments of the Rhine were investigated [109], a high accumulation of LREE but not of HREE together with the common legacy pollutants (Ni, Cu, Zn, Cd, Pb) was found, particularly downstream of Cologne along the Lower Rhine, indicating anthropogenically driven inputs of La and Sm from catalyst production and Gd inputs from municipal wastewater discharges. Similarly, in the sediments of Rio Tinto and Rio Oriel, which merge with the Atlantic Ocean in a typical estuary near the Gulf of Cadiz (Spain), [110] found substantial enrichment of Cu and rare earth elements (REE) in the cores as a consequence of former Cu mining and a fertilizer factory, which emitted Cu and REE. The REE concentrations in the estuary water were 1000 times higher than the ambient levels [110]. Compared to that, in the Chinese rivers, the Yangtze, the Yellow, the Sunhuajing, the Pearl, the Haihe, the Huahe, and the Liaohe, REE in sediments (<2 mm) rarely exceeded the crustal average (Table 6), although China has the majority of REE reserves in the world [29].

Table 6. Occurrence of REE in stream sediments of Aswan Lake [111], China’s large rivers [29], the Vistula [112], the Rhine [109] and the Ganges [113]. Medians of total concentrations (mg/kg), except for Aswan. In addition to the median, the concentration range is given for rivers in China.

Element	Aswan Lake	China’s Large Rivers	Vistula River	Rhine River		Ganges		
Location		n.a.	n.a.	upper	lower	main central	Porphyroids	Proterozoic
Fraction	Total, unsieved	HNO ₃ < 2 mm	Total < 0.02 mm	Total < 0.063 mm		Total < 0.18 mm		
Sc	25.7 ± 3.4	11.6 (1.32–23.1)	5.74	n.a.	n.a.	n.a.	n.a.	n.a.
Y	n.a.	14.6 (3.31–24.8)	12.7	n.a.	n.a.	n.a.	n.a.	n.a.
La	34.2 ± 6.5	31.1 (7.56–57.3)	19.4	29	72	86.1	40.5	30.2
Ce	81 ± 14	65.3 (16.5–123)	41.1	54	94	195	87.1	61.6
Pr	n.a.	7.57 (1.59–14.3)	4.79	6.2	10.5	n.a.	n.a.	n.a.
Nd	n.a.	29.3 (5.6–58.5)	18.9	23	39	46	28.2	26.8
Sm	8.7 ± 1.4	5.33 (1.09–11.0)	3.84	6.5	7.8	12.23	6.52	5.59
Eu	2.1 ± 0.5	0.87 (0.05–1.72)	0.82	1.17	1.29	1.86	1.41	1.40
Gd	n.a.	8.86 (1.64–16.8)	3.65	5.4	6.2	9.87	5.40	4.39
Tb	n.a.	0.65 (0.12–1.16)	0.51	0.75	0.76	1.68	0.93	0.75
Dy	n.a.	3.20 (0.53–4.96)	2.85	4.2	4.3	9.45	5.27	4.11
Ho	n.a.	0.57 (0.09–0.99)	0.50	0.79	0.81	1.88	1.05	0.80
Er	n.a.	1.40 (0.26–2.44)	1.29	2.18	2.26	5.77	3.07	2.32
Tm	n.a.	0.18 (0.06–0.38)	0.17	0.31	0.32	0.85	0.42	0.32
Yb	0.75 ± 0.14	0.96 (0.22–2.89)	1.03	2.00	2.12	5.05	2.38	1.84
Lu	0.45 ± 0.07	1.15 (<0.02–0.42)	0.15	0.28	0.31	0.77	0.34	0.27

n.a. = not available.

The geochemical survey of Austria covers the total composition of stream sediments (<0.18 mm), but the dataset had been restricted to La and Ce. The sediments are enriched in heavy minerals like monazite, bastnaesite, allanite, titanite, epidote, and apatite. The available datasets reveal concentration minima in limestone areas (La < 13 mg/kg and Ce < 24 mg/kg) and enrichment at the edges of crystalline rocks (La: 13–24 mg/kg, Ce: 24–45 mg/kg). Due to higher levels of REE in post-glacial sediments than limestones, La ranged within 25–55 mg/kg and Ce within 46–102 mg/kg [107]. In stream sediments of the Slovak Republic (<125 µm), Ce accumulated in the heavy mineral fraction with an average content of 61 ± 23 mg/kg. The 25 percentile was 50 mg/kg, the 75 percentile was 69 mg/kg, and the 99 percentile was 140 mg/kg. Here, concentrations below 48 mg/kg were typically found in Mesozoic carbonates and, to a lesser extent, Paleogene and Neogene sediments. In contrast, the above-average values were associated exclusively with crystalline units in the Tatra and the Paleozoic metamorphosed rocks of the Spišsko-gemerske ore mountains [108]. In the Campania region (Italy), stream sediments cover a wide range of geological facies, like alluvial sediments, volcano-sedimentary deposits, siliciclastic, and carbonate deposits, as well as limestones and dolostones. The median and range of 2389 stream sediments were 15.8 mg/kg for La (range 1.2–124.2) and 2.4 mg/kg for Sc (range 0.40–12.6) [114]. Similarly, sediment samples from small headwater streams to the Ganges in a remote area in the South-Western Himalaya (Table 6) reflect distinct geologic characteristics of the area. The REE contents decrease from the highly metamorphosed rocks of granitic parentage of the Main Central Thrust Zone MCTC towards a zone of porphyroids and finally towards a zone of Proterozoic metasedimentary sequence [113]. Unsieved sediments of the Aswan High Dam Lake (Egypt-Sudan) contain Fe, Co, Sm, and Eu in relatively uniformly distributed amounts, whereas for Al, Sc, La, Ce, and Th, a distinct increase downstream was noted [111], which could be largely explained by the late sedimentation of REE-enriched fine particles such as clays. Conversely, the distribution of REE in sediments 10 km downstream the Vistula (<5 µm, 5–10 µm, and 10–20 µm) was explored, and decreasing concentrations of REE with decreasing particle size were found, which suggests that accessory minerals are more critical than clay minerals in controlling the rare earth element distribution in this river [112]. This highlights the importance of considering particle fractions during geochemical studies on sediments, allowing further interpretations of processes related to element transport and sequestration.

4.2.2. Marine Sediments

Compared to sediments of terrestrial water bodies, the literature on REE concentration patterns in marine sediments is scarce. Ferromanganese concretions at the bottom of the seas are classified into hydrogenous, oxic-diagenetic, suboxic-diagenetic, and hydrothermal varieties due to their origin. The hydrogenous-type concretions (vernadite δ -MnO₂) occur as crusts on seamounts and are enriched in Fe, Co, and REE, particularly in Ce, whereas the abundance of REE in other types of deep-sea nodules is low. Versus mean crust values, the enrichment is maximum for Sm and decreases from Sm down to La and Sm up to Lu. The contents of REE in oxic-diagenetic nodules are at the same levels as in associated siliceous sediments [115]. In carbonate-dominated marine sediments, REE remain preserved and permit conclusions about the oxygenation during the sedimentation period. Hydrothermal fluid inflow causes a positive Eu anomaly, and well-oxygenated seawater leads to a negative Ce anomaly [116].

4.3. Coal and Coal Ash

REE concentrations in coal typically do not exceed the average crust concentration; however, lignite and peat often appear enriched in REE (Table 7). In coal from Saxony/Germany, REE occur in small, well-distributed Al minerals or are adsorbed on their surface [117] (Vogt 1994). The distribution of minerals and major, minor, and trace elements within the lignite seams is often very different from distribution in the enclosing sediments and associated inorganic horizons. In particular, in Alabama coals, Ce was found to be consistently associated with minerals, while Sc-Y-Yb were at least partially associated with organic matter. Yb was higher in the inorganic horizon than in the organic, but taken as ash-based data, the concentrations were higher in the organics [118]. Ce, Dy, Ee, La, Nd, Tb, and Yb were determined in brown coal and lignite used in Austria and the resulting bottom ash and fly ash [119]. Based on the dataset given by Wedepohl [105] for the continental crust, which allows the extrapolation of lacking elements, the sum of REE in the Austrian brown coals (75 samples) can be estimated at 94.5 mg/kg. The REE concentrations reached 107 mg/kg (25 samples) in imported hard coals from Poland and Australia. In bottom ash, REE were present with 223 mg/kg, and in fly ash with 243 mg/kg (Table 7), indicating a significant enrichment during combustion.

During coal combustion, REE are mainly concentrated in the coarse residues or at least equally partitioned between coarse residues and fine particles [120]. Alkaline fly ash samples from coal-fired thermal electric power plants contain ferromagnetic spherical particles and aluminosilicates. Most ferromagnetic fractions contain significant quantities of a spinel (magnetite, Fe_3O_4) and minor quantities of quartz, hematite, and magnetite. About 45% of the ferromagnetic fraction was leachable with 0.5 M HNO_3 and contained total REE concentrations similar to standard magnetite as an exterior coating of thin shells on fresh ferromagnetic particles [121]. REE minerals remain unchanged during coal combustion (below 1500 °C). In the slag, elemental mapping by EDAX (energy dispersive X-ray spectrometry) showed that the Al and P distribution still coincides with those of La, Ce, and Nd but not with Si. In addition, in the corresponding aluminosilicates, correlations between Al and the REE were much more pronounced than between Si and the REE [122]. In coal fly ash, most of the REE are dispersed in the Al-silicates glassy matrix, which impairs REE recovery through leaching [122,123]. Calcination pretreatment can increase their recovery substantially due to the removal of the organic matter, as demonstrated for coals of the Fire Clay and Western Kentucky seams that contained 502–1968 mg/kg of total REE, mainly as phosphate minerals like monazite [123].

Table 7. REE (mg/kg) in coal and coal ash (mean ± sd or median and range).

Element	East Alabama	West Alabama	Darco	Wall	Lignites *	Hard Coal *	Bottom Ash	Fly Ash	Argonne Coal	Argonne Coal Ash
Reference	[118]				[119]				[36]	[47]
Sc	3 (2–5)	2 (0.7–5)	3 (0.8–8)	1 (0.7–3)	6.6 ± 3.4	4.2 ± 3.3	16.2 ± 6.1	16.4 ± 8.1	2.18 (0.81–7.61)	20 (9.4–33)
Y	9 (7–11)	13 (7–21)	6 (3–13)	5 (2–10)	10 ± 7	9.6 ± 3.5	40.3 ± 16.6	46.3 ± 14.9	n.a.	39 (25–86)
La	14 (9–17)	3 (2–7)	5 (0.7–12)	5 (1–14)	18 ± 9	16.7 ± 12.2	42 ± 26	44 ± 18	6.1 (2.8–21.5)	64 (39–137)
Ce	n.a.	n.a.	n.a.	n.a.	30 ± 15	25.8 ± 23.1	84 ± 36	92 ± 28	11.4 (4.4–30)	n.a.
Nd	n.a.	n.a.	n.a.	n.a.	29 ± 15	42.5 ± 38.0	49 ± 33	62 ± 1	8 (2.3–11.9)	77 (39–113)
Sm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.14 (0.41–3.52)	8.1 (<3–14)
Eu	n.a.	n.a.	n.a.	n.a.	0.6 ± 0.3	0.43 ± 0.42	1.18 ± 0.63	1.15 ± 0.53	0.22 (0.08–0.67)	n.a.
Tb	n.a.	n.a.	n.a.	n.a.	0.6 ± 0.2	0.71 ± 0.52	1.19 ± 0.55	1.13 ± 0.48	0.14 (0.06–0.40)	n.a.
Dy	n.a.	n.a.	n.a.	n.a.	2.9 ± 1.7	2.43 ± 1.81	3.9 ± 2.5	3.1 ± 2.0	n.a.	5.5 (2.0–9.2)
Yb	0.8 (0.5–1.2)	2.6 (2–4)	0.6 (0.3–1.1)	0.3 (0.1–0.8)	1.6 ± 0.7	2.05 ± 1.43	1.56 ± 0.73	2.05 ± 1.43	0.50 (0.20–1.6)	n.a.
Lu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	16.2 ± 6.1	16.4 ± 8.1	0.13(0.04–0.22)	n.a.

* Lignites and hard coal used in Austria in 1988; n.a. = data not available.

