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Lanthanides

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LANTHANIDES

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and **Ahmed T. Mubarak**

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Meet the editors

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Ahmed T. Mubarak is currently a Professor of Inorganic Chemistry and leader of the Catalysis Research Group at the Chemistry Department, Faculty of Science, King Khalid University, Saudi Arabia. He is a member of the Saudi Chemical Society, Head of the Chemistry Department 2004–2008, Vice Dean of the Science Faculty 2008–2010, Dean of Research at King Khalid University 2011, and Vice President of King Khalid University for Research and Graduate Studies 2011–2015. He obtained his PhD in Chemistry in 1999 from Nottingham University, UK. He has authored and coauthored more than 50 articles in peer-reviewed and highly reputed ISI journals. He has also edited a few books and supervised and reviewed graduate students in both MSc and PhD degrees. He has participated in international and local conferences in the UK, USA, KSA, France and other countries. He is the main researcher in three big projects with King Abdulaziz City for Science and Technology, KSA, and one project with SABIC, KSA, on metallocene catalysis used for polyethylene production. He works with collaborators/researchers with mutual interests from many institutes and universities. His research interests are primarily in the areas of catalysts and using different techniques related to environments and petrochemical treatment using catalysis at the nanoscale, the growth of varying forms of nanostructured materials and their basic characterization by XRD, SEM, TEM, spectrophotometric techniques towards the correlation nature of heterogenous catalysis and nanocatalysis, their properties, and applications.

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Preface

This book deals with the topic of lanthanides through six chapters. The first chapter is a short introduction that explains the nature and purpose of the book and the logic and significance of its contents. The second chapter by Katarzyna Kiegiel et al. introduces novel apparatus solutions, for example membrane contactors in the extraction stage and different types of matrices (uranium ore, phosphorites, etc.). The chapter focuses on the fundamental actions aimed at ensuring continuity of rare earth element (REE) supply, i.e. exploration and exploitation of new deposits, reduction of consumption of these precious metals in technological processes, and their recovery from waste, which are very important from an economic point of view. The third chapter by Dariusz Sala and Bogusław Bieda from AGH University of Science and Technology, Management Department, Poland, describes the development of life cycle inventory (LCI) to REEs based on secondary sources, conducted according to ISO 14040 (2006) guidelines. This chapter comes with many figures and charts that indicate many aspects referring to uncertainty in the input parameters used to create the LCI of REE recovery processes from secondary sources. The focus of this study is defined in its goal and scope, and was developed using primary and secondary data. Chapter 4 concentrates on lanthanide soil chemistry and shows how the soil chemistry of REEs may support soil science investigations. In this chapter, the author tackles another important field of lanthanide science that addresses lanthanide elements or REEs as an active soil science research area, given their usage as microfertilizers, documented cases of environmental impact attributed to industry/mining, and their ability to identify lithological discontinuities and reveal active soil processes. Dmitry V. Ladonin in Chapter 5 studies the content of forms of lanthanides in soddy-calcareous soils at different distances from the Cherepovets steel mill (Vologda region, Russia). The author concludes that the individual properties of lanthanides are clearly manifested in their interaction with the soil components. The largest part of the fraction, bound to organic matter, contains medium lanthanides, while the heavy lanthanides are bound to Fe and Mn (hydr)oxides. The last chapter discusses ecological and physiological impacts of lanthanides on algae as primary producers in aquatic environments. This study summarizes knowledge of positive and toxic effects of lanthanides on algae to better elucidate their biological roles. Various applications and methods of use, including the possibility of remediation and lanthanide recycling, are also suggested.

This book will definitely encourage readers, researchers, and scientists to look further into the frontier topics of lanthanides and opens new possible research paths for further novel development. Finally, the book’s editors would like to express their appreciation to the contributors and the IntechOpen Author Service Manager. We hope this book will contribute much knowledge to lanthanides and their applications in our lives.

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Section 1

Lanthanides and Environment

Introductory Chapter: Lanthanides - A Quest for Solutions

Ahmed T. Mubarak and Nasser S. Awwad

Additional information is available at the end of the chapter

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1. Introduction

Lanthanides are a family of high electropositive metals that intervene between the *s* and *b* blocks. They are sometimes known as the rare earth metals, where rarity reflects the difficulty in obtaining an element in its pure form, which has been a challenging task to achieve due to similarity in their properties, the original isolation, and identification of the lanthanides. The cheap prices encourage scientists to use lanthanides in various applications. The coordination chemistry of lanthanides has shown promising opportunities to use lanthanide-based reagents or catalysts in the preparation and study of broad spectrum of applications to new materials in various fields [1].

Lanthanides have been the subject of many applications, such as, misch metals (alloy), removal of the impurities of sulfur and oxygen from different industrial applications, and as catalysts in the conversion of crude oil into a lot of products. Furthermore, the industry of ceramics uses oxides of lanthanide to color glasses and ceramics as well as optical lenses that used lanthanum oxide in binoculars and cameras. The most important application of lanthanides related to the nuclear applications is that they are used as control rods *via* absorption of neutrons to shut down the nuclear reactors. Lanthanides are considered promising materials as shielding for γ- and X-rays produced from the fission product in reactors.

Many researchers and scientists have come with conclusions that more efforts are needed to expand their quest toward the multidisciplinary character of the lanthanide research. Therefore, it is expected that these efforts will stimulate researchers to explore many more exciting discoveries in a variety of fronts to expand the body of knowledge available on lanthanide materials and explore new ways for their utilization in modern and futuristic applications. Hence, this book is going to give an insight into some of the applications taking place within the lanthanide research in recent times. It is a small effort to show interesting results of some valuable studies carried out by bright scientists and researchers in different parts of the world. We thank the authors for having agreed to participate in this book with their excellent contributions.

2. Summary of the book

The book is going to be divided into six chapters. The first one is going to be a short introduction to explain the nature and purpose of the book and the logic and significance of its contents. The second one is going to discuss the recovering and recycling of the rare earth elements (REE) and the economical importance for Poland, in particular, and the EU economy [2]. The chapter is going to focus on the fundamental actions aimed at ensuring continuity of REE supply, that is, exploration and exploitation of new deposits, reduction of the consumption of these precious metals in technological processes, and their recovery from waste, which are very important from an economic point of view. In addition, the chapter shows different methods and processes of separating and obtaining the rear earth elements from raw materials such as REEs ores, waste electronic equipment (WEEE), coal fly ash (CFA), and other resources. Some of these recovery techniques have shown a promising high purity extraction.

The third chapter describes the development of life cycle inventory (LCI) to rare earth elements (REEs) based on the secondary sources, conducted according to ISO 14040 (2006) guidelines. Monte Carlo (MC) simulation with the Crystal Ball (CB) spreadsheet-based software was employed to stochastic modeling of life cycle inventory. This chapter comes with many figures and charts to point out many aspects referring to uncertainty in the input parameters used to create LCI of REEs recovery processes from secondary sources performed. The focus of this study is defined in the goal and scope and developed using the primary and secondary data, and with uncertainty analysis, a final result is obtained in the form of value range. The results from this study suggest that MC simulation is an effective method for quantifying parameter uncertainty in LCA studies. The analyzed parameters are assigned with log-normal distribution. It is concluded that uncertainty analysis offers a well-defined procedure for LCI studies; early phase of LCA as deterministic analysis does not include uncertainty in the input data [3].

In the fourth chapter, attention is going to be directed to another important field of lanthanide science that addresses the lanthanide elements or rare earth elements (REEs) as an active soil science research area, given their usage as micro-fertilizers, documented cases of environmental impact attributed to industry/mining, and their ability to identify lithologic discontinuities and reveal active soil processes. In soil science, the uniqueness and importance of the rare earth elements (REEs) arise because their respective concentrations as a function of atomic number have been employed to (i) assess soil genesis, (ii) augment soil fertility, (iii) evaluate anthropogenic impacts, and (iv) are sufficiently mobile to infer the intensity of key pedogenic processes [4]. Rare earth element abundances in soils are influenced by (i) parent materials and organic matter contents, (ii) soil texture, (iii) pedogenic processes, and (iv) anthropogenic activities [5].

The fifth chapter describes a new study on the effect of lanthanides content in soddy-calcareous soils under anthropogenic impact at a different distance from the Cherepovets steel mill

(Vologda region, Russia). The study has shown that in soils near the steel mill, an increased content of Pr and Tb was found, while the content of other light lanthanides (from La to Gd inclusive) was less increased. The study concludes that the comparison of distribution diagrams of lanthanides constructed with used indicators allows deriving both qualitative and sometimes quantitative differences in the behavior of these elements and in the technogenic contamination of soils with lanthanides. Further, the soils of the investigated territory are contaminated with lanthanides due to the Cherepovets steel mill (CSM) activities. Moreover, a significantly increased content of praseodymium and terbium was found in soils near CSM. In these soils, less increase in the content of other light lanthanides, from lanthanum to gadolinium, was determined. Technogenic contamination also leads to an increase in the amount and to changes in extraction degree of acid-soluble forms of lanthanides from soils [6, 7].