5. Pedosphere

5.1. Occurrence in Soil

The concentrations of REE in soils depend on the soil parent material, climate, time, and biological activity determining soil genesis, weathering intensity, and consequently mobility and sequestration of REE in/on secondary minerals and soil organic matter [59,124–127]. Given that soils are composed of heterogeneously distributed primary and secondary mineral phases and organic compounds, soil REE signatures are an amalgamation of the signatures belonging to each mineral group. This might explain why the median level of REE in Chinese soils is not higher than elsewhere (177 mg/kg REE) and ranged from 85 to 523 mg/kg but with some hotspots with LREE enrichment [18,128]. Many soil-forming processes cause dramatic losses of REE; consequently, soils typically show lower concentrations than the parent material from which they are derived (Table 8). REE concentrations in soil reflect weathering intensity rather than rock type, given that observed differences in soil REE concentrations can rarely be related to variations in bedrock. Chemical weathering of the host rocks drives the dissolution of the primary REE-bearing minerals [127]. The mobilized REE either co-precipitate in secondary minerals, sorb to appropriate surfaces, or leach into adjacent water bodies. Secondary minerals formed during silicate weathering may absorb and concentrate the REE liberated from primary minerals [67,129]. Thus, excessive REE losses are typically related to intensive weathering of both primary and secondary mineral phases. The literature indicates that soils developed upon felsic rocks such as granite, gneiss, and quartz rocks, at least tend to contain higher concentrations of REE, especially LREE, than soils derived from mafic rocks (basalt), which tend to contain lower total REE concentrations but may be relatively enriched with HREE [124,125,130]. However, soils developed on tholeiitic basalts within the Tertiary newer volcanic province of Victoria (South Australia) showed anomalously high REE concentrations, which has been attributed to REE released during the earliest stages of weathering and subsequent sequestration in secondary phosphate or clay minerals [95]. Decreasing soil REE concentrations have been reported in the order basalt > clay slate > loess > sandstone, which can be largely explained by an increasing portion of REE-depleted quartz [131,132]. In underdeveloped lithosols of the Ditrau Alkaline Massif in the Eastern Carpathian Mountains, characterized by an intrusion body within pre-Alpine metamorphic rocks formed by nepheline syenite, syenite, and mazonite, Ion [133] found extraordinarily high concentrations of total REE (median 273 mg/kg). On the contrary, in highly weathered lateritic soils, the upper ferruginous horizons appeared significantly depleted in REE, but also showed distinct accumulation zones of REE, especially in the basal saprolite [127,134]. When the characteristics of Australian soil derived from the weathering of the Toorong Granodiorite were investigated, lower concentrations in soil than in the parent granodiorite were found, but REE enrichment in zones of intermediate weathering, highlighting the influence of weathering conditions on the content of REE in the soil [135]. Given that the mobility of REE in soils does not depend on dissolution and sorption processes only, but also on complexation and ligand exchange reactions [136], the presence of ligands often explains differences in the concentrations of total REE along soil profiles as well as the pattern of LREE and HREE [129]. In Japan, the highest total REE contents were found in red soils [124,125]. Andosols with elevated carbon and phosphate levels exhibited intermediate total REE but were enriched in heavy rare earth elements (HREE). Conversely, highly weathered Acrisols, which were also depleted in numerous soil cations and phosphate, displayed the lowest total REE concentrations (Table 8). Similarly, acidic spodosols and podzols are characterized by the downward migration of REE together with Al and Fe as organic complexes [82,137,138]. In podzols of cold temperate regions of Sweden, the loss in the eluvial E-horizon was significantly higher for LREE (80–85% of La) than for HREE (54–60% of Yb) and the B-horizons appeared to be enriched through REE reabsorption on secondary oxy-hydroxides, clay minerals and organic material. In contrast, higher losses of HREE relative to LREE reported in soils across different tropical and temperate soils [97,129,139] are typically related to the presence of carbonates and the

higher affinity of HREE to form stable aqueous complexes [129]. During weathering in a semi-arid Mediterranean climate (Cape Province, South Africa), the increase in REE with depth reflected the change from the acidic organic-rich upper layer to alkaline carbonate precipitates at deeper layers [97]. Similarly, high concentrations of REE in soils near reefs, with their high carbonate and organic carbon contents, are typically caused by REE co-precipitation with marine carbonates or scavenging with particulate organic matter [140]. In Germany, soils developed from loess had higher REE levels than soils derived from Pleistocene and Holocene sediments or organic material [141]. The aqua regia extractable REE correlated significantly positively with clay contents, cation exchange capacity, and soil pH but negatively with organic carbon, according to [141]. Possibly, differences in other physicochemical properties related to the bedrock impacted soil REE concentrations more strongly than differences in organic matter contents, or a higher carbon content fostered the leaching of REE. In contrast, Wiche et al. [58] found a positive relationship between soil organic matter and total REE contents in various soil types derived from the same parent material (gneisses). We emphasize that soil organic matter has a dual role in REE sequestration and leaching. A higher content of particulate organic matter may contribute to REE sequestration and accumulation in a given soil, whereas dissolved organic carbon favors the leaching of REE [136,142].

Table 8. Median concentrations and ranges (mg/kg dw) of total REE in the continental crust, Baltic soils, 25 agricultural soils of Sweden, 24 soils from apple orchards in Austria, 843 soils of Europe, topsoils in China and Japan, 43 soils of Parana state Brazil, and lateritic soils of east Cameroon.

Element	Earth Crust ^{1,2}	World Soil Average ³	Baltic Soils ⁴	Topsoils Sweden ⁵	Topsoils Austria ⁶	Soils of Europe ⁷	China ⁸	Andosols Japan ⁹	Cambisols Japan ⁹	Acrisols Japan ⁹	Soils of Brazil ¹⁰	Lateritic Soils Cameroon ¹¹
Sc	14	11.7	n.a.	4.9–17.6	12 (7–18)	9.1 ± 5.6	n.a.	28 (10–51)	17 (7–41)	13 (2–37)	31 ± 15	n.a.
Y	31	33.0	n.a.	5.5–33.2	23 (15–34)	n.a.	n.a.	24 (12–72)	16 (7–67)	9 (3–28)	28 ± 8	17 ± 10
La	35	27	33 (2.3–113)	11–68	47 (30–69)	26 ± 16	35 (7–184)	19 (3.8–51)	23 (10–120)	21 (4–55)	38 ± 14	12 ± 6
Ce	66	56.7	37 (3.7–167)	1.3–7.5	5.8 (4.3–7.9)	52 ± 31	75 (16–454)	42 (10–100)	66 (2–140)	58 (7–150)	96 ± 38	23 ± 13
Pr	9.1	7.0	4.3 (0.4–24)	9.3–53	22 (16–29)	6.3 ± 3.6	n.a.	4.8 (1.1–11)	5.0 (2–31)	4.1 (0.7–9.9)	9.1 ± 3.4	2.6 ± 1.5
Nd	40	26	16 (1.7–86)	0.9–4.6	4.1 (3.1–5.8)	22 ± 14	33 (7.6–62)	22 (6–45)	20 (8–120)	15 (3–36)	34 ± 13	9.9 ± 6.0
Sm	7.0	4.6	3.0 (<0.2–15)	0.2–0.8	0.9 (0.6–1.2)	4.3 ± 2.6	5.6 (1.6–26)	4.6 (1.4–9.7)	4.1 (1.4–26)	2.8 (0.4–5.9)	6.9 ± 2.7	1.9 ± 1.0
Eu	2.0	1.4	0.6 (0.06–2.3)	1.0–4.8	3.7 (2.6–5.4)	0.9 ± 0.5	1.1 (0.2–7.0)	1.3 (0.7–2.2)	1.2 (0.6–8.1)	0.8 (0.2–1.3)	1.6 ± 0.7	1.2 ± 0.3
Gd	6.1	3.9	2.8 (0.24–13)	0.15–0.65	0.5 (0.4–0.8)	4.2 ± 2.7	n.a.	4.7 (1.6–9.5)	3.7 (1.4–22)	2.1 (0.5–5.9)	5.7 ± 2.3	1.7 ± 0.7
Tb	1.2	0.63	0.4 (<0.05–2.0)	0.90–3.76	n.a.	0.6 ± 0.4	0.77 (0.2–2.7)	0.8 (0.3–1.4)	0.7 (0.3–3.0)	0.4 (0.1–1.0)	1.0 ± 0.4	0.3 ± 0.1
Dy	4.5	3.6	2.3 (0.24–10)	0.20–0.74	0.5 (0.3–0.7)	3.6 ± 2.4	n.a.	4.5 (1.7–9.4)	3.3 (1.4–15)	1.5 (0.5–5.0)	5.7 ± 2.2	2.5 ± 0.9
Ho	1.3	0.72	0.4 (0.05–2.0)	0.63–2.2	1.3 (0.9–2.0)	0.7 ± 0.5	n.a.	0.8 (0.4–1.7)	0.6 (0.3–2.4)	0.3 (0.1–0.9)	1.1 ± 0.3	0.7 ± 0.4
Er	4.9	2.2	1.3 (<0.15–5.0)	0.09–0.33	n.a.	2.1 ± 1.4	n.a.	2.5 (1.1–5.9)	1.7 (0.8–5.7)	1.0 (0.4–2.9)	3.2 ± 1.1	1.9 ± 1.4
Tm	0.4	0.37	0.2 (<0.05–1.0)	0.60–2.3	n.a.	0.3 ± 0.2	n.a.	0.3 (0.2–1.1)	0.3 (0.1–0.7)	0.2 (0.1–0.4)	0.5 ± 0.2	0.4 ± 0.3
Yb	3.1	2.6	n.a.	0.09–0.34	0.2 (0.1–0.3)	2.1 ± 1.3	2.6 (0.7–8.5)	2.3 (1.1–6.3)	1.7 (0.7–4.4)	1.1 (0.5–2.7)	3.4 ± 1.1	2.6 ± 2.2
Lu	0.8	0.37	0.2 (<0.05–1.0)	4.9–17.6	n.a.	0.3 ± 0.2	0.45 (0.1–1.2)	0.4 (0.2–1.1)	0.3 (0.1–0.6)	0.2 (0.1–0.4)	0.5 ± 0.2	0.4 ± 0.3

¹ [30] Hu and Gao (2008); ² [5] Tyler (2004); ³ [143] Kabata-Pendias (2011); ⁴ [144] Reimann et al. (2000); ⁵ [145] Eriksson (2001); ⁶ [86,146] Sager (2016, 2020); ⁷ Data calculated based on the Foregs dataset [147] (Salminen et al. 2005); ⁸ [18] Liang 2005; ⁹ [124] Yamasaki et al. (2001), [125] Takeda et al. (2004); ¹⁰ [148] Licht (2005); ¹¹ [127] Braun et al. (1998). n.a. = data not available.

5.2. Mobility and Speciation in Soil

Despite the relatively high REE concentrations in soil (Table 8), under most pedological conditions, their mobility is low (Table 2). The mobility of REE in soils is a function of their ionic radii and speciation in solution, pH, Eh, water fluxes, and the nature of secondary intermediate minerals formed under different conditions [5,95]. Sorption on clay minerals [149–152], phosphates [17,104,153], Fe-/Mn-hydroxides [11,18,154–156], Al hydroxides [156], and soil organic matter (SOM) [72,104,136,154,157,158] decrease the solubility and mobility of REE in soils. Conversely, the presence of inorganic and organic ligands such as sulfate, carbonates, fluorides [9,159], carboxylates [14,73,77,160,161], humic and fulvic acids [136,158,162] can counteract sorption and foster their presence in the soil solution. However, there is also evidence that REE(III)–humate may bind on the surfaces of Fe-/Mn-oxyhydroxides, lowering its abundance in soil solution [155,157]. Dong et al. [163] estimated that of the total REE in soil, 1.8–26.5% of REE are bound into soil organic matter. Although REE sorbed onto mineral surfaces represent a relatively small element pool in soil [72], this pool is susceptible to slight physicochemical changes and contributes significantly to the mobilization/stabilization of REE in soils. Based on the point of zero charges given by [164], clay minerals account for a significant proportion of REE chemisorption over a wide pH range (pH 4–8), whereas carbonates and hydrous Fe-hydroxide minerals are predominantly relevant in soil environments with relatively high pH (pH 7–10), aluminum oxides contribute to REE sorption in slightly-acidic to circumneutral pH ranges, and in strongly acidic soils (pH 2–5) REE sorption onto manganese oxides becomes increasingly important [165,166].

The concentrations of REE in soil solution typically lie between 0.1 and 0.5 µg/L for a single element and rarely exceed 1 µg/L for the sum of all REE [73,167]. At comparable DOC concentrations in soil solutions, REE mobility in soil is inversely related to soil pH [168,169]. Fluctuations in soil water contents may locally change the redox potential and pH of soils, thus strongly affecting the mobility and speciation of REE [158]. In the soil solution, REE can occur in a variety of chemical forms, such as ions [16], dissolved complexes [153], and colloidal forms [136,158]. In wetland soil solution or shallow groundwater, ultrafiltration shows that REE are mainly concentrated in the high-molecular-weight fraction and the colloid phases, which consist of Fe and organic matter. Soil organic matter has many negatively charged groups per unit dry weight, and a high capacity to adsorb or chelate divalent and trivalent cations. In soil systems rich in organic matter, about 46–74% of REE mobility in soils derives from the interactions with humic compounds [167] but strongly varies depending on pH, redox conditions, type, contents, and composition of the organic compounds [170,171].

Davranche et al. [158] demonstrated that REE are released from wetland soils mostly bound to colloidal organic matter related to the organic matter desorption caused by the rise in pH imposed by the reducing reactions during the flood season. The stability of REE-(Tb, Yb, and Gd)-complexes with humic substances may be especially high in neutral to moderately alkaline (pH 8–9) conditions [163]. The stability of HREE with most inorganic and organic ligands typically increases with increasing atomic number and consequently decreasing atomic radius [172], leading to a fractionation of HREE in soils relative to LREE. Given that HREE form more stable complexes with many soil constituents than LREE do [173–175], SOM often appears to be enriched in HREE relative to LREE [82,175,176]. Ma et al. [177] observed a strong positive Ce-anomaly in REE patterns of organic matter, probably because complexation capacities and formation constants of humic acids are higher with Ce than with the other LREE [178]. In podzols, the percentage of total REE in general, and especially of HREE bound to organic matter, increases with soil depth [82,176] due either to the preferential complexation or the migration of HREE-complexes [82,176].