The sixth chapter discusses ecological and physiological impacts of lanthanides on algae as primary producers in aquatic environments. This study summarizes knowledge of positive and toxic effects of lanthanides on algae in order to better elucidate their biological roles. Various applications and methods of use, including the possibility of remediation and lanthanide recycling are also suggested [8–10]. The study arrived at a brief conclusion, which stated that algae are very important, being at the very beginning of the food chain. Their relationships with metals therefore affect other living organisms. Their ability to accumulate lanthanides may have an impact on the surrounding environment, representing both a threat and an opportunity, with the potential for further study and use, as bioaccumulation abilities and beneficial or toxic effects of lanthanides differ in individual algal strains. Algae in combination with lanthanides offer a wide variety of applications. They can be used as bioindicators, fertilizers, toxin detectors, or for phytoremediation and recycling. Therefore, understanding the relationships between algae and lanthanides is very important, once we understand the molecular mechanisms of their effects.

3. Conclusion

Although the presented book is not providing a comprehensive treatment by any means to its topics, it is still a very important tool to direct attention to some of the advanced trends of the lanthanide research. This book will encourage readers, researchers, and scientists to look further into the frontier topics of lanthanides applications and uses to reach the needed efforts to develop their quest toward the multidisciplinary character of lanthanide research.

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Chapter 2

Perspective of Obtaining Rare Earth Elements in Poland

Katarzyna Kiegiel, Agnieszka Miśkiewicz,
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Additional information is available at the end of the chapter

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Abstract

Along with the increasing development of electric and electronic industries, the demand for rare earth elements is also growing due to their high position in many applications. In Poland, there are minerals containing REE; however, the concentration of these elements in raw materials is rather low, so they do not have a big impact on the national economy. The potential source of REE is secondary materials; among them are phosphogypsum, uranium tailings, and the waste electrical and electronic equipment (WEEE). Lanthanides as accompanying metals of uranium in Polish uranium ores were leached in the technology of uranium recovery from these resources. The recovery of REE from pregnant liquors was conducted by solvent extraction and ion exchange. Novel apparatus solutions like membrane contactors in extraction stage were tested. Different types of matrices (uranium ore, phosphorites, etc.) were used.

Keywords: rare earth elements, phosphogypsum, uranium deposits, waste electrical and electronic equipment, separation of lanthanides

1. Introduction

The group of rare earth elements (REE) is considered as 1 of 20 critical mineral raw materials important for the EU economy [1]. Due to the high demand for these metals, their resources are systematically exhausting. Actions aimed at ensuring continuity of REE supply, that is, exploration and exploitation of new deposits, reduction of consumption of these precious metals in technological processes and their recovery from waste, are very important from an economic point of view. The REE are widely used in the industry. For example, Nd, Pr, Sm, Tb, and Dy constitute the most important component of magnets used among others in mobile computers, mobile phones, cameras, electric motors, hybrid cars, and equipment for magnetic resonance; La, Ce, Pr, and Nd are used for the production of batteries of hybrid vehicles and hydrogen-absorbing alloys; Eu, Y, Tb, La, Dy, Ce, Pr, and Gd are a part of luminophores used in mobile phones, tablets, LED diodes, and energy-saving light bulbs; Ce, La, and Nd are added to the powders for polishing of screens of TV sets, monitors, tablets, mirrors, and computer processors (in the form of nanoparticles) [2]. The new applications of REE are still being found, and in the most of cases, it is impossible to replace them by other materials.

In Poland, the concentration of REE in minerals is rather low; their impact on the national economy is small. Potential sources of these metals are secondary materials such as phosphogypsum,

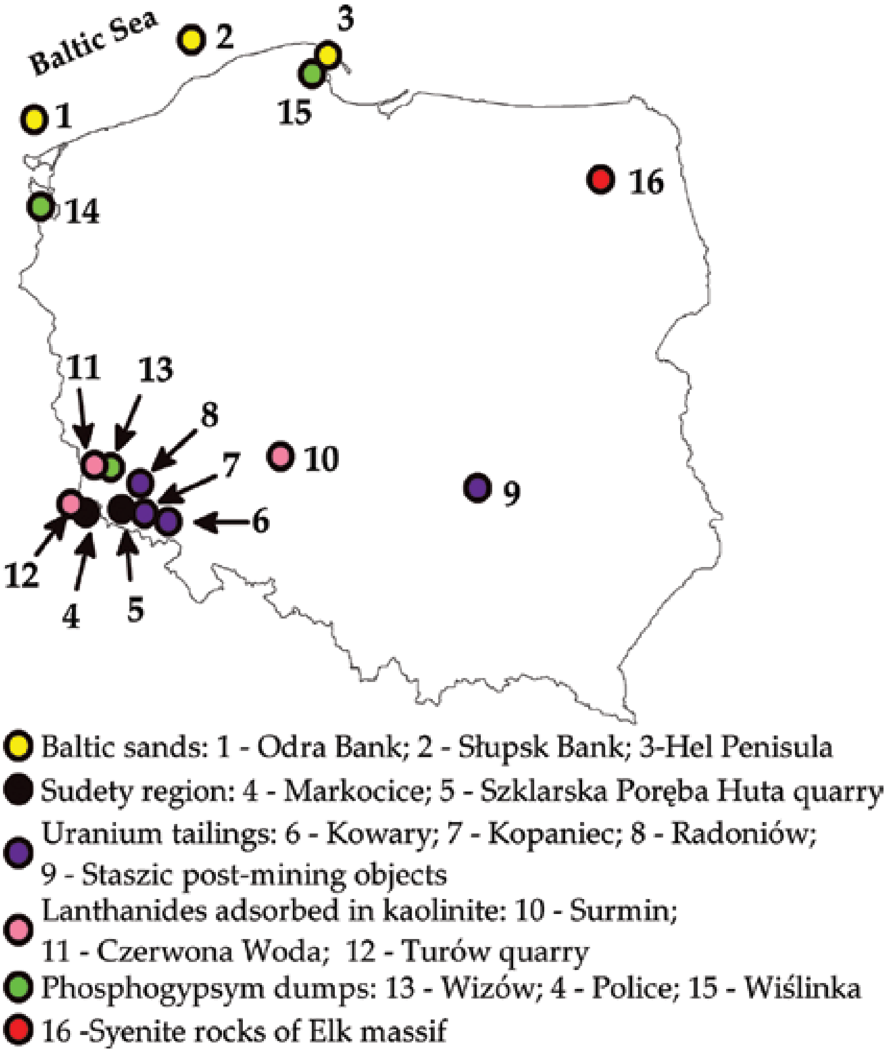

Figure 1. The location of potential REE raw materials in Poland.

the uranium tailings, and the waste electrical and electronic equipment (WEEE). In this chapter, the perspectives of recovery of REE from the Polish reserves are presented. The location of potential REE resources in Poland is shown on **Figure 1**.

2. Rare earth elements in Poland: natural sources

Natural resources of lanthanides in Poland were identified in alkaline intrusive Elk massif, Baltic sands, granite rock of Szklarska Poręba Huta quarry and Michałowice quarry (Karkonosze massif), pegmatites of Bogatynia (Sudety mountains), and Lower Silesia kaolinite [3–6].

The Elk alkaline massif belongs to group of intrusive centers within the crystalline basement of the precambrian Baltic shield (northeastern Poland). It is composed mainly of syenite rocks such as nepheline syenite (E2, E3), fold-less syenite (E3), amphibola syenite (E4), monzogabbro (G1), and quartz syenite (K1, P1, P2). The whole massive is about 400 km^2 in areal extent and the lanthanide-bearing rock is buried beneath 800–900 m of sedimentary rocks. For all rocks of Elk massif light REE enrichment has been found [3].

In the 1950s of the last century, a geological survey was carried out (seven drills has been digged, near the Elk city). It was showed that the concentration of lanthanides in this region is in the range of 207 up to 1224 ppm. The highest average concentration of lanthanides (963.9 ppm) is related to amphibola syenite, on a depth 950–1639 m, and the lowest one (354.7 ppm) is related to monzogabbro. The whole REE bearing layer is located on the depth 900–2500 m [3]. Distribution of the %REO (rare earth oxides) content depending on the depth of residual resources was shown on **Figure 2**. The calculation was done on the basis of the data published in the Geological Survey [3].

For all rocks of Elk massif light REE enrichment has been found and almost all samples have negative Eu anomaly [3].

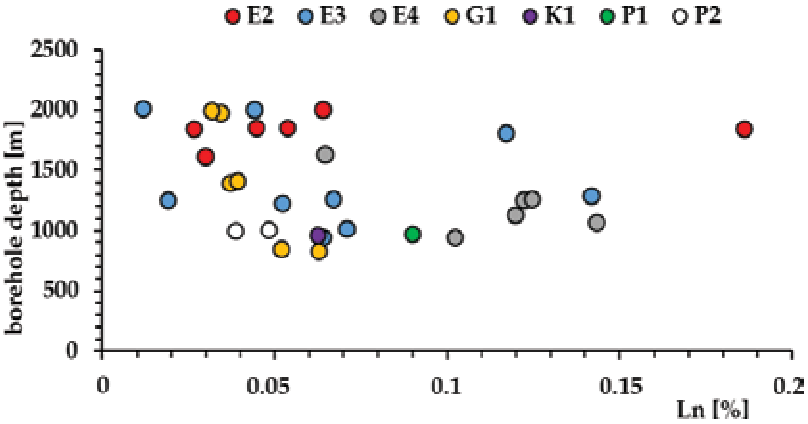

Figure 2. Distribution of %REO depending on the borehole depth (calculation based on data [3]).