6. REE in the Hydrosphere

6.1. Speciation in Solution

The concentrations and speciations of REE predominantly depend on processes at the water/rock or water/soil interface governed by the physicochemical parameters of the water and the composition of soil/rock [5,153,179–194]. Truly dissolved REE typically represent a minor fraction of REE in the solution [136,158] because free REE^{3+} ions strongly interact with oxides or they are attracted to sorption surfaces, especially oxides and organic matter [157,166,190,195]. Under most physiologically relevant pH conditions (pH 5–7), REE show weak hydrolysis [196], and their solubility and chemical speciation are governed by complex formation with PO_4^{3-} , CO_3^{2-} , SO_4^{2-} , Cl^- , and F^- [197], where REE compete with other cations depending on ionic strength and pH [82,196]. At 3.5% salinity, it was found [198] that REE preferentially form complexes with carbonates but with slight differences between LREE and HREE. Lanthanum preferentially (86%) occurred in the form of MCO_3^+ and MCO_3^{2-} , 7% was present in free ionic form, and 7% was bound as hydroxide/sulfate/chloride/fluorides. In contrast, only 0.5% of Lu remained uncomplexed, 96% was present as dissolved carbonate species, and 1.5% formed hydroxide, sulfate, chloride and fluoride complexes. Accordingly, in groundwater with low Nd concentrations (0.22–0.80 ng/L), high pH (pH 6.9–8.6) and low DOC contents (0.08–0.15 mg/L) speciation modeling revealed that NdCO_3^+ and $\text{Nd}(\text{CO}_3)_2^-$ accounted for the majority of dissolved Nd (70–92%). In contrast, the species NdOH^{2+} , NdCl^{2+} , NdF^{2+} , NdSO_4^+ and NdHPO_4^+ were found to be negligible [153]. Yttrium and Ho have similar ionic radii and charge, but in an aqueous solution, Y–Ho fractionation takes place by preferential Ho-scavenging onto Fe-oxyhydroxides relative to Y as well as the preferential incorporation of Ho into CaCO_3 [62]. The higher stability of HREE carbonate complexes compared to complexes with LREE explains the HREE enrichment in hypersaline groundwaters in Australia, while in seawater and most other natural waters, the concentrations of REE typically decrease with increasing atomic number with respect to average shale [136,153]. Given that the complex stabilities of REE with organic compounds are much higher than with inorganic ligands, the chemical speciation of REE is strongly influenced by DOC and POC [198], determining the element's distribution between dissolved and colloidal forms. Many ultrafiltration studies demonstrated that REE in the dissolved fraction occur as colloid-borne particles [180,182,183,189,191,199–202]. In arctic glacial meltwaters and glacial-fed river waters from Western Greenland, the truly dissolved amount of REE obtained after ultrafiltration of 10 kDa was just 1/1000 of the total [203]. There is broad evidence that humic/fulvic acids act as carrier phases of dissolved REE [60,136,191,204–207]. For humic acids, increasing REE binding from pH 2 to pH 10.5 was demonstrated [136], similar to the complexation of REE with acetic acid, thus suggesting carboxylic groups with low pKa (pKa 5–6) as the primary binding sites. However, bidentate complexation with phenolic groups (with higher pKa > 8) cannot be completely ruled out [136]. The stability of REE complexes with humic substances is exceptionally high at moderately alkaline (pH 8–9) conditions [163]. However, more than 95% of the REE present in river water acidified to pH 3 was found in their complexed form with organic compounds [185], indicating that related complexes may occur over a wide range of biogeological relevant pH conditions, depending on the composition of DOC and consequently the prevailing functional groups. The binding of polydentate ligands is entropically favored compared to that of monodentate ligands. Simple carboxylic acid groups tend to form weaker monodentate complexes in environments with high REE concentrations, whereas multidentate complexation might be more relevant when REE concentrations are low [205]. In particular, enrichment of middle mass REE seems to be associated with the monodentate complexation, while HREE enrichment may derive from complexation with stronger binding sites [205].

6.2. Limnic Water Bodies

The total REE abundances in water depend on the watershed limnology, stream hydrology, climate, groundwater, landscape, and anthropogenic impact [106]. Therefore,

compared to their relatively equal distribution in the earth's crust, the concentration of REE in limnic water bodies varies by several orders of magnitudes. Typical ranges between 1 ng/L and a few hundred ng/L for a given element from this group (Table 9) depend on weathering, the source materials, and the removal during the formation of auto-genic, biogenic, and inorganic solids such as carbonates and oxyhydroxides [62,195,208]. Acidic conditions may favor higher total REE concentrations [60]; however, the processes involved depend not solely on REE solubility but are often influenced by other biogeochemical processes solution-surface chemistry governed by pH in concert with Eh, TOC, and salinity [106,209]. In general, freshwater contains higher REE concentrations than seawater because in river water the REE are associated with inorganic nanoparticles and colloids [51]. [51] compared REE concentrations in freshwater and saltwater samples from Germany and the Netherlands and found 26–280 ng/L (total REE plus yttrium) in freshwater, whereas in saltwater, the concentrations rarely exceeded 10 ng/L. In the Canadian St. Lawrence River and the Athabasca River, less than 20% of REE were found to be present in dissolved forms [210]. At the river mouth of the Amazonas, the concentrations of soluble Fe and REE rapidly decline with increasing salinity through the removal of dissolved Fe and co-precipitation of REE [182]. In the Karstic groundwater system of Guizhou (SW China), which is dominated by limestones and dolomites, the sum of dissolved REE was <0.15 µg/L (range 0.03–0.99 µg/L) [209]. In Lake Baikal, the sum of total REE varied from 0.02 to 2.16 µg/L as a function of season and year [106], and model calculations demonstrated that REE are predominantly present in the form of carbonate and humic complexes [211].

REE are commonly used as tracers for geochemical processes in natural water bodies. The normalized patterns of the abundance of the REE can be used to trace the origin of suspended matter in river waters [106], given that anomalies in water might be related to the source rocks of the watershed [199]. Based on $^{147}\text{Sm}/^{144}\text{Nd}$ ratios, the origin of Rhine water downstream of Basel could be identified [199]. Depletion of both LREE and HREE is typical for phosphate inputs; however, chemical weathering and sorption processes during element transport lead to extensive fractionation between river water's dissolved REE composition and river-suspended particles. Tropical rivers usually show MREE enrichment, whereas temperate rivers show enrichment of HREE (Table 9) and negative Ce-anomalies concerning chondritic normalization [203]. In the coagulation region of river colloids, more Ce is precipitated than La and Nd [182]. In addition, in oligotrophic and oxygenated river waters, negative Ce anomalies and positive Y anomalies may derive from Ce co-precipitation and oxidation on FeOOH and less sorption of Y than other REE onto particulate matter [199,212] governed by pH and DOC [209]. On the contrary, LREE often appear to be enriched in arctic lakes and rivers that usually do not develop positive Eu anomalies because processes of Eu reduction do not take place in low-temperature environments [203]. In the Karstic groundwater system of Guizhou (SW China), most river water samples exhibited enrichment of MREE and negative Eu and Ce anomalies, whereas the suspended matter and surface sediments showed positive Ce and Eu anomalies [209]. From volcanic ash, siderophore-promoted transfer of REE and Fe into glacial meltwater, river, and ocean water has been observed [213].

In addition to geochemical processes, REE fractionation patterns in water are significantly influenced by biological activity altering the physicochemical water properties and cycling of specific REE species from the water phase [214]. It was demonstrated [62] that phytoplankton liberates REE from Fe-rich particles and accumulates both Ce(III) and Ce(IV), which may counteract the formation of a Ce anomaly even under oxic conditions. In addition, anthropogenic inputs of REE with wastewater discharge may strongly alter REE signatures of stream waters, primarily through the medical application of Gd-chelates [51,103,199,203,215]. [216] investigated the fate of cerium dioxide (CeO_2) nanoparticles in municipal wastewater during activated sludge treatment.

Table 9. Concentrations of dissolved REE (ng/L) in water samples from tropical and temperate rivers compared with groundwater collected around Bergen and Oslo (Norway).

Source	Groundwater ¹	Mississippi ²	Sepik ²	Fly ²	Amazon ²	Amazon River Mouth ³	Luce ⁴	Fraser ⁴	Dordogne ⁴	Garonne ⁴	Columbia ⁴	Sacramento ⁴
Region	Norway	USA	New Guinea		South America	Guyana	Scotland	Canada	France		North America	USA
Y	110–130	n.a.	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
La	46–57	3.9	38	35	40	47	192	97	48	47	30	8.1
Ce	8–13	7.3	85	81	111	118	451	155	77	81	58	11
Pr	1–8	1.4	13	12	n.a	n.a	n.a	28	11	5.2	9.9	7.2
Nd	31–37	7.3	57	55	73	76	264	88	37	38	23	11
Sm	3–8	21	15	15	17	20	59	25	7.3	8.2	44	2.5
Eu	n.a	0.7	4.4	3.3	4.1	4.9	15	7	1.3	1.6	1.6	1.0
Gd	6–9	3.6	17	17	19	22	58	53	0.8	8.8	6.5	5.1
Tb	1	0.5	2.3	1.9	n.a	n.a	n.a	43	1.3	1.2	1.2	0.5
Dy	n.a	4.5	13	11	22	19	43	n.a	n.a	n.a	n.a	n.a
Ho	2–3	1.2	2.3	2.2	n.a	n.a	n.a	7	1.2	1.6	0.9	0.4
Er	7–9	4.1	6.1	5.3	11	11	24	14	4.3	4.1	n.a	n.a
Tm	1–2	0.6	0.8	6.7	n.a	n.a	n.a	n.a	0.6	0.6	n.a	n.a
Yb	14–18	3.9	4.6	4.6	8.4	9.3	20	n.a	3.7	3.6	4.5	2.5
Lu	3–4	0.7	0.8	0.5	1.0	1.2	n.a	n.a	0.7	0.6	0.7	0.3

¹ [217] Reimann et al. (1996); ² [208] Hannigan and Sholkovitz (2001); ³ [82] Sholkovitz (1993); ⁴ [101] Protano and Riccobono (2002). n.a. = data not available.

6.3. REE in Seawater

In seawater, the level of total REE steadily increases with depth, because they are transported to the sea floor by settling particles, which finally form nodules at the bottom. Thus, for 15–750 m depth, 12.0 ng/kg had been reported for the Pacific, and 14.7 ng/kg for the Atlantic Ocean, resp., for 100–3500 m depth 23.9 ng/kg for the Pacific and 25.0 ng/kg for the Atlantic Ocean, and finally 30.6 ng/kg for the Atlantic deep-sea. Differences and uncertainties are mainly influenced by Ce oxidation/precipitation, which had been observed to be higher in the Pacific than in the Atlantic Ocean [115]. The carrier phase is probably biogenic amorphous silica of diatomea. In the interstitial water of the deep-sea sediments, the rare earth concentrations are lower than in the overlying bottom water. Hydrothermal solutions are strongly enriched in LREE relative to seawater and display a pronounced positive Eu-anomaly [8], which is also evident in hydrothermal iron oxide crusts.

Nevertheless, with respect to mean crust abundances, the seawater is enriched in HREE and depleted in LREE because of the complexation with organic and inorganic ligands [182]. The main species in oxygenated seawater are carbonate complexes. The stability of carbonate and lactate complexes and the hydrolysis constants of the REE increase almost monotonically from La to Lu [115]. During flood periods, reducing conditions and a rise in pH causes a mobilization of REE from their particulate phase, which mainly consists of dead or living organic matter. Bacteria, diatomeae cells, and algae cell surfaces represent significant binding sites for REE due to the prevailing carboxylic and amino functional groups [218]. Thus, thin organic coatings strongly affect the adsorption behavior of suspended particles in seawater, similar to limnic water bodies. Given that the monocarboxylate complexation constants substantially increase from LREE to HREE, the formation of soluble REE-carboxylate complexes might explain the enrichment of HREE in seawater [218].

6.4. Groundwater

The concentration of REE (sum of La–Lu) in groundwater rarely exceeds a few $\mu\text{g/L}$ and typically ranges between 1 and 100 ng/L for specific representatives of this group [67,217]. Water samples from Norwegian bedrock groundwater boreholes drilled in Paleozoic and Precambrian igneous or metamorphic aquifers (pH range 7.22–8.95) contained a sum of dissolved REE concentrations of about 162 $\mu\text{g/L}$ [219], which could be largely explained by the geological setting which led to REE enrichment in top and bottom soils [220]. In hypersaline groundwaters in Australia, 33–152 $\mu\text{g/L}$ REE and enrichment of HREE due to higher complex stability of HREE-carbonate complexes compared to LREE were reported [153]. Colloidal particles may facilitate or retard REE migration along groundwater flow paths, which is highly dependent on the reversibility of the sorption process. Colloid particles in deep groundwaters mainly consist of quartz, clays, iron hydroxides, calcite, and humic substances [221]. At the Mizunami Underground Laboratory (Japan), it was found that up to 60% of the REE, particularly LREE, were associated with suspended particles, especially carbonates and Fe/Mn oxides [221]. Within the Dead Sea fault system (Israel), the northern spring is dominated by Ca-HCO_3 . Further south, they contain sulfate from the dissolution of gypsum or high Na and Cl contents from ancient brines or meteoric waters dissolving halites. According to PHREEQC modeling, most well waters were undersaturated with gypsum and halites, but some were oversaturated with dolomite and calcite. The REE were either complexed by carbonate, chloride, or fluoride. The amount of REE^{3+} and $[\text{REECl}]^{2+}$ species decreased with increasing molecular weight, whereas the amounts of $[\text{REE}(\text{CO}_3)_2]^-$ increased, and $[\text{REECO}_3]^+$ remained constant. The well waters grouped due to their low redox potential ($-0.40 < \text{Eh} < -0.25$) had a distinctly positive Eu anomaly but no Ce anomaly. In contrast, the other group ($-0.1 < \text{Eh} < +0.26$ V) had a strong Ce anomaly and was enriched in the middle REE [62].

7. Biosphere

7.1. Plant Availability and Accumulation of REE in Herbaceous Plants

In all studies reported, LREE represented more than 90% of the total REE content of plants, indicating that the concentrations in plants largely reflect the abundance of REE in soils (Table 10). However, the literature indicates large differences in the total accumulation level and LREE/HREE ratios among different plant species (Table 10) and even individuals of the same species growing on the same soil [7,222]. Due to strong interactions of the trivalent elements with soil, cell, and tissue constituents, shoot REE concentrations are typically very low and range from a few ng/g to 1 µg/g (Tables 10 and 11). Some herbaceous plants hyper-accumulate REE, of which ferns (up to 3358 µg/g REE) and species from the Phytolaccaceae (*Phytolacca americana*: up to 623 µg/g REE) were the most profoundly studied [37,223,224]. With regard to the element distribution among different plant tissues, there is broad evidence that the REE concentrations decrease in the order root > leaf > stem > grain/fruit [5,9,10,18,31,55,59,140,225] and are higher in old leaves compared to young ones [146,226]. Notably, root concentrations are strongly biased by REE³⁺ absorbed onto the apoplast, and the evaluation of root uptake requires desorption with ionic solutions or EDTA [160].

Compared to vegetative organs, REE in reproductive plant parts are only occasionally detectable or orders of magnitude lower compared to concentrations in plant leaves [18,146,227,228], indicating restricted REE allocation from soil to the plant and vegetative plant parts to the fruits (Tables 10 and 11). Dicots typically show higher shoot REE concentrations than monocots (Table 10, [74]), which could be attributed to a higher accumulation of Ca in dicots compared to grasses [229] and differences in below-ground functional traits related to nutrient acquisition, particularly of P, Fe, and Mn [14,55,74].

Table 10. Median and range of shoot REE concentrations ($\mu\text{g}/\text{kg}$) in different herbaceous plant species and hay samples from Germany and Austria.

Species	<i>Fagopyrum esculentum</i>	<i>Helianthus annuus</i>	Legumes	Cereals	<i>Agrostis capillaris</i>	<i>Miscanthus giganteus</i>	<i>Phalaris arundinacea</i>	Hay Samples		Apple Leaves
Region	East Germany ¹				Sweden ²	East Germany ¹		Bohemian Massive, Austria ³	Limestone Alps, Austria ³	Austria ⁴
Sc	52 (14–1395)	60 (4–100)	30 (14–80)	39 (5–110)	n.a.	33 (20–56)	44 (3–328)	10 (<10–100)	11 (<10–550)	<20 (<20–50)
Y	425 (33–842)	112 (44–455)	31 (9–100)	33 (4–227)	30	36 (10–71)	42 (6–524)	39 (5–195)	218 (22–3294)	27 (9–241)
La	564 (47–1119)	204 (91–540)	44 (17–171)	56 (5–318)	110	56 (13–111)	65 (10–887)	94 (22–306)	330 (10–3747)	62 (18–516)
Ce	963 (76–1826)	358 (159–748)	85 (29–296)	86 (10–491)	150	103 (28–207)	120 (20–1824)	166 (28–695)	601 (40–7494)	88 (26–612)
Pr	98 (8–179)	14 (18–78)	9 (3–35)	10 (1–54)	17	12 (3–23)	14 (2–203)	19 (3–77)	69 (2–1559)	11 (3–90)
Nd	356 (27–626)	161 (74–309)	40 (11–134)	42 (4–233)	91	49 (11–94)	58 (8–835)	71 (90–292)	251 (7–5829)	40 (11–492)
Sm	65 (6–116)	30 (14–53)	8 (2–25)	7 (1–45)	10	9 (4–17)	12 (6–162)	14 (2–56)	46 (2–1117)	8 (2–66)
Eu	18 (4–33)	8 (3–12)	3 (2–26)	6 (1–51)	1	3 (1–5)	6 (1–60)	8 (3–11)	12 (2–219)	9.2 (4.7–26)
Gd	79 (6–134)	32 (19–74)	8 (3–27)	10 (2–64)	10	13 (3–21)	12 (2–135)	13 (2–54)	46 (2–1019)	7 (2–75)
Tb	11 (1–20)	2 (2–9)	1 (<1–3)	2 (<1–16)	1.0	2 (<1–3)	2 (<1–53)	2 (<1–8)	7 (<1–142)	1.0 (0.2–9.9)
Dy	56 (5–110)	20 (8–46)	6 (2–16)	6 (1–36)	5.1	6 (2–12)	10 (3–123)	n.a.	n.a.	n.a.
Ho	11 (1–23)	4 (2–9)	1 (<1–3)	1 (<1–17)	1.0	1 (<1–3)	2 (<1–65)	1 (<1–7)	7 (1–133)	0.9 (<0.1–7.1)
Er	32 (3–58)	16 (8–29)	4 (1–10)	5 (1–28)	3.1	8 (1–12)	7 (<1–96)	4 (<1–20)	23 (3–389)	2.5 (0.4–16.5)
Tm	4 (<1–7)	2 (1–4)	0.5 (<0.5–2)	1 (<0.5–4)	2.9	0.6 (<0.5–2)	0.8 (<1–67)	n.a.	n.a.	n.a.
Yb	20 (2–40)	10 (4–18)	3 (1–9)	3 (<0.5–16)	1.9	4 (2–8)	5 (0.5–74)	n.a.	n.a.	n.a.
Lu	3 (<0.5–6)	2 (0.5–4)	0.5 (<0.5–1.3)	0.6 (<0.5–3)	0.3	0.5 (<0.5–1.8)	0.8 (<0.5–59)	0.4 (<0.4–2)	3.1 (<0.5–54)	<0.3 (<0.1–1.2)

¹ Concentrations were calculated based on 15 shoot samples of *F. esculentum*, 20 shoot samples of *H. annuus*, 20 samples of *M. giganteus*, 6 shoot samples of *P. arundinacea*, 15 shoot samples of selected legumes (*Lupinus albus*, *Lupinus angustifolius*, *Trifolium pratense*, *Medicago sativa*) and 29 shoot samples of cereals (*Zea mays*, *Hordeum vulgare*, *Avena sativa*) collected in the area of Freiberg (Saxony, Germany) and analyzed according to [58] Wiche et al. (2017a); ² [169] Tyler and Olsson (2001b); ³ [230] Sager (2013a); ⁴ [146] Sager (2020); n.a. = data not available.

Generally, the plant availability of REE increases with increasing concentrations in soil solution, which is inversely related to soil pH [142,169,231,232]. However, relationships between total concentrations in soil and physicochemical parameters such as soil pH or operationally defined soluble soil fractions are usually weak when variability in REE concentrations among plant species are compared [7,74,167], suggesting that chemically mediated soil–plant relationships rather than soil properties control the availability of REE. Soil-associated factors determine the initial distribution of REE in mobile and labile forms in the soil and influence the plants’ nutritional status, which in turn controls the release of protons, carboxylates, siderophores, and other element solubilizing compounds in the rhizosphere [14,71,78]. There is evidence that rhizosphere acidification and complexation of REE with carboxylates and siderophores increase the mobility of REE in soil and consequently alter the plant availability of REE [14,55,73]. In this view, the higher shoot content of dicots compared to grasses (Table 10) could be explained by a higher carboxylate release and rhizosphere acidification in P-efficient dicots than in P-inefficient monocots [14,55,78].

A higher portion of dissolved and exchangeable REE in the rhizosheaths is related to a higher root adoption of REE, whereas plant uptake is substantially reduced when REE are present in a complexed form in the soil solution [14,17,55,72,159,233,234]. This is because plant uptake of REE is mediated mainly, but not solely by Ca^{2+} , Na^{+} , and K^{+} channels [72,160,235,236], which transport REE^{3+} , and most likely discriminate stable metal-complexes relative to the free ionic form. Carboxylate release by plant roots plays a vital role during both element acquisition and the detoxification of potentially toxic trace metals such as Al^{3+} and REE^{3+} through complexation external to the roots [12,14,55,177,237–240]. REE accumulation in plants must be understood as a consequence of processes during nutrient acquisition and detoxification of metals through extracellular complexation that overlap in the rhizosphere in time, space, and function. For a given REE, complex stabilities, and thus, the degree of element exclusion, typically increase in the order of monocarboxylates < dicarboxylates < tricarboxylates and are higher for HREE than for LREE. In addition, complex stability is strongly influenced by rhizosphere pH, governing the protonation of the carboxylic acid head groups, rendering them continuously ineffective for complexation when the pH decreases below the pKs of the carboxylates. Thus, plants that release less tricarboxylates and/or strongly acidify the rhizosphere contain higher REE concentrations, especially HREE [14,55]. This might be why REE accumulation often correlates positively with Al uptake in plant shoots and highlights the dual role of phosphate in REE availability. Phosphate supply may control the precipitation of REE internal of the roots [17,241] and controls the amount and composition of ligands and metal solubilizing compounds by plant roots depending on plant species and the nutritional status [71,78]. It could be demonstrated [55] that REE accumulation in plants reflects changes in carboxylate release triggered by the P-nutrition status across a variety of plant species with different P-acquisition efficiency. In P-efficient species characterized by a higher carboxylate release under conditions of P-deficiency [71,78], REE accumulation declines with declining P-supply, whereas in P-inefficient, phosphophilic species such as *Brassica napus* and *Triticum aestivum*, REE accumulation increases with declining P-supply. Relationships between P-efficiency and REE accumulation could also explain the high REE accumulation in some species from the Proteaceae growing on extremely P-impooverished, acidic soils of Australia [226] and the relatively high REE accumulation in crop species that strongly acidify the rhizosheaths such as *F. esculentum* (Table 10). Notably, there is evidence that plant species which hyperaccumulate REE rely on the release of weak ligands, such as amino acids, which increase mobility through complexation but do not strongly interfere with uptake and translocation [242,243].

Other factors affecting the mobility of REE in soils are plant–microbe interactions, especially the REE absorption on cell surfaces, and the influence of metabolic compounds released, such as bacterial metallophores [244]. Some components of these exudates, such as sugars, flavonoids, and carboxylates, may further influence microbial growth and the rhizosphere metabolome [245–247] that can, in turn, alter REE availability through

the release of metabolites and intra- or extracellular sequestration [248–251]. It could be demonstrated [252,253] that mycorrhizal infection affects the accumulation of REE in Chinese milk vetch (*Astragalus sinicus*), maize (*Zea mays*), and millet (*Sorghum bicolor*).

Once REE are taken up by the root cells, root–shoot translocation is strongly influenced by interactions/adsorption to a variety of cell structures, such as cell walls and plasma membranes [243,254] and proteins [255], limiting their transport through the roots and transfer to the shoots. Organic ligands like carboxylates and amino acids facilitate REE transport in the xylem, leading to preferential enrichment in the aerial parts [256]. In the xylem sap, REE are transported almost entirely complexed with amino acids or carboxylates [242]. Given that complexation and ligand exchange reactions play a prominent role during the mobilization, uptake, and transport of REE, it is reasonable that the related processes during uptake and translocation have opposing effects on the bulk REE pattern in plants when HREE are discriminated relative to LREE during plant uptake from the rhizosheaths [55], while LREE are discriminated relative to HREE during the long-distance transport [257]. Indeed, only slight and not systematic fractionations of LREE and HREE are observed in contradictory studies [126,234,235]. Processes during uptake sometimes fractionate only one specific REE, as demonstrated for Eu [234,258], Sm, Tb, and Nd [258]. When the evaluation of REE accumulation in plants growing in their natural growth environment is desired, it has to be noticed that REE availability is significantly influenced by interspecific root interactions [73,74,259] that impact not only the total level of REE accumulation but also the fractionation pattern of REE in plant communities. In addition, plant recycling modifies REE speciation since uptake preferentially affects weakly bound REE pools, which are returned into the soil as REE bound into organic matter [5,30]. Hence, plant recycling induces a well-known enrichment of element budgets in the topsoil, especially in the forest context, and influences plant uptake and accumulation [30,126].