The lanthanides mineralization has been also found in the Baltic marine sands, which are enriched in heavy metals, from the Odra and Slupsk Bank and from Hel Peninsula. All the samples were enriched in LLn_2O_3 (light lanthanides oxide). The highest REE (including Y and Sc) content is related to heavy minerals of Hel Peninsula sands (1371.2 ppm) and Odra Bank (up to 8787.7 ppm) [4].

In southwestern Poland (Sudety Mountains) REE occurrences are associated with uranium- and thorium-bearing rocks. In Szklarska Poręba Huta quarry, lanthanides are associated with Nb, Ta, and Li pegmatites and granites. The total concentration of %REO is 0.5 wt%, and prospective resources are estimated at 305 tonnes of these metals. In Markocice (near Bogatynia), REE content has been estimated at 150 tonnes, with average REO concentration of 1.5 wt%. In this area, lanthanides occur in metamorphic cover with the main REE bearing minerals such as zirconolite, gadolinite, fersonite-formanite, aeschynite, uraninite, monazite, zircon, and xenotime [5, 6].

The occurrence of lanthanides, which are adsorbed in kaolinite (Surmin, Czerwona Woda, and Turów), has been found in the area of Lower Silesia (southwestern Poland). The average concentration of lanthanides in this mineral is 288.7 ppm for Surmin, 106.9 ppm for Czerwona Woda, and 41.6 ppm for Turów. These clays are enriched in light lanthanides [7].

3. Potential secondary materials for REE recovery

3.1. Uranium tailings

Uranium mining and uranium tailings are also rich sources of metals from the lanthanide group. Uranium mining residues in Poland were studied under various projects demonstrating the presence of REE and possibility of their extraction. The investigations were conducted in the Sudety region—Kowary (adit and sorting station), Radoniów (small and big dump), Kopaniec (dump), and in iron sulfide deposit in Rudki ("Staszic" mine) in the Holy Cross Mountains—where the soil and water from the mine pit lake and surrounding soils were analyzed. For waste materials from the Sudety region, the average concentration of Ln (excluding Tm) was as follows: Kowary adit, 64.9 ppm; sorting place, 95.9 ppm; Radoniów, 77.3 ppm (big dump) and 109.8 ppm (small dump); and Kopaniec dump, 103.9 ppm, with majority of light lanthanides (calculation based on data from [8]). For the Staszic post-mining objects, the average concentration of Ln was 993.3 ppm in water from open pit lake and 82.6 ppm in soils (calculation based on data [9]). All tested samples were enriched in medium lanthanides [9].

3.2. Phosphoric fertilizer manufacturing process: imported phosphates, phosphogypsum, and phosphoric acid

One of perspective secondary materials for recovery of REE is phosphate ores, which are used in the production of phosphoric acid. Phosphate ores can be divided into two main types according to their origin: sedimentary and igneous phosphate rocks. Sedimentary phosphate rocks (phosphorites) are found in Florida, Morocco, and the Middle East, while igneous phosphate rocks in the Kola Peninsula (Russia) and in Brazil [10]. The REE content in phosphate rocks depends on the type of rocks; in sedimentary phosphate rocks, it is 0.01–0.1 wt%, while in igneous phosphate rocks it is much richer (1–2 wt%). Apatite is the main phosphate mineral in most phosphate deposits [11]. These phosphate ores generally contain only 0.1–1% Me_2O_3, but they are present in huge quantities, c.a. 67 billion tonnes and are spread around the world; thus they have the potential to be an important source of REE. In apatite ores, REE either take the place of Ca^{2+} in the apatite itself or is presented as mineral inclusions in the ores. REE can be extracted from apatite ores during the production of phosphoric acid. In the technological process, c.a. 70% of REE present in the raw material is transferred to insoluble gypsum in precipitation process. In phosphoric fertilizer manufacturing process in Poland, phosphate rocks imported from Morocco, Tunisia, and Syria are used. The example concentration of lanthanides in these materials is presented in **Table 1**.

Phosphogypsum is primarily $CaSO_4{\cdot}2H_2O$, but it also contains impurities such as fluoride, heavy metals, and naturally occurring radionuclides such as ^{210}Po, ^{226}Ra, ^{234}U, ^{238}U, and ^{210}Pb [13]. The composition of impurities within phosphogypsum can vary greatly depending on the source of the phosphate rock used in phosphoric acid production.

Phosphogypsum waste generated during production of phosphoric acid process in Poland is stored on the heaps in Police, Wizów, and Wiślinka near Gdańsk. It is estimated that every year, all plants in Poland produce about 2.2–2.6 mln tonnes of phosphogypsum. In Wizów, apatites originating from the Kola Peninsula (Russia) were processed. The phosphate rock coming from the Kola region contained an average 0.8–1.0 wt%. lanthanide oxides (as Ln_2O_3). Phosphogypsum waste generated in the Wizów Chemical Plant in south-western Poland was stored on a huge heap in the vicinity of the plant. The phosphogypsum stored in Wizów mainly consists of calcium sulfate hemihydrate which undergoes physical and chemical changes during storage [14]. The analyses of the composition of this waste showed that the average content of lanthanides was in the range 0.3–0.7 wt%. (as Ln_2O_2). It was confirmed that this waste is a potential raw material for the manufacture of 6–10 kt of REE [15]. The phosphogypsum waste heap in Wiślinka (northern Poland) is located between the Martwa Wisła River and farm fields, close to the Gdańsk agglomeration. It contains about 16 million tonnes of phosphogypsum stored on 40 ha of land. The phosphogypsum waste heap is the result of production of phosphorite fertilizers by phosphoric fertilizer industries in Gdańsk. The concentration of lanthanides in phosphogypsum stored in Wiślinka is collected in **Table 2**.

Lanthanides	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**
Origin of phosphorite	**Concentration, ppm**											
Morocco	90	38	14	62	13	3	18	3	18	4	14	13
Syria	26	22	4	18	4	1	5	1	4	1	4	3
Tunisia	64	100	13	55	11	3	12	2	9	2	6	5

Table 1. Concentration of lanthanides in the phosphates of different origin [12].

3.3. Fly ash from coal combustion in conventional power plants

Fly ash is considered as a potential future source of lanthanides and other valuable metals (e.g., uranium, thorium, aluminum, etc.).

Usually concentration of metals in solid fossil materials such as anthracite, hard coal, and lignite is not very high. During combustion or co-firing processes, a lot of valuable metals is concentrated several times in coal fly ash (CFA) [16, 17].

Poland is the second biggest consumer of coal in European Union countries. Polish energy mix has been shown in **Figure 3**. Almost 80% of electric energy comes from combustion of hard coal, lignite, and biomass [18].

Only 25% of CFA that comes from Polish coal-fired power plants is utilized, and 75% is disposed as a waste material. Fly ash is used mainly as an admixture for concretes and cements or for production of synthetic zeolites. In the fly ash, 81 metals have been analyzed, including REE, which concentration is much higher than in raw material.

Average concentration of lanthanides in coal and lignite is not very high (in Polish solid fossil fuel is approximately 100 ppm of Ln), but during combustion process the total concentration of lanthanides grows 3–4 times [16]. Assessment of Polish fly ash, which comes from combustion of solid materials (biomass, hard coal, and lignite), showed that concentration of REE (including Y and Sc) is in the range 101.1–443.3 ppm, always with majority of LL_2O_3 fraction [17, 19].

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb
Concentration, ppm	40	53	8	34	7	2	9	1	7	2	5	4

Table 2. The concentration of lanthanides in phosphogypsum stored on Wiślinka heap [15]

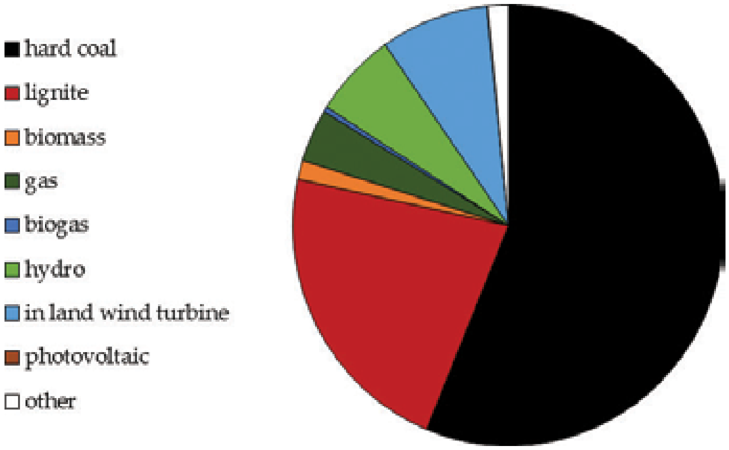

Figure 3. Polish electricity production energy mix (in shares %).

3.4. Waste electrical and electronic equipment (WEEE)

In view of the growing demand for rare earth elements (REE) and requirements of environmental protection, the treatment of waste electrical and electronic equipment becomes a very good secondary source of the REE in a modern economy. Recycling of the waste electrical and electronic equipment is also one of the possibilities of obtaining the rare earth metals and limiting their purchase from China. According to the European Commission, waste electrical and electronic equipment is one the fastest growing waste streams in the European Union, with almost 9 million tonnes produced in 2005 and probably will increase to more than 12 million tonnes by 2020 [20].

Also in Poland, a potential raw material of the rare earth elements is secondary material, which is a waste of electrical and electronic equipment (WEEE). In the recycling process of WEEE, developing an appropriate scheme for the management of WEEE by improvement of collection and treatment of electronics scrap is very essential. In Poland, the new WEEE Act has been in force from January 1, 2016 (dated September 11, 2015) [21], which transposes the European Directive WEEE 2 (No. 2012/19 / EU) [22]. The European Directive WEEE 2 introduces, among others, increased obligations to collect and process WEEE–65% of weight from 2021 and a new division into six groups of WEEE from 2018, as well as the obligation to collect WEEE free of charge in the place of delivery of new equipment. Stores also have the obligation to collect small WEEE without any quantitative restrictions if the dimensions do not exceed 25 cm. The European Directive WEEE 2 groups a total of 10 categories of waste electrical and electronic equipment (WEEE) [22]:

- Large household appliances
- Small household appliances
- IT and telecommunications equipment
- Consumer equipment
- Lighting equipment
- Electrical and electronic tools
- Toys, leisure, and sports equipment
- Medical devices
- Monitoring and control instruments
- Automatic dispensers

It is estimated that about 11 million tonnes of WEEE such as computers, laptops, TV sets, LCD glass panels, fridges and mobile phones, smartphones, batteries, car batteries, accumulators, fluorescence lamps, magnets, etc. are produced in Europe annually, which accounts for 22% of the total volume of WEEE generated in the world [1]. The largest growth rate among WEEE is seen in the use of IT and telecommunications devices, for example, mobile phones and laptops [1]. The recovering and processing of the WEEE have become very important because of the huge amount of the collected WEEE in Poland and in the European Union. Only 25% of the mass of WEEE produced in the EU-27 is stored and processed, and the remaining 75% is not processed. In Poland, an overall of 1.48 kg per capita of WEEE was collected in 2008 and 4.39 kg per capita in 2014; it is roughly 168,900 tonnes of WEEE. In 2021 Poland will be obliged to collect 11 kg per capita [23].

Based on the data of the Chief Inspectorate for Environmental Protection (CIEP), Poland, there are a lot of Polish Organisation of Electrical and Electronic Equipment Recovery (OEEER), for example, Elektroeko, the European Recycling Platform, AURAEKO, Biosystem Elektrorecykling, CCR RELECTRA, Electro-System, DROP, and TOM, which are responsible for meeting the collecting and recycling obligations on behalf of enterprises [23]. In Poland, there are also a number of companies collecting and processing WEEE, which cooperate with companies belonging to OEEER, for example, Elektrorecykling Sp. z o.o. [24], REMONDIS Electrorecycling Sp. z o.o. [25], Baterpol S.A. [26], and P.P.H.U. POLBLUME Zbigniew Miazga [27].

A total of 168,932 tonnes of WEEE was collected in the country, including 159,756 tonnes (94.56%) from households and 9175 tonnes (5.44%) from other sources in 2014. The largest volume of this waste is composed of large household appliances, 79,562 tonnes (47.09%), and IT and telecommunication equipment (e.g., computers, laptops, mobile phones, etc.), 24,965 tonnes (14.72%). The smallest part is composed of wastes of automatic dispensers, 115 tonnes (0.06%) [28].

4. Hydrometallurgical process of REE recovery

In order to separate the individual REEs, at first they have to be recovered from the raw material such as REE ores or the WEEE, in hydrometallurgical process. The technological scheme of REE extraction from minerals usually consists of grinding and cracking mined ore, preliminary enrichment to produce mixed REO concentrates, and then further concentration, separation and purification of REE oxides. To concentrate the REE extracted from minerals, the methods such as flotation, gravity separation, electrostatic separation, or magnetic processes are used [2].

Various methods and solutions are used for the extraction of REE from solid materials. As lixiviants, inorganic acids, alkalines, electrolytes, and chlorine gas are used. The leaching reagent should be selected to fit specific characteristics of the source material, for example, acids are commonly used to extract REE from silicate ore mineral such as gadolinite, eudialite, and allanite, and the alkaline reagents and sulfuric acid are mainly used to leach REE from phosphate ore minerals like monazite and xenotime. Electrolyte solutions are used to extract of REE from ion adsorption clay deposits. The chlorination process can be used to treat majority of rare earth minerals.

The obtained solution is a mixture of various REE with other metals, present in the raw material. The separation of individual metals is one of the most major challenges in hydrometallurgy. Currently the solvent extraction is the most preferable method of purification due its continuous nature and possibility to handle large amounts of diluted post-leaching solution. Selection of the ligand used for forming the organic soluble metal-ligand complex can have profound effects on separation of metals and overall process efficiency and economics. Generally all three major classes of extractants: acidic, neutral, or basic extractants can be utilized for separating rare earths [29].

The extraction step is always followed by scrubbing. The organic phase from extraction step is contacted with scrubbing solution in order to remove any undesirable solutes that are entrained in the organic solution and improve the purity of valuable elements. Typically scrubbing is carried out by using water, dilute acid, or base solution. It is worth to note that a relatively high amount of valuable metals may pass to the scrubbing solution. For this reason, it should be recycled back to extraction stage and mixed with the feed aqueous solution.

The metals extracted to the organic phase should then be stripped back to aqueous phase for further recovery. The stripping is the reverse operation to the extraction. As a stripping solution, typically concentrated acid, alkaline, or salt solutions are used. Likewise extraction, stripping may be performed in a one-stage, two-stage, or multi-stage process [30].

REE can be separated using ion-exchange techniques. The separation of lanthanides can be achieved by using the combination of chelating eluents that are selective for individual lanthanides with resins that is characterized by little selectivity. The other possibility is the extractions with the chemically modified resins; among them are resins coated with extractant [31].

Several REE can be separated basing on their redox properties [31]. The example is cerium and europium which have been isolated on an industrial scale using reduction-oxidation reactions. Cerium (III) was oxidized to +4 that forms sparingly soluble oxides or hydrates. The precipitate was separated to give pure cerium solid (99% of purity) and cerium free liquor. Europium was reduced to +2 and precipitated as sulfate from mixed rare earth elements solution. The purity of europium obtained in this way was >99%.

The industrial process of purification of lanthanum, gadolinium, terbium, and dysprosium uses fractional crystallization techniques. This method is based on the different solubility of rare earth bromate, nitrate, and sulfate complexes. A lot of repetition of crystallization is necessary to obtain pure metal. For example, the lanthanide with 99.98% purity was obtained from a mixture of REE with using ammonium nitrate after 16 repetitions of crystallization ([31], and references therein).

Summarized, the separation of REE is the most difficult aspect of their production. The expanding global demand of these metals is the reason for the intensive increase of research in this field.

5. Separation of REE from polish resources

Initiating the nuclear power program in Poland generated interest in domestic uranium resources and the study of the recovery of uranium from Polish uranium ores [32, 33]. Most

Polish uranium ores are black shale and sandstone-type deposits [34, 35]. Uranium is usually accompanied by other valuable metals, among them REE [36]. These metals could be recovered at the same time as uranium, to improve the economy of processing of low-grade uranium ores predominated in the country. The content of lanthanum in Polish ores is 31–62 ppm in dictyonema shales and 4–53 pm in Triassic sandstones. The studies performed in the scope of national projects have shown 66% efficiencies of leaching of La from dioctynemic shales by 10% H_2SO_4 at 80°C [36]. The leaching under elevated pressure (2, 3, 5, 7 bar) did not improve the efficiencies, however shortened the time of process from 8 to 2 hours. Zakrzewska-Koltuniewicz et al. developed the second-order regression models to predict the leaching efficiencies of valuable chemical elements. They carried out the statistically designed experiments to investigate the recovery of U, V, and Mo chemical elements and representative lanthanides like La and Yb from low-grade uranium ore using sulfuric acid as a leaching reagent [37]. Lanthanum can also be extracted from sandstones with high efficiency (80%) at temperature 60°C with 10% HCl [38].

Very interesting, the novel method used for processing Polish uranium ores was a leaching in the membrane contactor with helical flow equipped with tubular metallic membrane. In this process, lanthanum was co-extracted with uranium from dictyonema shales with 78% of efficiency [39]. The process was carried out at ambient temperature, and the yield of leaching was higher than obtained in the stationary reactor with heating and mixing. The additional advantage of using the membrane contactor is a possibility of conducting two processes: leaching and solid-liquid separation in one apparatus.

The post-leaching solution obtained from the separation of solid residue from liquid is a mixture of various metal ions. The further purification and separation of metals can be achieved by solvent extraction followed by stripping to aqueous phase or by ion exchange. By using solvent extraction, we cannot avoid some of the problems associated with this process. A third phase between aqueous and organic phases is often formed in solvent extraction process. It is related to the solubility of the metal-extractant complex in the organic solution. The formation of the third phase may cause many difficulties; first of all, it leads to organic solvent loss. The minimization of the formation of the third phase can be achieved by addition of a modifier to the organic phase [40] or by application of membrane contactors, a multistage mixer-settler arrangement with concurrent flow of two phases—aqueous and organic [41].