7.2. Physiological Responses of Plants to REE

It is generally assumed that REE are neither essential nor strongly toxic for plants [5,243]. However, all REE exhibit ionic radii very similar to that of the hydrated Ca^{2+} ion [16], closely follow Ca during plant uptake [160], and have the potential to replace and compete with Ca in a variety of physiological processes [260]. REE interfere with multiple types of Ca^{2+} channels, alter membrane stabilities, and inhibit many Ca^{2+} -dependent enzymes [16,261]. In physiological research, cations of REE have been widely used as probes in studies on Ca channels [262,263] for characterizing Ca^{2+} binding sites in plant tissues and spatial distribution of protein complexes [264,265]. They displace Ca at Ca-binding sites at biological molecules due to their higher charge density, thus inhibiting the efflux of extra- and intra-cellular Ca [2]. Consequently, the REE influence the processes of cell division, like DNA structure or mitotoxic effects, resulting in a decrease in cell division activity [266–268]. Detrimental effects from REE are frequently observed when plants are exposed to high concentrations [38]; at low concentrations, REE produce hormesis effects on organisms, which is characterized by stimulatory effects at low doses and inhibitory effects on high doses [243]. In fact, greenhouse and field studies demonstrated that low levels of plant-available REE seem to promote plant growth and biomass formation of several crops [5,268], while high concentrations of plant-available REE may reduce plant growth, root elongation, and biomass formation [2,5,257,261,269,270]. Low application rates of REE to plants have been widely reported to promote biomass production and growth in plants through increasing the chlorophyll content, enhancing gas exchange via increased efficiency of the PS II electron transfer chain, and increasing the photosynthetic rate and stomatal conductance. The positive effect of low-dose additions is not due to a fertilizer effect as such but due to stimulation activated by low doses of oxidative stress, enhancing catalase, superoxide dismutase, and thiol-based redox regulation [31,32,268,271–274]. This forms the scientific basis for the utilization of REE-enriched fertilizers that have recently been implemented in agricultural fields to improve crop growth and agronomic performance, especially in China [2,275].

Given that the presence of REE stimulate carboxylate release in plants, similar to Al [13], it is reasonable that microdoses of REE positively affect processes during nutrient acquisition in the rhizosphere, which is an important subject for future studies. Elevated levels of application, however, may cause toxic effects on plants [9,33,34,276] caused by detrimental oxidative stress, decreased membrane permeability, and increased electrolyte leakage as well as imbalance of nutrient homeostasis [26,274]. The degree of damage seems to depend on the concentrations of REE applied and the time of exposure [276]. In an Australian study [9] neither positive effects nor adverse effects on plant growth of *Vigna radiata* and *Zea mays* were found, when treated with a commercial REE fertilizer at rates recommended in Chinese agriculture. Higher rates, however, led to foliar damage in maize and mung bean and reduced growth and nutrient uptake of *Vigna radiata*, while *Zea mays* was only slightly affected. Recently, the effect of Gd and Y application on soil-grown maize was also investigated [34]. While there were no effects of low concentrations (0.1–1 mg/L), high concentrations (10 mg/L) resulted in severe phosphate deficiency symptoms in maize. A database was created, including 703 La-induced hormetic-like dose responses, including maximum biological responses followed by growth restrictions versus La concentrations, containing 37 taxa [277]. With increasing concentration, a maximum response appeared at first (median effect 125%, max 150%), followed by a steady decline of growth versus La concentration in the substrate. The maximum biological response concentration was 1–5 times lower than the no-observed-adverse-effect levels, where inhibitory response versus concentration began. The stimulation effect was usually lower under optimum pH conditions. Effects of La-chloride and La-nitrate seem to be the same, but scales differ widely. The magnitude of hormesis differed only marginally between experiments of 0–7 days of interaction and 8–31 days of interaction, remaining beneficial after ceasing stimulation by maximum response after the end of chronic exposure. Examples have been given for rice (*Oryza sativa*), beans (*Phaseolus vulgaris*), horseradish (*Armoracia rusticana*), and others [277]. The effects of Ce, especially CeO₂ nanoparticles, on the metabolism and growth in higher plants have been intensely reviewed [274]. Unlike the ionic form, the nanoparticles possess catalytic radical scavenging activities mimicking superoxide dismutase and catalase and have beneficial effects through the alleviation of oxidative stress [26]. The kind of added compound, like nano-CeO₂, Ce(NH₄)₂(NO₃)₆, Ce(NO₃)₃, or CeCl₃, had obviously different effects, but differences between soil and hydroponic growing media were marginal [274]. In hydroponic culture, the addition of 1–5 mg/L Ce had a positive effect on paprika (*Capsicum annuum*), tomatoes (*Lycopersicon esculentum*), cucumbers (*Cucumis sativus*), but negative effects on Liliaceae, onions (*Allium cepa*), peas (*Pisum sativum*), and tobacco (*Nicotiana tabacum*). Vegetables and wild herbs may be less responsive to Ce than cereals, fruit tree, and pastures [274].

7.3. REE Accumulation in Woody Plant Species

In trees, concentrations in leaves are higher than in woody parts and rarely exceed 1 µg/g for a specific element from this group (Table 11). 1.1 µg/g La in plant individuals have been reported from the genus *Acer* (maple), which is considered a REE accumulator [278]. Compared to herbaceous plant species, the leaves and branches of woody plants generally show much less variability in REE concentrations [279] (Tables 10 and 11), which could be attributed to different functional traits related to nutrient acquisition in concert with deep and extensive root systems that integrate over very different REE pools in soil.

Table 11. Rare earth concentrations found in leaves and woody parts of different tree species (median and range, µg/kg); n.a. = data not available.

Species	<i>Picea abies</i>		<i>Pinus silvestris</i>	<i>Populus nigra</i>	<i>Malus domestica</i>		<i>Fagus silvatica</i>				<i>Pinus densiflora</i>		<i>Castanea crenata</i>	
Region	Sweden ¹	Russia ²	Germany ²	Bulgaria ³	Austria ⁴		Sweden ¹				Korea (Chungcheonbukdo) ⁵			
Sampling details					May	Aug.	Jul.	Sep.	Litter Nov.	Litter prev. year	Leaf litter	Woody parts	Leaf litter	Woody parts
Sc	n.a.	17.3	15	n.a.	<20	<20	32	42	n.a.	327	40	60	160	20
Y	150–770	64	150	140 (50–710)	22 (9–281)	27 (8–378)	21	26	65	195	n.a.	n.a.	n.a.	n.a.
La	150–250	194	160	220 (79–1093)	58 (15–521)	80 (26–784)	44	49	130	370	370	640	5920	1010
Ce	250–550	210	310	330 (120–1120)	70 (22–759)	121 (45–1134)	66	84	235	700	500	880	3360	560
Pr	30–60	23	35	39 (2–156)	9 (3–92)	15 (5–154)	8	10	26	79	80	130	1090	140
Nd	100–250	74	130	157 (71–628)	31 (10–586)	54 (18–594)	55	67	181	560	270	450	3900	500
Sm	20–40	15	21	32 (13–235)	6 (2–70)	10 (4–123)	5	6	17	52	50	80	670	80
Eu	5–15	7	6	12 (4–86)	8 (4–26)	14 (9–37)	9	10	15	26	20	20	180	30
Gd	10–230	14	32	33 (13–209)	5.4 (1.6–81)	7.8 (2.8–136)	5	7	18	53	50	70	760	90
Tb	5–15	2	6	4.1 (1.6–22)	0.6 (0.2–11)	1.0 (0.4–18)	n.a.	n.a.	2.2	6.9	100	10	10	10
Dy	25–50	11	24	21 (9–91)	n.a.	n.a.	4	5	12	36	40	50	570	50
Ho	5–15	2	60	3.9 (1.6–26)	0.6 (<0.2–8)	0.8 (0.4–13.5)	1.0	1.0	2.2	6.8	n.a.	n.a.	n.a.	n.a.
Er	15–30	7	16	11 (4.6–55)	1.5 (0.4–19)	2.5 (1.0–31.3)	2	2	6	20	n.a.	n.a.	n.a.	n.a.
Tm	n.a.	2	6	n.a.	n.a.	n.a.	0.2	0.3	0.9	2.7	n.a.	n.a.	n.a.	n.a.
Yb	15–30	7	16	8 (3–26)	n.a.	n.a.	2	2	6	17	n.a.	n.a.	n.a.	n.a.
Lu	2.5–5.0	1	3	1.1 (0.5–6.3)	0.2 (<0.2–1.3)	0.3 (0.2–1.9)	0.2	0.3	0.8	2.5	n.a.	n.a.	n.a.	n.a.

¹ [280] Tyler (2005); ² [281] Markert and Li (1991); ³ [282] Djingova (2001); ⁴ [146] Sager (2020); ⁵ [283] Gautam et al. (2019); n.a. = data not available.

Species from the Juglandaceae and Euphorbiaceae, especially *Carya tomentosa*, *Carya cathayensis*, and *Glochidion triandrum*, have been described as hyper-accumulators of REE, as these species accumulate up to 2296 µg/g REE in their leaves [2,284]. However, until recently, the number of REE hyperaccumulating tree species is relatively low. In leaf samples collected from *Populus nigra italica* growing on six different soil types in Bulgaria [282], the highest REE concentrations were found on humic carbonatic soils (sum of REE: 2.24 µg/g) and the concentrations declined in the order humic carbonatic soils > brown mountain soils (1.68 µg/g) > leached chernozems (0.95 µg/g) > alluvial soils (0.72 µg/g) > leached cinnamomic forest (0.60 µg/g) > calcareous chernozems (0.46 µg/g). The transfer of REE from an andosol (pH 4.2–5.0) into different plant parts of *Populus sieboldi*, *Thea sinensis*, *Sasa nipponica*, and *Taxodium japonicum*. *Taxodium japonicum* was characterized by lower REE concentrations and showed the highest REE concentrations in the roots and the lowest in the stems. Conversely, *Populus sieboldi* had the highest total concentrations and higher concentrations in the leaves than in the stems, which suggests efficient transport mechanisms in this species [278].

Once REE are taken up, similar to Ca and Si, REE are highly immobile and accumulate over time, particularly in the leaves. Consequently, the highest concentrations typically appear in senescent leaves, as it was demonstrated in beech tree (*Fagus silvatica*) and leaves from apple tree grown at the experimental orchard at Klosterneuburg, Austria (Table 11) [146]. Specifically, senescent apple leaves collected in August showed REE concentrations that were a factor of roughly twice as high than fully developed leaves sampled at the end of May (Table 11). Leaf samples from Swedish beech trees showed similar concentration ranges. However, the beech trees and apple trees grew on substantially different soils, suggesting that the stage of leaf senescence is probably more important than the composition of the soil or the plant species. This highlights the need for considering leaves of the same age when a comparison in the accumulation of different species is desired. In addition, the input of labile-bound, potential plant-available REE by leaf litter might be especially relevant in forest ecosystems characterized by high humus accumulation and relatively slow turnover rates. Microbial decomposition and the related mass losses can lead to REE enrichment in the humus and liberate REE from the organic matrix over time [283].

7.4. REE Accumulation in Ferns, Mosses and Lichens

Ferns strongly accumulate REE and could be used as indicator plants or for phytomining applications [7,243,285,286]. Some species of the Genera *Dicranopteris* [37,258], *Blechnum* [287], *Pronephrium* [288–290], *Athyrium* [223], *Stenoloma*, *Woodwardia* [287], *Dryopteris* [278], and *Asplenium* [278] accumulate up to 3359 mg/kg of the sum of REE in their shoots. In areas of relatively high abundance of REE in soil, the leaves of *Dicranopteris dictatoma* and *Dicranopteris linearis* contain 100–1000 times higher REE concentrations than other plants [37,126,258,291]. [278] reported 40 µg/g La and 14 µg/g Ce in the leaf mesophyll tissue of *Asplenium ruprechtii*. *Dicranopteris pedata* is a perennial fern native to southern China and forms a mat-like layer in rare earth mine tailings. It enriches REE under non-contaminated soil conditions, preferably in the above-ground part, by forming complexes with carboxylates and histidine in cells and in the rhizosheaths and sequestration of REE in the chloroplast membrane and the thylakoid [243].

In Norway, high REE concentrations were observed in *Pteridium aquilinum* that contained similar La concentrations as the underlying soil [279]. In ferns, generative germination does not occur at the surface of the fern but at an intermediate and independent mobile pre-germ, which dies after fertilization, whereas the green leaves carry only spores. It is generally assumed that ferns protect their root systems rather than the leaves, and the accumulation of non-essential elements in leaves might not harm the plant individual as long as photosynthesis can proceed [292]. Thus, metal transport to leaves and stems minimizes metal stress without touching the generative proliferation because the leaves contain just spores, and fertilization takes place inside a pre-germ [292].