Ion exchange proved also itself as an effective separation method of metals from water solutions. Danko et al. proposed to use Dowex 1X10 and Dowex 50WX4 for valuable metals extraction from pregnant leach liquors from extraction of Polish ore. The recovery of lanthanides was 99% [42].

6. Separation of REE from waste and products of phosphate fertilizer industry

The process of the recovery of REE from phosphogypsum has been studied in Poland for over 30 years. As a leaching solution, a concentrated sulfuric acid, nitric acid, or their mixture have been applied. For separation of rare earth elements, different methods have been used: precipitation and extraction in liquid-liquid systems with the participation of an organic phase as well as crystallization methods, among others [43, 44]. Results of this work confirmed higher efficiency of leaching lanthanides from phosphogypsum by the application of nitric acid (c.a. 90%) than sulfuric acid (c.a. 60%). However, in the case of using nitric acid, an additional waste threatening the environment is generated.

The possibility of recovery of REE from phosphogypsum stored in Wizów heap with simultaneous recovery of P_2O_5 and production of anhydrite cement was also a subject of work [14]. The technology was examined at laboratory scale by the processing of 1 Mg/h of phosphogypsum. The technological flowsheet consisted of three steps: (i) leaching of lanthanide from the phosphogypsum using sulfuric acid at a concentration of 15%, (ii) crystallization of the rare earth concentrate (containing up to 25% Ln_2O_3) from the leach solution, and (iii) recrystallization of gypsum. In this way, insoluble high-quality anhydrite, phosphoric acid, and concentrate of rare earths concentrate containing more than 90% of oxides were products of the process. The composition of the rare earth concentrate is presented in **Table 3**.

The leaching of valuable metals from phosphogypsum stored in Wiślinka heap was also studied. The experiments were performed in laboratory scale. Lanthanum and other REEs were recovered with high efficiencies (**Figure 4**). Initially, the phosphogypsum was treated with 30% NaOH at 60°C, and then the solid residue was leached with 10% HCl at 60°C [12, 45].

Zielinski et al. studied the recovery of lanthanides from Kola apatite used for the phosphoric acid production in Polish phosphoric fertilizer factory [46]. It was found that a stage of the hydration of hemihydrate provides the best conditions for the recovery of lanthanides. In this stage for the removal of lanthanides, a solvent extraction has been applied and consequently a precipitation-stripping process for the removal of lanthanides from the solvent has been employed. As a result, a concentrate enriched with lanthanides has been obtained in which lanthanides were recovered with an efficiency of 80–85%. The similar results were obtained by the El-Didamony et al. in the studies of reduction in the concentration of radionuclides in phosphogypsum by using suitable organic extractants. This process was accompanied by reduction in the concentration of REE up to 80.1% [47–49].

Component	**%**	**Component**	**%**
La_2O_3	24.8	Dy_2O_3	0.2
CeO_2	50.5	Tb_4O_7	0.1
Nd_2O_3	15.9	Ho_2O_3	<0.1
Sm_2O_3	1.9	Er_2O_3	<0.1
Gd_2O_3	0.9	Tm_2O_3	<0.1
Eu_2O_3	0.44	Yb_2O_3	<0.1
Y_2O_3	0.3	Lu_2O_3	<0.1
ThO_2	0.2		

Table 3. The composition of the concentrate of REO [14]

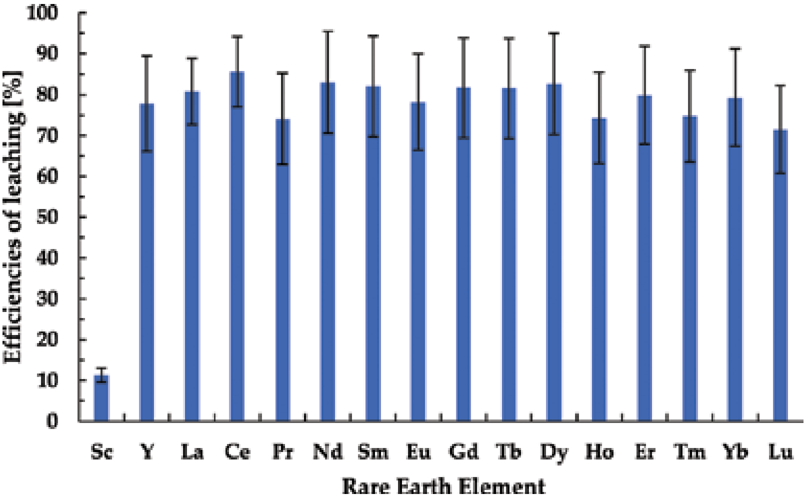

Figure 4. The efficiencies of leaching REE from phosphogypsum stored in Wislinka heap, Poland.

The possibilities of separation of rare earth elements from phosphoric acid solution have been also investigated [50]. A strongly basic ion-exchange resin with quaternary ammonium functional groups (Dowex 1) has been used for this purpose. The effect of temperature and resin cross-linking on the column performance and the ion-exchange reactions of phosphate complexes of several rare earths were determined. It was found that the resolution increases with increase of temperature, and the best separation was obtained at temperature of 85°C.

A separation of lanthanides form phosphoric acid through a crystallization process has been also investigated [51]. The effect of temperature and H_3PO_4 concentration on lanthanide solubility was tested. As a result of the experiments, highly crystalline solids of lanthanide phosphates were obtained.

7. Recovery of REE from WEEE

A complete strategy of recycling of waste electrical and electronic equipment consists of policies of waste management, research and development in new methods of processing, and challenges in elaboration of new technologies. For many countries, mainly those having limited access to mineral resources of REE, the development and improvement of the recycling processes of valuable metals from WEEE are significant aspects from the economic and environmental point of view. In Poland, obtaining a concentrate of REE from the discussed secondary raw material on an industrial scale is currently an economic issue. Unfortunately, about 70% of collected WEEE waste is processed in China [52].

In general, waste electrical and electronic equipment (WEEE) is a mixture of different materials and can consist of steel, printed circuit boards, batteries, permanent magnets, hard drives, plastic, aluminum foils, phosphors, photovoltaic materials, cables, separators, active materials, carbon, organic binders, organic solvents, salts, additives, valuable metals, etc. Very important steps for the hydrometallurgical recovery of metals from a wide range of WEEE are mechanical pretreatment and dismantling.

Usually, a recycling of different types of waste electrical and electronic equipment is very complex because of the complexity of the material; the content of metals, for example, low-grade or high-grade material; the solubility and/or thermal stability; etc. Recovery of REE from WEEE using pyrometallurgical treatment is energy demanding, and often, the final products that are obtained require another processing to get pure compounds of the material [53]. As an alternative to pyrometallurgical processes, the metallurgical industry has been examining for hydrometallurgical treatment, due to some benefits related to hydrometallurgical processing, mainly for low-grade and chemically difficult streams [53].

Rare earth elements are used in the production of metal alloys (25%), catalysts (16%), permanent magnets (23%), polishing materials (11%), glass (7%), and materials containing phosphors (7%). The applications of these metals should provide the opportunities for strategic recycling and material recovery after their use. Recycling of spent fluorescent lamps can be a useful secondary source of Y, Eu, and Tb, and recycling of permanent magnets, which are used in water and wind energy as well as in HEV and EV vehicles, can become an important source of secondary acquisition of Nd, Pr, Dy, and Tb [54–56].

The amount of REE depends significantly on the type of waste electrical and electronic equipment (WEEE) and can range from several hundred ppm to several dozen percents. Particularly rich in rare earth elements are wasted permanent magnets of type $Fe_{14}Nd_2B$ (about 24% of Nd) or Sm_2Co_5. Some magnets of this type include additionally about 5% of Dy [1].

Usually, the processes of obtaining rare earth from permanent magnets are preceded by pretreatment, which includes such operations as mechanical disassembly of waste, physical separation, grinding to the proper grain size, thermal treatment, pyrometallurgy, hydrometallurgy, etc. Methods are adequate to the particular type of waste electrical and electronic equipment. The basic technologies include such unit processes as rare earth recovery through thermal or hydrometallurgical processing. For example, the recovery process of the neodymium from the $Fe_{14}Nd_2B$ magnet scrap consists of the extraction of neodymium with liquid magnesium, the separation of the liquid phase from the solid phase, and the evaporation of liquid magnesium. After these operations, the obtained final product contains about 96% of Nd [57].

The recycling and separation processes of Nd and Dy from permanent magnet scrap has been also studied by a hydrometallurgical method using liquid emulsion membranes in an integrated process [58]. In this method, the removal of ions is the result of processes taking place in one apparatus, that is, the production of liquid emulsion membranes and extraction. The extraction process involves the steps of transporting metal ions of Nd and Dy through the membrane phase of the emulsion to the phase of internal droplets, where they are separated by the extraction.

Nickel-metal hydride batteries (NiMH) that are used in the production of hybrid vehicles are another secondary source of valuable rare earth elements. The typical NiMH car batteries contain approximately 3 kg of REE, 11 kg of nickel, and 1.5 kg of cobalt. A hydrometallurgical technology has been carried out for the recovery of valuable metals from spent car NiMH batteries in a continuous countercurrent solvent extraction process using a mixer-settler system in a pilot plant scale [59].

At the Institute of Mechanised Construction and Rock Mining, Warsaw, Poland, a method for recovery of yttrium and europium from used phosphors was developed, that is the subject of the patent PL-200095, 2008 [60, 61]. Acidic leaching, hydrolytic precipitation, and/or solvent extraction methods have been used in the recovery of Eu and Y from waste fluorescent lamps containing ~0.3% Eu and 7% Y. The best results of leaching efficiency were reached in 3 M HCl or 3 M HNO_3 at 80°C, about 90% for Eu, and 95% for Y [62].

A mixture of fluorescent lamps of a different kind was processed for the recovery of REE especially Y and Eu [63].

The high efficiency of oxide containing 99.96% REE (94.61% yttrium, 5.09% europium, and 0.26% of the other REE) was reached in solution with 35 vol% Cyanex 923 in kerosene using mixer-settler systems of three extraction and four stripping stages.

8. Summary: current status and perspectives

Due to the depletion of natural resources, increased environmental pollution, and dependence on suppliers from China, the recovery of valuable metals from WEEE is currently of great importance. Broadly understood economic development and new technologies in the electrical and electronic market are beneficial for people, but they also harm the surrounding environment and, consequently, all of us. Therefore, the intensively developing industry of recovery of metals from secondary sources has many positive aspects such as less hazardous waste, reduction of greenhouse gas emissions and CO_2, or a reduction in the use of natural resources and thus reducing the destruction of the natural environment.

Despite the small amount of recycling of REE, the worldwide production of these metals currently exists at about 130,000 metric tonnes of REO equivalent content per year, with the 2014 REE market worth about US$2051 million [64]. A large amount of REE is used in the production of catalysts, glass, lighting, and in the metallurgy industry, 59% in 2011, and the remaining 41% in new increasing markets such as magnets, batteries, and ceramics [64].

Development of modern technologies both in the field of electronics and green motorization is heavily dependent on rare earth elements. Also in Poland, the constantly growing consumption of REE is observed. Poland does not actually have its own REE natural deposits. The demand for these metals is mainly covered by import from China, West Europe, and USA. Alternative sources can be rich hard coal resources and a large share of fossil fuels in energy production. No wider studies on the occurrence of REE have been conducted in the country so far, for example, for the assessment of the hard coal deposits and power fly ashes as reasonable sources of lanthanides. Fragmentary data not allow to determine the full volume of REE in Polish hard coal.

A prospective direction in obtaining REE from domestic resources can be processing of WEEE. In recent years the interest of small entrepreneurs in this subject is noticeable. Many small companies have been established, dealing primarily with the collection and segregation of electric and electronic waste materials. With the help of national assets and money from EU structural funds, many innovative projects in the field of metal recycling are carried out. Innovative REE recovery projects can meet the expectations of satisfying the demand for these valuable, irreplaceable metals in today's life.

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Chapter 3

Life Cycle Inventory (LCI) Approach Used for Rare Earth Elements (REEs) from Monazite Material, Considering Uncertainty

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Additional information is available at the end of the chapter

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Abstract

This study describes the development of life cycle inventory (LCI) to rare earth elements (REEs) based on the secondary sources, conducted according to ISO 14040 (2006) guidelines. Monte Carlo (MC) simulation with the Crystal Ball (CB) spreadsheet-based software was employed to stochastic modeling of life cycle inventory. The number of simulations was set at 10,000. The study scope considered LCI associated with REE concentrate production from New Kankberg (Sweden) gold mine tailings production (input gate) to the final delivery of rare earth elements (end gate) to reprocessing/beneficiation for rare earth element recovery. For the presented case, lognormal distribution has been assigned to scandium (Sc), dysprosium (Dy), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), holmium (Ho), erbium (Er), terbium (Tb), thulium (Tm), ytterbium (Yb), and lutetium (Lu). The MC simulation (10,000 trials) for the sum of analyzed REEs used for CB is presented in the form of statistics. Sensitivity analysis (SA) presented in the form of tornado charts and spider charts was performed. The results from this study suggest that uncertainty analysis is a powerful tool that should support and aid decision-making and is more trusted than the deterministic approach.

Keywords: rare earth elements (REEs), life cycle inventory (LCI), life cycle assessment (LCA), Monte Carlo (MC) simulation, Crystal Ball® (CB), sensitivity analysis (SA), uncertainty

1. Introduction

This chapter presents the utility of MC simulation with the Microsoft Excel with a CB extension software used to LCI modeling under uncertainty based on the public dissemination data from environmentally friendly and efficient methods for extraction of rare earth elements from secondary sources (ENVIREE)—ERA-NET ERA-MIN-funded research project [1]. Recently, rare earth elements (REEs) have received increased attention due to their importance in many high-tech and clean energy applications, although very limited life cycle assessment (LCA) studies have been conducted [2].

Life cycle assessment (LCA) is one of the tools that is increasingly being used to examine the environmental impact of a product through its entire life cycle [3]. Udo de Haes et al. [4] highlighted LCA as a global tool, while a wide range of LCA applications are presented in [5]. The increasing application of LCA as a tool for making policy decisions as well as material and design choice and need for robust and up-to-date information for such studies is also presented in [6, 7].

2. Uncertainty in LCA

Uncertainty is a pervasive topic in LCA and can be defined in various ways [8]. In [9], definition of uncertainty given by [10] is quoted: "Uncertainty is defined as incomplete or imprecise knowledge, which can arise from uncertainty in the data regarding the system, the choice of models used to calculate emissions and the choice of scenarios with which to define system boundaries, respectively."

LCA is an analytical tool which needs intensive data: methodological choices, initial assumptions, and degree of data uncertainty have a profound effect on validity of LCA results [11], and existing quantitative uncertainty methods in LCA require also a huge amount of accurate data [12]. Problem of aleatory uncertainty or "lack of knowledge" and epistemic uncertainty or "variability" [13] is discussed in [14], when it is highlighted that quantification for the aleatory uncertainty is usually performed using the MC. Detailed description of the combination of sources of uncertainty (parameter, model, and scenario uncertainties) and methods (deterministic, probabilistic, possibilistic, and simple methods) to address them is presented by [15]. According to the [16] discussed municipal solid waste incineration model, it is suggested that uncertainty is due to data gap or inaccurate data.

The LCI analysis involved the collection and calculation of data and procedures to quantify the relevant input and output of the product system. Very often large amounts of data required for LCI [17, 18] are affected by uncertainty [19, 20]. The main sources of uncertainty presented in [21, 22] is quoted in [23, 24]. With respect to parameter uncertainty, the common practice in LCA consists in representing uncertainty parameters by single probability distributions, e.g., a normal distribution is characterized by an average and a standard deviation [25, 26], while in [8], uncertainty is defined as geometric standard deviation of intermediate and elementary exchanges at the unit process level. To obtain a result, different statistical methods can be applied. The most well-known sampling method is MC simulation (e.g., [18–26]) easily applied to LCA [27], while a most sophisticated method is the Latin hypercube (LH) method, where the sampling strategy is not entirely random but utilizes stratified probability distributions [27]. MC simulation is also recommended in the IPCC 2006 Guidelines [28, 29]. Most software for LCA is by now able to deal with uncertainties, in most cases on the basis of MC simulation [27–29]. LH sampling performs better that random sampling when the output is dominated by a few components of the input factor and better that random sampling for estimating the mean and the population distribution function [30]. Moreover, LH sampling (data compression techniques) can reduce computer time [15] and may reduce the required number of simulation [27]. It is important that a sufficient number of replications be used in a simulation. The number of replications of simulation affects the quality of the results. In general, the higher the number of replications, the more accurate will be the characterization of the output distribution and estimates of its parameters, such as the mean [19, 20]. According to [31], it is suggested that statistical accuracy of the simulation increases with an increased number of trials.

As pointed out in, the number of runs will vary from problem to problem, at least 1000 runs (see *Introduction to LCA with SimaPro* [32]) to thousands [23, 24, 30, 33]. In discussion of stochastic flow shop scheduling metaheuristic model for vessel transits in Panama Canal that used 200 runs in MC simulation model, which stated that the change in the 95% confidence interval width for makespan was negligible, is presented.

The problem of number of runs in MC-based approaches was also considered by [34], who analyzed the fuzzy uncertainty propagation using matrix-based LCI and proposed the number of runs between 100 and 10,000. According to [35] in the analysis of the IBM, daily trading volume stocks used a Poisson distribution via the MC simulations based on 1000 repetitions. Also [36] applied 1000 iterations to estimate the uncertainties of life cycle impact assessment (LCIA) results introduced by the statistical variability or temporal, geographical, or technological gaps in the LCI data. In the same work to estimate the combined uncertainty for IPCC-derived greenhouse gas inventory, the MC simulation with 5000 iterations was used [36]. In [36], when probabilistic scenarios are analyzed, using Microsoft Excel with CB for MC method for each scenario, uncertainty analysis involved 20,000 MC simulations. Finally, [37] presented relative results between compact neighborhoods cells in Mexico City involved 100,000 MC simulation.

3. Material and methods

The framework of LCA, structured according to International Organization for Standardization ISO 14040 [38] standard, is described in [39].

3.1. Goal and scope of the study

The goal of this study was to provide LCI under uncertainty calculus on the probabilistic MC approach for the primary data delivered from the secondary REE recovery process following the guidelines in ISO 14040:2006 standard.