Compared to ferns, the literature on REE concentrations in lichen and mosses is very scarce. The available literature indicates that Bryophytes and lichen accumulate lower REE concentrations than ferns. Still, the concentrations reported are generally higher (Table 12) than in many vascular plants, possibly due to the utilization of atmospheric REE inputs [104,293,294]. The REE accumulation was investigated in *Hypogymnia physodes* (monk's hood lichen), Sphagnum mosses, and *Polytrichum commune* (great golden maidenhair. A moss) in two forest ecosystems situated in Germany and Russia [293]. The concentrations decreased in the order *Hypogymnia physode* > *Sphagnum spec.* > *Polytrichum commune*. In the forest biosphere reserve Kalinin, Sphagnum moss accumulated lanthanides 3-fold, and the lichen *Hypogymna physodes* up to 10-fold compared to other vascular plants. Moreover, plants collected from study sites in Germany with a higher atmospheric REE deposition exhibited higher REE concentrations than in Russia, which suggests the high impact of atmospheric deposition upon REE accumulation, especially lichen (Table 12) [293,294].

Table 12. REE ($\mu\text{g/kg dw}$) in selected mosses (*Hylocomium splendens*, *Polytrichum commune*, *Polytrichum formosum*, and *Sphagnum spec.*) and the lichen *Hypogymnium physodes*.

Species	Bryophytes					Lichen
	<i>H. splendens</i>	<i>P. commune</i>	<i>P. formosum</i>	<i>Sphagnum spec.</i>		<i>H. physodes</i>
Region	South Sweden ¹	Russia ²	Germany ²	Russia ²	Germany ²	Russia ²
Sc	n.a.	27.9	25	37.7	36	196
Y	120–134	91	250	230	590	580
La	248–285	240	260	265	720	910
Ce	466–519	260	510	440	1410	1870
Pr	53–59	29	58	61	100	180
Nd	373–431	95	220	20	600	580
Sm	35–37	18	39	40	110	110
Eu	93–105	9	8	10	13	30
Gd	36–039	20	54	50	130	120
Tb	4.7–5.2	3	11	9	26	22
Dy	23.5–25.3	17	41	42	99	100
Ho	4.5–4.9	3	11	8	25	20
Er	12.7–13.7	10	28	25	66	62
Tm	1.6–1.9	2	5	5	11	12
Yb	10.1–12.0	10	27	24	65	62
Lu	1.5–1.7	1	4	4	10	10

¹ [5] Tyler (2004); ² [293] Markert and Li (1991).

7.5. REE in Fungi

The accumulation of REE in fungi depends on the fungi species and increases with a higher REE mobility in the soil [295]. Some mushrooms hyper-accumulate trace elements, but it seems that REE concentrations in mushrooms are rather affected by the chemical composition of the ambient soil rather than physiological traits and may vary strongly depending on interactions with plant roots and temperature [50]. At the current time, no species with a specific REE accumulation has been identified so far, nor are there significant differences between boletus and lamellar-type mushrooms. Compared to most vascular plants, the level of REE accumulation in fungi is 1–2 orders of magnitude lower and typically does not exceed 10 $\mu\text{g/kg}$ (Table 13). However, wild mushrooms, both boletus and laminar types, collected in Poland contained up to 200 $\mu\text{g/kg}$ total REE (dry weight), possibly due to REE pollution from coal burning [50]. Generally, concentrations of most elements in mushrooms decrease from spore-forming parts of caps to the remaining parts of caps to stipes [296].

Table 13. REE concentrations found in fungi collected in a Swedish beech forest ($\mu\text{g}/\text{kg dw}$) [280] (from Tyler 2005).

	<i>Amanita citrina</i>	<i>Hydnum repandum</i>	<i>Lactarius biennius</i>	<i>Clitocybe odora</i>	<i>Collybia butyracea</i>	<i>Collybia peronata</i>
Y	1.6–4.7	1.3–1.6	2.2–2.5	2.8–5.6	1.7–2.1	4.8–7.6
La	2.1–3.2	1.6–2.2	2.6–3.2	2.8–4.0	1.9–2.6	6.7–10.8
Ce	4.1–5.2	2.8–3.6	5.0–6.2	4.5–6.7	3.6–4.9	12.7–20.0
Pr	0.5–0.7	0.4–0.5	0.6–0.8	0.7–0.9	0.4–0.6	1.5–2.4
Nd	3.7–4.3	2.3–3.5	4.2–5.5	5.0–6.3	3.5–5.0	10.9–18.5
Sm	0.3–0.6	0.2–0.3	0.5–0.6	0.5–0.8	0.3–0.5	1.0–1.8
Eu	0.1–0.2	<0.1	<0.1	<0.1	0.1–0.2	0.3–0.5
Gd	0.4–0.6	0.3	0.5–0.6	0.5–0.8	0.4–0.6	1.1–1.9
Tb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dy	0.3–0.7	0.2–0.3	0.4–0.5	0.4–0.8	0.3–0.4	0.9–1.4
Ho	0.1–0.2	<0.1	0.1	0.1–0.2	<0.1	0.2–0.3
Er	0.2–0.3	0.1–0.2	0.2	0.1–0.2	0.1–0.2	0.5–0.8
Tm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Yb	0.2–0.3	0.1–0.2	0.2	0.2–0.4	0.3	0.4–0.8
Lu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

In a Swedish beech forest (soil pH 3.2–3.6), six varieties of macro-fungi contained far lower REE concentrations and other trivalent or tetravalent elements compared to beech leaves. This either means their uptake from the mycelium is excluded or that REE are transported to the sporophores [280]. In a controlled greenhouse experiment, REE accumulation in winter oyster mushrooms (*Pleurotus ostreatus*) was not statistically significantly influenced by changes in substrate properties. In contrast, *Cyclobe cylindracea* showed significant positive correlations between substrate and tissue concentrations. In the case of *Cyclobe cylindracea*, the REE in the substrate correlated only with the productivity, but the REE in the substrates also influenced the incubation period, earlyness, antibiological efficiency in *Pleurotus ostreatus*. The reduction in hemicellulose, cellulose, and lignin in the substrate led to increased REE accumulation in *Pleurotus ostreatus*, whereas *Cyclobe cylindracea* responded to hemicellulose reduction only [295]. The fast-growing edible ectomycorrhizal basidiomycete *Suillus luteus* prefers sandy soils below pine trees. It is highly tolerant to Cd, Cu, and Zn. It accumulates up to 20 $\mu\text{g}/\text{kg}$ REE, especially in the cuticle, possibly as a consequence of siderophores release during nutrient acquisition [296], which promotes REE mobilization [73,244].

7.6. Aquatic Biota

Aquatic biota are adapted to living in environments where nutrients and REE are mainly dissolved in the water body, especially in cases of filter feeders, algae, or floating plants with roots floating on the water surface (e.g., duckweeds, =*Lemnoidae*). However, in aquatic macrophytes rooted in sediments, element pools in the substrate might be of similar relevance for element uptake as for terrestrial plants. It is not yet clear how much of the REE accumulated originate from the substrate or dissolved REE pools. REE accumulation was explored in seagrass meadows adjacent to mangroves, sandy beaches, and coral reefs in Brazil [140]. The authors found that *Halodule wrightii* accumulated higher REE contents in roots than in shoots. In contrast, *Cymodocea nodosa* exhibited higher shoot accumulation than in roots, suggesting preferential uptake of REE in *Cymodocea nodosa* from the water column. Similar to terrestrial plants, chemical speciation strongly impacted REE availability to aquatic organisms, given that the lowest REE accumulation in seagrass appeared near coral reefs characterized by the highest REE concentrations in the soil. Here, REE appeared almost entirely as carbonate complexes that are likely excluded during uptake, and the remaining REE^{3+} might compete with Ca^{2+} during uptake and translocation [140]. Free-floating macrophytes, such as species from the *Lemnoidae* (duckweeds), solely depend on dissolved elements in the growth environment, and may hyper-accumulate REE [51]. Duck-

weeds grown in different ambient waterbodies in Northern Germany and the Netherlands contained 0.276 to 5.74 mg/kg dw of REY (=REE + Y). All freshwater-grown duckweeds followed a REY-pattern similar to the water, but strong positive Gd-anomalies in 7 out of 10 water samples were not reflected in plant uptake. REY accumulation was about 1000-fold and showed a positive linear relationship to Mn (but not to Ca), presumably because of the same uptake mechanism by macrophage proteins or chelation with phosphatic polyanions [51].

Similarly, mussels filter large quantities of water and are known to accumulate REE from water and floating particles. 649 samples of *Mytilus galloprovincialis* mussels collected along the Portuguese Atlantic coast [297] contained the highest concentrations (2.67 mg/kg dw) downstream of Lisbon, which is most likely caused by erosion and leaching of REE from agricultural sites. Notably, the mussels showed strong positive Gd anomalies at all locations due to the widespread use of Gd-chelates in medical applications in Portugal [297].

8. Anthroposphere

8.1. Economics

China, as the dominant rare earth raw material supplier, accounted for more than 95% of global production between 2000 and 2010 and 60–70% between 2010 and 2020 [243,298]. Here, REE mining has resulted in 302 abandoned mines till 2010 ([243]. Globally, the resources of REE are estimated at 43% in China, 17% in Russia, and 12% in the USA, and further in Australia, India, Brazil, and Greenland. Monazite is also found in Africa, particularly in Namibia. The most prominent rare earth mining sites are Bayan Obo in China (>83% of China's total REE reserves), Mount Weld in Australia, and Mountain Pass in the US [299–301]. Compared to LREE and HREE, for scandium, no mines exist, but Sc enrichments have been found in New Caledonia, together with >0.5% Co and >2% Ni [302]. Secondary sources of rare earth ores are electronics and industrial waste residues, pyrometallurgical process slags, red mud, phosphoric acid by-products, coal by-products, mine tailings, and acid mine drainage. From an economic point of view, an outlook coefficient has been defined, which equals the sum of critical (and more valuable) REE (sum of Nd, Eu, Tb, Dy, Er, Y) over the sum of excessive REE [303]. REE are critical for photovoltaic modules, optoelectronics, computers, screen displays, lasers, ceramics, and medical X-ray and magnetic resonance image scanning systems [26]. In 2020, about 23% of the global rare earths production was used for Nd-Fe-B permanent magnets, which contain about 30% of rare earths, mainly Nd with up 1/3 Pr beneath some Dy and Tb. In 2019, the volume of waste from electrical and electronic equipment reached 53.3 million tons, with an increasing tendency to contain large amounts of Cu and REE [304]. Consequently, REE play an increasingly vital role in industry, especially in green high-technology applications, such as wind turbines, hybrid cars, electric cars, and batteries [286]. Compounds of Nd, Sm, Pr, and Ce are used for permanent magnets, La, Ce, Nd, and Pr for rechargeable batteries, and the preparation of high-temperature superconductors [305]. Some REE are used as catalysts for chemical reactions, especially the cracking of crude petroleum and Gd and Dy for medical applications [231,293]. In addition, La is used in glass production to change color, refractive index, and UV absorption [306]. From an economic view, based on current demand, REE are classified as critical (Nd, Eu, Tb, Dy, Er, Y), uncritical (La, Pr, Sm, Gd), and excessive (Ce, Ho, Tm, Yb, Lu) [93]. China was the first country in the world to use commercial rare earth-enriched fertilizers applied to crops in various forms. The release of REE-enriched fertilizers into cultivated soil in China 2002 had already amounted to 5200 tons [2]. Since the beginning of the millennium, about 43–85 million tons of REE have been spread as REE-based fertilizers across 4 million hectares [18].

8.2. Ore Formation, Technical Enrichment Methods, and Recovery of REE

On a global scale, REE-phosphate deposits of bastnaesite, monazite, and xenotime, and ion-adsorption REE deposits are considered most viable for REE-extraction with conventional mining techniques [90,298]. In addition, industrial and municipal wastewater,

ashes, sludges, and tailings may contain high amounts of rare earths representing significant secondary REE resources and material for REE recycling, which is vital for improvement of a circular economy [123,304,307].

The Bayan Obo deposit (China) contains bastnaesite and monazite, with magnetite and hematite as the dominant iron minerals. REE recovery can be achieved by leaching with H_2SO_4 and subsequent solvent extraction with procedures adjusted depending on the concentrations of other accompanying elements, such as Ca, Fe, and Cu. At Mount Weld (Australia), REE contents reach 15.4%, mainly as phosphate minerals encapsulated in iron minerals. Also, the rare REE-bearing ores from the Southern African region contain REE in an iron mineral matrix, appearing as coatings on hematite/goethite or in the form of small, disseminated particles [299]. In a laboratory trial, an African ore with high portions of FeOOH and MnO was reduced with stoichiometric amounts of anthracite in an Ar atmosphere to obtain metallic iron. In contrast, the REE, together with Th and U, moved to an oxidic slag. CaO was used as a fluxing agent to decrease the slag liquidus temperature and viscosity. The procedure was optimized for 30 min heating at 1700°C and 0.5% lime addition to enrich the rare earth oxides to 13.8%. In the slag, REE were mainly bound to a Ca-silicate phase that was leachable with HCl , resulting in 94% recovery [299].