3.1.1. Functional unit

The FU, central concept in LCA, is the measure of the performance delivered by the system under study [3, 18]. The FU has been defined as 1000 kg of a secondary source to be excavated and processed as the input for all subsequent processes.

3.1.2. Data quality and collection

As noted above, very often LCI required a lot of data [17, 18] that are well correlated to the study context [40]. Data quality is discussed widely in literature [17, 23, 40–44]. In [45] analyzed uncertainty in a comparative LCA of hand drying systems pointed that data collection is one of the limitations in their LCA analysis. The databases presented in this study are affected to several uncertainties. According to [41], the basic uncertainty in data quality considerations of the inventory of rare earth concentrate processes comes out with data obtained from the literature studies. Large uncertainties exist for the infrastructure and also for particle emissions, fresh water use, and land use [41]. Another reason for the uncertainties is the nature of the chemicals used for the recovery of the REEs from the concentrate after flotation and beneficiation processes (e.g., collector, conditioner, depressant) due to production system characterized by diverse practices and technologies [41, 46], as well as various laboratory methods.

The primary data used in the study is obtained from the Deliverable D1.2 Report on the physical-chemical properties of available materials for the recovery of REE and Deliverable D1.3 chemical and mineralogical data of secondary REE sources [1]. The secondary data used in the study is obtained from the following sources:

- The subject literature—scientific publications
- Expert consultations and knowledge of the process

4. Results and discussion

The MC simulations for evaluation parameter uncertainty involve the following steps [47]:

1. Select a distribution to describe possible values of each parameter.
2. Specify properties of each parameters.
3. Generate data from the distribution.
4. Use the generated data as possible values of the parameter in the model to produce output.

The REEs can be grouped into two different categories based on their atomic numbers. REEs with atomic numbers 57–63 are classified as light-rare earths (LREEs), and REEs with atomic numbers 64–71 are classified as heavy-rare earths (HREEs) [48]. However, the term "rare" earth is a misnomer; they are relatively abundant in the Earth's crust; however, they are typically dispersed and only rarely occur in concentrated and economically exploitable mineral deposits [49].

The literature on the flotation of monazite is rather scarce. The available literature focused on the separation of monazite from xenotime, bastnaesite, rutile, and zircon [50] or on the Rhône-Poulenc liquid-liquid extraction process for separation of the REEs from monazite [51] and the Shanghai Yue Long Chemical Plant monazite concentrate treatment in the process similar to the Rhône-Poulenc process [11], both described in [49].

Monazite and xenotime from titania-zircon paleo beach placers in Australia, in the 1980s, were the third most important source of REEs in the world [52]. According to [53], in Australia, monazite typically has associated radioactivity due to thorium content (by substitution up to 30%). Until 1995, rare earth production in Australia was largely a byproduct of processing monazite contained in heavy mineral sands [54].

In addition to Australia, monazite deposits in Brazil, India, Malaysia, Thailand, China, Thailand, Sri Lanka, South Africa, and the United States constitute the second largest segment [49]. Present-day production is from India, Malaysia, Sri Lanka, Thailand, and Brazil [52]. Moreover, approximately 500 t of monazite per year was produced from 1952 to 1994 as a byproduct of titania-zircon production from Pleistocene sands near Green Cove Springs in Florida [52].

The Carolina monazite belt, from which a total of about 5000 t of monazite was produced between 1885 and 1917, has considerable placer reserves that average 0.25 kg/m^3 of monazite [55]. Bear Valley, Idaho, where monazite- and yttrium-bearing euxenite was mined by dredging, contains an estimated 10,000 t of REOs along with significant niobium and tantalum, on the basis of data from [56]. At Baotou, the largest producer of rare earths in China, the bastnesite concentrates contain a small amount of monazite [49].

According to ENVIREE project, flotation tests have been carried out on the flotation tailing from New Kankberg to find out if the REEs can be recovered [57]. The results indicate that most of the REEs are in monazite. *Monazite* is the second most important rare earth, after bastnaesite, and is a rare earth phosphate mineral that contains various amounts of thorium [50]. Sample from the flotation tailing was delivered to the ENVIREE project. After delivery of samples and their homogenization, they were analyzed. As mentioned above, ICP-MS analysis of samples was investigated, in order to test the availability of REE extraction. The results are presented in **Table 1** [1].

In this study we concentrate on a set of 16 REEs, denoted as critical [58] (European Commission 2014), namely, Sc, Dy, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Er, Tm, Tb, Yb, and Lu. MC, an uncertainty propagation method [59], required definition of the mean, type of statistical distribution, and standard deviation (SD) for each parameter [59]. In this study, the uncertainty analysis was modeled using probability distributions considered to be lognormal (term *lognormal distribution*) was derived from [60], according to the criteria proposed by [18] that "heavy metals is a sum parameter in the form of Pb, equivalents of following heavy metals: As, B, Cr, Cu, Hg, Mn, Mo, Ni, Pb and Sb," and according to the estimations published by [61], as well as following the [62, 63] indication, that environmental parameters in LCA studies are independent and usually follow the lognormal distribution as do the impact results [59]. Other studies showed that the lognormal distribution has been used by [9] for the variability assessment by means of bootstrap technique (applied for the computation of the median absolute deviation (MAD) for measure of the *variability* in statistical analysis). As pointed out by [62], the lognormal distribution has an upside-down bathtub-shaped hazard rate [64, 65], and no negative values are possible [18]. Lognormal distribution always remains positive, and it is consistent with the data available in the ecoinvent database and the pedigree matrix approach, as suggested by [45]. In addition, it is interesting to note that according to analysis, the trace element concentrations in gold processing have been concluded that concentration distribution of the elements between the grinding stages and the discharge stages was not uniform probably due to the different physical and chemical processes at various stages [64, 65].

REEs	Distribution type	Atomic number	μ_g	σ_g	Quality	Reference
Scandium (Sc)	Lognormal	21	0.41	1.10	0.41	CB® result
Yttrium (Y)	Lognormal	39	3.25	1.10	3.27	CB® result
Lanthanum (La)	Lognormal	57	12.13	1.10	12.19	CB® result
Cerium (Ce)	Lognormal	58	23.86	2.39	23.89	CB® result
Praseodymium (Pr)	Lognormal	59	2.39	1.10	2.4	CB® result
Neodymium (Nd)	Lognormal	60	9.78	1.10	9.83	CB® result
Samarium (Sm)	Lognormal	62	1.74	1.10	1.75	CB® result
Europium (Eu)	Lognormal	63	0.45	1.10	0.45	CB® result
Gadolinium (Gd)	Lognormal	64	1.27	1.10	1.28	CB® result
Terbium (Tb)	Lognormal	65	0.14	1.10	0.14	CB® result
Dysprosium (Dy)	Lognormal	66	0.49	1.10	0.49	CB® result
Holmium (Ho)	Lognormal	67	0.08	1.10	0.08	CB® result
Erbium (Er)	Lognormal	68	0.22	1.10	0.22	CB® result
Thulium (Tm)	Lognormal	69	0.03	1.10	0.03	CB® result
Ytterbium (Yb)	Lognormal	70	0.17	1.10	0.17	CB® result
Lutetium (Lu)	Lognormal	71	0.02	1.10	0.02	CB® result

μ_g = geometric mean value; σ_g = geometric standard deviation.

Table 1. Overview of the rare earths taken into account in the study (all values in ppm).

Finally, in this study to address uncertainty in the inventory data, analyzed REEs were fitted by lognormal distributions based on the real data summarized in **Table 1**. The CB lognormal distribution tab windows included the lognormal distributions of each of the 16 analyzed REEs after defining the geometric mean value (μ_g) automatically which calculated (matches) the standard deviation (σ_g) and lower as well as upper boundaries of lognormal distribution. There is lack of critical details in literature on how experimental data (e.g., σ_g) with regard to probability distributions for the REEs in monazite was calculated. Moreover, lack of expert knowledge and transparency makes it extremely difficult for other researches to carry out their studies [48]. As noted above, *monazite* is the second most important rare earth, after bastnaesite [48]. The results of the performed simulation (10,000 runs) can be presented in the form of frequency charts shown in **Figure 5**.

4.1. Uncertainty analysis: MC simulation results

The literature includes many studies and papers dealing with the uncertainty analysis. According to [66], the uncertainty analysis can vary from a qualitative assessment (where parameters are assigned a low, medium, or high level of uncertainty) to a semiquantitative assessment in which parameter values are bounded [66].

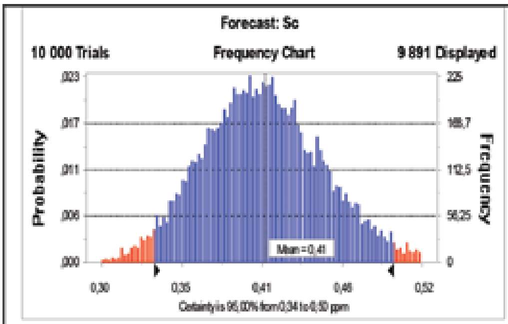
Several studies have presented examples of the utilization of MC simulation in LCA studies; however, according to [67], MC and fuzzy set theory have been applied in a limited number of LCA studies. According to [25] the LCA data, in general, is full of uncertain numbers, and these uncertainties, for instance, are caused by uncertain measurement or uncertainty about how representative a data is for the analyzed problem [25]. Bieda [23] depicted that the reliability of LCA results may be uncertain, to a certain degree, and this uncertainty can be pointed out using MC method. In order to obtain robust conclusions about LCA results, the uncertainty needs to be sufficiently accommodated [68], and in order to apply the MC approach, it is needed to translate own information about uncertainty into a standard distribution type [32].