REE in apatites are mainly recovered during phosphoric acid and superphosphate fertilizer production. Here, phosphogypsum remains yield a residue containing silica, Al-sulfate, Fe-sulfate, and gypsum and about 4 kg of REE per ton. REE recovery from phosphogypsum involves leaching with dilute H_2SO_4 , HCl , or HNO_3 after mechanical activation by grinding and/or ultrasonic treatment [308,309]. Co-precipitation with CaSO_4 is prevented by adding a cation exchange resin to the suspension, which favors desorption and dissolution and can be easily separated from the suspension of the finely ground phosphogypsum by sieving at 0.5 mm. The stripping of the cation exchange resin is achieved by ammonium nitrate, which is finally recovered by precipitation of the REE with ammonium carbonate. The remaining gypsum can be calcined to produce various types of cement [310]. On the other hand, phosphate sorption from brewery waste has been achieved by CeCl_3 co-precipitation [311].

Ion adsorption rare-earth ores are formed through the weathering of original rocks and subsequent migration of REE along with rainwater and groundwater until they are adsorbed onto clay surfaces (halloysite > illite > kaolinite > montmorillonite) and particulate organic matter [140,312,313], thus forming ion-adsorption rare-earth ores that are the primary sources of REE, particularly in southeast Asia [152,313]. In Brazil, at the Serra Verde adsorption deposit, weathering of a primary granite by F-CO_2 -alkali-rich hydrothermal fluids led to strong enrichment in the kaolinized part of the profile with REE absorbed to clay minerals [300]. From these clays, REE can be desorbed with salt solutions at low pH.

Batch adsorption/desorption experiments from halloysite, illite, kaolinite, and montmorillonite clays demonstrated increasing REE recovery with decreasing pH and complete recovery from kaolinite and montmorillonite with 0.11 mmol/L ammonium sulfate at pH 2.5 and 92% of final release of REE from halloysite and illite at pH 3–4 [312].

The tailings at New Kankberg, Sweden, contain phosphates like monazite, apatite, xenotime, and berlinite that predominantly contain LREE. Here, the enrichment and recovery of REE are achieved by using phosphate flotation and magnetic separation of the paramagnetic monazite from the non-magnetic apatite. In the Covas tailings in Portugal that originate from scheelite and wolframite mining of tungsten and contain 14% calcite, flotation was not efficient, and REE were successfully recovered by gravimetric techniques and subsequent magnetic separation. Finally, the REE were leached with acid and separated by solvent extraction. From dilute nitric acid, REE are extracted with Cyanex923, a commercially available mixture of 4 trialkylphosphinoxides, and tetraoctyl-diglycol-amide (TODGA) in kerosene. In contrast, REE extraction from dilute sulfuric acid is achieved with bis-2-ethylhexylphosphoric acid (DEHPA) and Cyanex572. Finally, tripping from the organic phases is achieved with HCl [314], from where the REE can be precipitated as oxalates and converted to oxides by thermal treatment [314].

Acid mine drainage can be highly mineralized with REE when strongly acidic water from sulfide oxidation attacks adjacent REE-containing rocks, which can yield another valuable secondary source of REE. At the Tharsis mining district in southwest Spain, acid mine drainage contained up to 8.8 mg/L REE (median 1.7 mg/L) [315]. More than 0.5 mg/L of total REE were reported in mine discharge from the Lower Kittanning coal seam, Pennsylvania [303]. A two-step enrichment procedure was proposed to scavenge REE from acid mine drainage, in which Al and Fe are removed as carbonates at pH 5, then the REE as carbonates at pH 7, whereas Ca and Mg will remain in solution [303]. From purely inorganic solutions, REE could be recovered by absorption on zeolite and desorption with dilute acids as results with ^{153}Gd radioactive tracers suggest [316]. This could be particularly interesting for the REE recovery from process waters with low concentrations of other metal ions [316], but has probably low relevance for REE recovery from complex solutions.

8.3. Environmental Pollution with REE

Environmental risks related to REE pollution predominantly arise from the increasing use of REE in end-of-life consumer products such as cars, electronics, and the resulting waste streams. In addition, the excessive use of REE chelates in medical treatments, REE in feed additives, and the impurities of phosphate fertilizers and their use as catalysts in oil refining are significant anthropogenic input sources that increase REE levels in soils and stream waters [210]. Gd-DTPA (-diethylenetriamine-pentaacetate) or Gd-DTPA-bismethylamide are used in medicine as a contrast medium for magnetic resonance imaging. The original complexes leave the human body unchanged via urine and also pass through biological wastewater treatment plants [63]. When the REE removal efficiency of six treatment plants across Canada were investigated [210], the findings revealed that, despite high removal rates for ionic forms, 0.16–0.33 $\mu\text{g/L}$ of REEs from urban wastewater (initially ranging between 0.9 and 7.0 $\mu\text{g/L}$) persisted in the effluents. Notably, only 50% of chelated Gd was removed. In the USA, 60–80 tons of REE are currently emitted into the atmosphere by oil refining every day [261]. Monitoring of REE-containing particle emissions in five Spanish towns [248] found higher REE concentrations in the coarse (PM₁₀) fraction than in PM₅, often related to industry [248]. CeO₂-nanoparticles, as a catalytic additive in diesel fuel, result in a component of diesel exhaust particulate matter, leading to the emission of CeO₂ nanoparticles in the exhaust [26,305]. However, aerosol REE emissions from tobacco measured indoors [317] not only exceeded the average outdoor levels of La and Ce, but also REE emissions measured near industry or heavy traffic areas (Table 14).

The increasing demand for REE in industry results in the expansion of mining sites and activities related to refining, transportation, processing, and waste disposal [243]. In China, REE mining has resulted in 302 abandoned mines till 2010. In addition to elevated REE concentrations in soils, groundwater, and stream water, in operating mining areas, chemicals used in the refining process of REE ores are often involved in diseases and occupational poisoning of local residents by water pollution and farmland destruction [243,318]. In addition, wind-propelled dust diffusion is an important form of pollution in mining areas, especially near open pits [319]. In the Bayan Obo REE deposit, located in Inner Mongolia in China, the migration of REE-containing mineral dust contributes to road dust and atmospheric particulates touch the entire region [319]. Notably, REE from anthropogenic sources are of particular environmental concern because they are emitted in ionic forms [168], accumulate in soils and water bodies, and have high mobility and availability to organisms, including intake by humans [26,243,298]. The REE contents were compared in 301 vegetable samples collected from a mining area in Shandong and a control area 70 km apart [320]. The average content of the sum of REE from vegetables in the mining area was significantly higher (0.094 mg/kg fw) than in the control area (0.039 mg/kg fw). Vegetables produced in Fujian and the Jiangxi mining district reached up to 3.58 mg/kg and 6.37 mg/kg, which is one order of magnitude higher than the national standard for China (0.7 mg/kg fresh weight) [320]. Thus, in the mining-affected region, the estimated daily intake of REE from vegetables was estimated to be 2.4-fold higher (0.65–0.76 $\mu\text{g/kg}$ per

day) than in the control area (0.27–0.31 µg/kg per day) [320]. In addition to REE pollution which is directly related to activities in REE mining and ore processing, REE pollution is frequently reported in areas where polymetallic sulfide ores are mined due to sulfide oxidation, soil and water acidification, and consequently, leaching of REE together with other trace metals from solid mineral phases. In the southwest of the Iberian Peninsula (Spain) and at the “metalliferous hills” close to Massa maritima (Tuscany, Italy), mining of sulfide ores caused excessive acidification of soil and stream waters and mobilization of REE, so that the REE concentrations in water samples downstream are orders of magnitude higher than the ambient levels [101,318,321].

Table 14. Effect of tobacco smoke on indoor aerosols (median and range, ng/m³) [317].

Element	Homes of Non-Smokers	Homes of Smokers	Restaurants	Bars	Discotheques	Outdoor
Cd	0.1 (0.01–1.3)	0.8 (0.1–3.0)	2.6 (1.2–7.7)	3.7 (1.7–27)	9.7 (5.3–16)	n.a.
Ce	0.4 (0.1–36)	9.6 (0.2–71)	18.5 (5.5–48)	24 (17–290)	50 (28–130)	(0.1–0.6)
La	0.2 (0.01–14.4)	5.9 (0.2–39)	10.6 (2.3–23)	15 (8–170)	23 (13–60)	(<0.1–0.3)

n.a. = data not available.

In addition to REE inputs from industry and mining, REE patterns in agricultural soils are strongly impacted by fertilization practices, primarily through the application of phosphate fertilizers. In mineral N- and K- and Mg fertilizers, REE concentrations are typically orders of magnitude lower than in the soil and appear only occasionally detectable with concentrations below 1 mg/kg [322]. However, fertilizers produced from carbonates and phosphorites may contain significant amounts of REE (Table 15). Here, the REE concentrations are widely fluctuating, both due to different elemental compositions of the mine and rock processing and can range from below detection limit up to higher than found in the soils [62,323–325]. Otero et al. analyzed 7 N fertilizers and 14 NPK fertilizers available in Spain. Fertilizers with phosphate from phosphorites showed a positive correlation between P contents and the sum of REE [322]. Contrary to the phosphate component, Abdel Haleem et al. [45] found the primary source of REE in limestone. In di-ammonium phosphate produced from phosphorites from Jordan, Al Hwaiti et al. [325] found 11–18 mg/kg Y, and Tyler [5] found 0.26% total REE in super phosphate produced at the Kola peninsula. In addition to unwanted REE inputs, in China, REE-enriched fertilizers have been extensively applied to increase crop production [268,324], which substantially increased the REE contents of soils [305] with not yet foreseeable effects on public health.

Table 15. REE in fertilizers and fertilizer components (mg/kg), according to Raven and Loeppert [323] (1997), Abdel Haleem et al. [45] (2001), Otero et al. [322] (2005), and Turra et al. [38] (2019).

Fertilizer	La	Ce	Sm	Eu	Yb
N-only	<0.5–1.2	<3	<0.1	<0.2	<0.2
K-only	<0.5	<3	<0.1	<0.2	<0.2
Mg-only	<0.5–0.8	<3	<0.1	<0.2	<0.2
Ca-carbonates	6.1–19.5	10.4–16.9	1.3–1.7	0.2–0.4	0.1–7.6
Mg-carbonates	3.0–7.6	5–21.8	0.5–1.7	0.1–0.3	0.1–1.3
Fe-carbonatite	27	51	1.3	0.3	0.2
Phosphorite	74–147	104–142	20–63	3.2–65	0.1–34
Superphosphate	18–1011	9–2240	145	0.3–30.3	–
P-fertilizers	29–149	61–408	17–34	0.7–10.5	6.7–8.7

8.4. REE in Food Production and Products of Animal Origin

REE have been rarely determined in tissues and products of animal origin because their contents are mainly at or below the detection limit of direct ICP-MS aspiration. Given that REE concentrations in biota decrease as the trophic level increases [326], REE concentrations in food plants are typically higher than in meat [295] or other products of animal origin

and are lower in fish species than in phytoplankton, zooplankton, and algae [326]. Thus, for human nutrition, cereals and vegetables contribute the strongest to the average daily intake of REE. Rice (*Oryza sativa*) is the most important staple food in southeast Asia. When 64 rice samples with regard to the REE concentrations were characterized [324], the highest concentrations (350 µg/kg) were found in rice from Pakistan and the sum of REE concentrations decreased in the order Pakistan > Sri Lanka (75 µg/kg) > India (30 µg/kg) > Australia and Thailand (11 µg/kg) > US (6 µg/kg) > Italy and China (<2 µg/kg). The reason for the significant differences observed is hardly resolvable and might be due to different REE contents in fertilizer, soil properties, rice cultivars, or other agricultural practices [324].

In China, the calculated average daily intake was calculated as 0.32–0.90 µg/kg per day, which is orders of magnitude below the critical value of 70 µg/kg per day [298]. Dai et al. [298] compared REE concentrations in 346 foods of plant origin and 349 foods of animal origin that were sampled all over China. Among samples of animal origin, foods of aquatic origin had on average 6.35 times higher REE concentrations, especially LREE, than from terrestrial origin, with the highest REE concentrations in shellfish food (605 µg/kg wet weight) and lowest REE levels in milk (18.4 µg/kg) and meat (22.8 µg/kg). Oysters and mussels collected along the entire coast of China contained 0.62–4.96 mg/kg (dw). They largely reflected the concentrations in the habitat that were partly influenced by human activity [301]. Compared to oysters and mussels, REE in crustaceans were significantly lower (0.10–1.95 mg/kg) and did not exceed 0.05 mg/kg in fish [301]. There is evidence that REE as artificial feed additives may slightly positively affect weight gain in pig farms [327]. However, the increased intake has adverse effects on product quality, given that the additives increase the REE concentrations in meat and eggs [52,328].

In the case of milk and dairy products [329,330], feeds and potable water for dairy cows indeed derive from local sources, and differences in geology might also lead to local differences in REE contents and signatures. Sager and Hobegger [331] investigated the effects of individual feeds (hay and silage from different regions) on REE concentrations in milk of cattle farms in Austria. The hay samples were collected across the Bohemian Massif (igneous rocks). The Danube Lowlands (Quaternary and Tertiary clays) and the limestone Alps (Table 10) showed no significant differences in plant REE concentrations among the study sites. However, in the silage, REE concentrations were 10-fold higher than in the initial hay, indicating REE enrichment during fermentation [331]. Thus, the use of hay could be especially problematic in the nutrition of animals when plant material from REE-polluted areas is used. In contrast, REE concentrations in maize silage were substantially lower [331]. Possibly, the hay contained a large portion of herbaceous dicots that typically show higher REE concentrations than grasses (Table 10). The REE concentrations in the milk did not reflect the differences in REE concentrations of the feed, suggesting that REE concentrations in milk are influenced by lactation period rather than individual feeding, differences in geology or type of milk [331].

Because Africa is short of milk, infant formulas are imported and diluted with local water to feed babies. Milk and formulas, even sold in open pits at the market, are clean with respect to REE (Table 16). Due to the plant-based origin, the elemental pattern of soy drinks as substitutes for milk is close to green plants and differs from milk in many ways, but milk from different domestic animals exhibited no significant differences in REE concentrations and pattern within the obtainable precision (Table 17) [332–334]. In spite of limitations of achievable detection limits (from instrument and blanks), the soy drink composition is closer to the apples, and tomatoes closer to milk, with respect to REE contents (Table 17). In cheese, only Y, La, and Ce were present at concentration levels above the detection limit (Table 16). Processed cheese may contain higher concentrations than raw cheese (Table 16). Higher levels in processed cheese are due to the addition of phosphates as fluxing agents [330]. REE contained in chocolate can be expected at higher level than in cheese, but lower than in green plants [335].

Table 16. Median and range of REE concentrations ($\mu\text{g}/\text{kg}$) in milk powder and infant formulas sampled in Tanzania [329] and cheese from [330].

Product	Type	Unit	Y	La	Ce	Nd
Milk powder (Infant)	Informal market	$\mu\text{g}/\text{kg dw}$	<1	<2	2 (<3–6)	<1
	Formal market		4 (<1–14)	5 (<2–14)	4 (<2–10)	1.2 (<1–5)
Milk powder (skimmed)			2 (1–2)	3 (3–6)	9 (7–11)	2 (1–2)
Milk powder (full cream)			2 (1–2)	2 (<2–10)	<2	1.2 (<1–4)
Cheese	Hard cheese	$\mu\text{g}/\text{kg fw}$	0.3 (0.1–1.2)	3.8 (0.8–60)	0.5 (0.4–1.0)	n.a.
	Semi-hard cheese		0.2 (0.1–1.3)	2 (0.2–16)	0.4 (0.4–0.8)	n.a.
	Soft cheese		<0.1	1.3 (0.2–17)	<0.4	n.a.
	Curdled milk Cheese		0.5 (0.1–5.6)	2.6 (1.6–40)	1.1 (0.5–2.5)	n.a.
	Processed cheese		3.2 (0.6–7.1)	7.7 (0.2–24)	1.2 (0.4–4.1)	n.a.
	Cream cheese (cows)		0.1 (0.1–1.3)	2.4 (0.8–62)	<0.4	n.a.
	Sheep + goat cheese		0.1 (0.1–0.9)	4.8 (0.5–29)	<0.4	n.a.

Table 17. Rare earth concentrations in human nutrition, given in $\mu\text{g}/\text{kg}$ in dry mass.

	Infant Formulas ¹	Cow Milk ²	Goat Milk ²	Sheep Milk ²	Soy Drink ²	Apples ³	Tomatoes ⁴
H ₂ O (%)		85.6 $\pm$ 2.2	86.7 $\pm$ 2.2	80.8 $\pm$ 2.9	88.5 $\pm$ 3.9	83.3 $\pm$ 2.4	93.3 $\pm$ 1.1
Y	5 (<1–14)	<1 (1–4)	n.a.	n.a.	n.a.	3.4 (1.3–14)	<1
La	4 (<2–9)	2 (<2–19)	<2 (<2–23)	<2	9 (2–30)	8.4 (1.2–58)	<4
Ce	5 (<2–10)	3 (<2–10)	<2 (<2–46)	<2 (<2–69)	11 (5–59)	9.1 (2–218)	<8
Pr	<1 (<1–1)	<1 (<1–8)	<1 (<1–5)	<1 (<1–7)	2 (1–8)	1.2 (0.2–25)	<1
Nd	2 (<1–5)	<1 (<1–23)	<2 (<2–20)	<2	8 (2–30)	4.9 (<1–88)	<5
Sm	<1	1 (<1–6)	1 (<1–4)	<1 (<1–5)	2 (1–6)	<2 (<2–5)	<2
Eu	0.1 (0.1–0.2)	0.1 (0.1–1.2)	<0.1 (<0.1–0.4)	<0.1 (<0.1–0.7)	1.3 (0.3–1.8)	0.5 (0.1–3.2)	<0.2
Gd	<1 (<1–1)	<1	<1 (<1–1.5)	<1 (<1–2.9)	4 (1.7–7.8)	0.8 (0.2–12)	<1
Tb	<0.1 (<0.1–1)	<0.1 (<0.1–0.6)	<0.1	<0.1	0.6 (0.2–1.0)	<0.1 (0.1–2.4)	<0.2
Dy	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ho	0.1 (<0.1–0.3)	<0.1 (0.1–0.4)	<0.1	<0.1	0.3 (<0.1–0.5)	0.1 (<0.1–1.1)	<0.1
Er	<0.3	<0.3	<0.3	<0.3 (<0.3–0.7)	2.1 (0.7–4.4)	0.3 (<0.3–3.4)	<0.3
Tm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Yb	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Lu	<0.3	<0.1	<0.1	<0.1	0.7 (<0.1–1.4)	<0.1 (<0.1–0.5)	<0.2

¹ [329] Sager et al. 2018, ² [332] Sager 2016, ³ [146] Sager 2020, ⁴ [228] Sager 2017. n.a. = data not available.

8.5. Essentiality and Toxicity of REE

Compared to other elements from the transition metals, REE are neither strongly toxic nor essential for most biota [5]. As an exception, however, in the highly acidophilic, autotrophic bacteria *Methylophilium fumariolicum* SolV La, Ce, Pr, and Nd are used as a co-factor instead of Ca to provide catalytic properties to a pyrroloquinoline-dependent methanol dehydrogenase, a key enzyme for both methylotrophs and methanotrophs [336], whereas salts of REE with higher atomic numbers than Nd are less supportive of growth. Thus, it is reasonable that the number of REE-dependent species will increase in the near future. Over the last decades, REE have been most profoundly studied with regard to their toxic effects at high concentrations. There is increasing evidence that at low exposure levels, REE promote growth and have protective effects. These hormetic effects were not only demonstrated in plants, but there is increasing evidence in other taxa, such as mammals [26,305].

It is generally assumed that oxidative stress may underlie the toxicities of all REE. Although REE occur only in the trivalent state (except Ce and Eu), they act on redox mechanisms like reactive oxygen species formation and lipid peroxidation, indicated by increased superoxide dismutase, catalase, glutathione peroxidase, glutathione transferase, and lipid peroxidase activity in the presence of REE [337]. In addition, exposure to high REE doses may have neurotoxic effects, indicated by decreased activity of acetylcholinesterase and

blocking of K-type Ca^{2+} channels, at least in different taxa of invertebrates and mammals [306,337]. Due to the large number of individual elements in this group that typically appear together in environmental compartments, the elucidation of processes is particularly challenging. It is not yet clear if the effects observed are triggered by a specific element only or result from interaction effects. Recent studies in environmental research tend to report the sum of REE or at least the sums of LREE and HREE, whereas the toxicological database about REE in plants, animals, and human tissues reviewed by [305,338] is mainly confined to Ce and La and with less information on Gd and Nd and no information on other representatives from this group. Given that single representatives share very similar chemical properties but have slight differences in charge density, it is reasonable that the differences in toxicity of individual REE do not only depend on different paramagnetic properties influencing physiological processes [305,338], but also on slight differences in bioavailability based on different mobility and transport properties internal of the organism (Sections 7.1 and 7.2). When the toxicity of Nd, Gd, and Yb in a *Daphnia magna* mobility test was compared [339], apparent differences in REE bioavailability were found, but the toxicity of the mixture of REE was similar to the individual REE, indicating no interaction effect. For La, the LD50 in *Daphnia magna* was 552 $\mu\text{g/L}$ for 14 days. However, there are significant differences in the response of organisms to REE, as was demonstrated [337] in a study showing how crustaceans are less sensitive to GdCl_3 than rotifers and cnidarians. Cao et al. [168] found that the sensitivity of soil microbes to La decreased in the order actinomyces > bacteria > fungi, which could be attributed to the release of metal-chelating siderophore produced by species from the actinomyces that are typically involved in extracellular detoxification [244]. Li et al. [340] explored differences in La toxicities between selected soil invertebrates in an artificially REE spiked soil and reported LC50 (4 weeks) that decreased from *Eisenia andrei* (Lumbricidae) 1850 mg/kg > *Enchytraeus crypticus* (1650 mg/kg), *Folsomia candida* (1690 mg/kg) > *Porcelio scaber* (960 mg/kg), indicating a higher REE tolerance in lumbricidae than isopodids. The REE concentrations in the invertebrates increased linearly with increasing concentration in the soil. Still, the survival of the mites *Oppia nitens* was not affected up to 5820 mg/kg, suggesting an extraordinarily high REE tolerance in this soil microarthropod. Lethal concentrations of more than 1000 mg/kg may only appear in areas of severe REE pollution; however, it was also demonstrated [340] that lower REE contents may already negatively affect reproduction rates with comparable low EC50 in *Eisenia andrei* and *Porcelio scaber* (529 mg/kg and 312 mg/kg, respectively) and higher EC50 in *Enchytraeus crypticus* and *Folsomia candida* (1010 mg/kg and 1220 mg/kg REE, respectively). In *Mytilus galloprovincialis* mussels treated with La and Gd as LaCl_3 or GdCl_3 , REE in mussel tissue increased linearly with increasing exposure concentrations, gills, and digestive tubules developed histopathological injuries, and the tested individuals showed a lower metabolic activity, inhibition of acetylcholinesterase and increased antioxidant enzymes like glutathione peroxidase, glutathione-S transferase, and superoxide dismutase. Notably, when exposed to intermediate REE concentrations (60 $\mu\text{g/L}$), a further increase in REE concentrations reduced the activity of antioxidative enzymes, which could be a consequence of enzyme inhibition [306].

Compared to invertebrates, animal studies often lack significance due to a short observation time (1–2 months) and a lack of information on long-term effects. In mammals, organ pathologies, cytogenic and embryologic damages, and growth inhibition caused by rare-earth exposures have been recognized at high exposure concentrations [338], as well as hormetic effects at low concentration levels [26] (Rim 2016).

In humans, advanced REE exposure is especially critical for workers and residents in mining districts as well as workers in the field of ore refining and e-waste processing. In addition, CeO_2 nano-particles from diesel engine exhausts and tobacco smoke represent significant REE sources. Increased REE levels in hair seem to be related to increased REE intake and could be used as an indicator of exposure [338]. In the respiratory tract, Ce, La, and Nd have been found to be cytotoxic to pulmonary alveolar macrophages, leading to pneumoconiosis and interstitial lung disease [338]. Occupational exposures to

rare earth oxide dust have already been associated with pneumoconiosis since 1982 [320]. Thus, the EPA derived an inhalation reference concentration of 900 ng/m³ for CeO₂ with increased incidence of alveolar epithelial hyperplasia in rats [317]. Long-term exposure to REE may cause liver function decline and hypertension. Cytogenic REE toxicity effects, which arise from the inhibition of mitotic activity, mitotic aberration, and induction of micronuclei, have been described [26,338]. The use of Gd as a contrast agent in magnetic resonance imaging promoted nephrogenic systemic fibrosis, and there is evidence that Gd is enriched in femoral bones and the brain [26]. In China, the use of REE micro fertilizer gave rise to concerns about the relationships between increased REE levels in soil and the intelligence of children [242]. Thus, a daily allowable intake of 4.2 mg for rare earth oxides (=3.6 mg as elements) has been proposed [301]. Concomitantly, diseases associated with oxidative stress from REE have led to investigations about the use of CeO₂ nanoparticles as anti-cancer therapeutics. Given that brain tumor tissues often exhibit excess levels of La, Ce, Gd, and Lu [305], and cancer cells have a high intrinsic load of mutation and chromosomal abnormality, they are more sensitive to DNA damage, the accumulation of Ce could lead to apoptosis [26]. Thus, the hormetic effects of REE represent a significant field for further research, coupled with a reduction in REE emissions and remediation of polluted environmental compartments.

9. Conclusions

Until recent, data on REE occurrence and speciation have not been regarded as relevant for environmental concerns. But in view of increasing utilization of REE in magnets, semiconductors, catalysts and others, contaminations, pollution, and dissipation into the environment will increase. Utilization of Gd-DTPA in medicine or REE-containing fertilizers in Chinese agriculture lead to remarkably higher concentrations. More toxicity studies will emerge. This review should give a background about occurrence and mobility in environmental items, as well as about possible sources. In future works, the environmental impacts of REE should be increasingly looked at to reveal interactions with Fe, Al, alkaline earths, and in particular with fluoride. The latter yields both complexes and precipitates and is itself bio-active.

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