In this study each REE is independent (uncorrelated) of the others and comes from the same source (i.e., laboratory). Uncorrelated means that deviations for all products (elements) are independent [45]. In carring out the MC simulation used CB (10,000 runs) obtained histograms, shown in **Figure 1**, statistics, as well as percentiles reports presented in **Tables 2** and **3**, respectively, are present the results obtained by MC simulation for the sum (total) of the Sc, Dy, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Er, Tm, Tb, Yb, and Lu. The confidence interval is 95%. This means that 95% of the results lay within this range [25]. Total forecast value amounted to the geometric mean value of the 56.59 ppm contained between 51.20 ppm and 62.58 ppm (see **Figure 2**). After 10,000 runs, the standard error of the mean is 0.04. The entire range which expressed the 95% confidence interval is from 45.78 ppm to 69.17 ppm. Range width is 23.38 ppm. The number displayed in the upper right corner of the histogram showed 9887 data points inside 2.6 SD of the mean [19, 20]. Just below the horizontal axis at the extremes of distribution, there are two small triangles, called endpoint grabbers [19, 20]. The certainty range (confidence interval) is displayed at the lower center of the frequency charts—the area of the histograms covered by them is darker [19, 20]. A detailed description of the simulation performed using CB is given in [19, 20, 23, 24]. The outcomes of the MC simulation listed in **Table 3** indicate that, for example, the chance that the total REEs will be less than 56.49 ppm is only 50% [19, 20].

4.2. Sensitivity analysis

The definition of sensitivity analysis (SA) given by [30] is "the study of how the uncertainty in the output of model (numerical or otherwise) can be apportioned to different sources of uncertainty in the model input." According to suggestion [45], SA isolates the main drivers of impact (and possibilities for improvement) and should be included in complete assessment of uncertainty. It is worth pointing out that Kolb [69] noted that theoretical methods are sufficiently advanced, so that it is intellectually dishonest to perform modeling without SA (see [30]). According to [70], SA of a result is most often studied parameter by parameter, while according to [71], SA helps decision-makers to understand the impact of chosen allocation method and boundary setting on LCA results.

The result of this SA with the confidence level of 95%, created on the basis of SRCC and sorted in descending order, where positive correlation coefficients indicate that the acceptance of the stricter assumptions can be associated with obtaining the higher forecast probability [23, 24], for the data presented in **Table 1**, is shown in **Figure 3**. Positive coefficient signifies the existence of positive correlation, whereas the negative coefficient signifies negative correlation


Forecast: Sc
10 000 Trials
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Probability
,023
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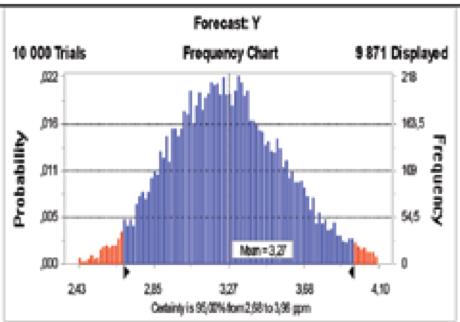
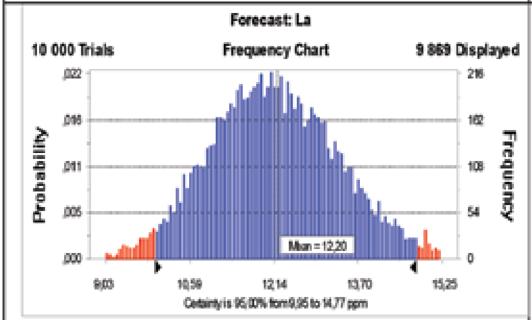
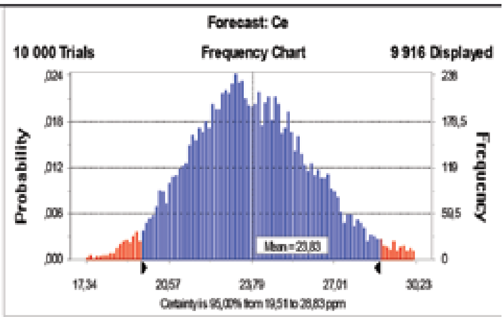
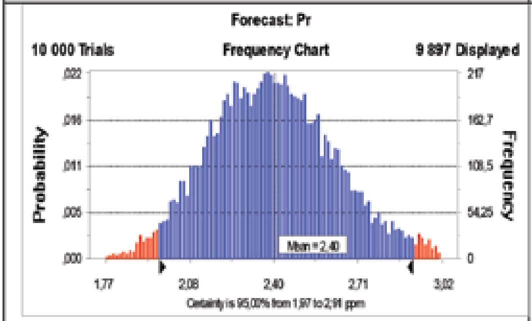
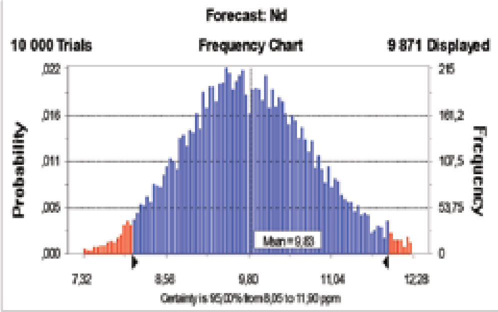
,000
Frequency
225
168,7
112,5
56,25
0
Mean = 0,41
0,30
0,35
0,41
0,46
0,52
Certainty is 95,00% from 0,34 to 0,50 ppm

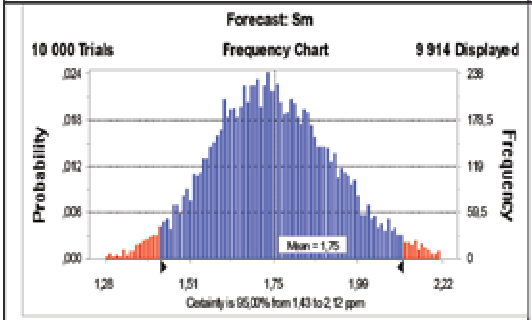

Forecast: Y
10 000 Trials
Frequency Chart
9 871 Displayed
Probability
,022
,016
,011
,005
,000
Frequency
218
163,5
109
54,5
0
Mean = 3,27
2,43
2,85
3,27
3,68
4,10
Certainty is 95,00% from 2,68 to 3,96 ppm

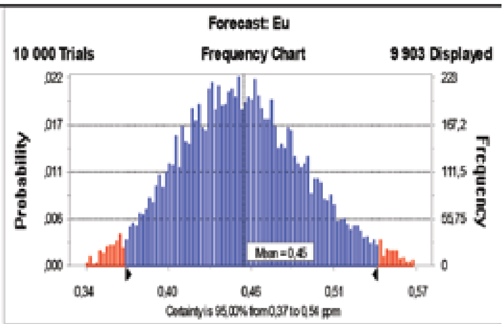

Forecast: La
10 000 Trials
Frequency Chart
9 869 Displayed
Probability
,022
,016
,011
,005
,000
Frequency
216
162
108
54
0
Mean = 12,20
9,03
10,59
12,14
13,70
15,25
Certainty is 95,00% from 9,95 to 14,77 ppm


Forecast: Ce
10 000 Trials
Frequency Chart
9 916 Displayed
Probability
,024
,018
,012
,006
,000
Frequency
238
178,5
119
59,5
0
Mean = 23,83
17,34
20,57
23,79
27,01
30,23
Certainty is 95,00% from 19,51 to 28,83 ppm


Forecast: Pr
10 000 Trials
Frequency Chart
9 897 Displayed
Probability
,022
,016
,011
,005
,000
Frequency
217
162,7
108,5
54,25
0
Mean = 2,40
1,77
2,08
2,40
2,71
3,02
Certainty is 95,00% from 1,97 to 2,91 ppm


Forecast: Nd
10 000 Trials
Frequency Chart
9 871 Displayed
Probability
,022
,016
,011
,005
,000
Frequency
215
161,2
107,5
53,75
0
Mean = 9,83
7,32
8,56
9,80
11,04
12,28
Certainty is 95,00% from 8,05 to 11,90 ppm


Forecast: Sm
10 000 Trials
Frequency Chart
9 914 Displayed
Probability
,024
,018
,012
,006
,000
Frequency
238
178,5
119
59,5
0
Mean = 1,75
1,28
1,51
1,75
1,99
2,22
Certainty is 95,00% from 1,43 to 2,12 ppm


Forecast: Eu
10 000 Trials
Frequency Chart
9 903 Displayed
Probability
,022
,017
,011
,006
,000
Frequency
223
167,2
111,5
55,75
0
Mean = 0,45
0,34
0,40
0,46
0,51
0,57
Certainty is 95,00% from 0,37 to 0,54 ppm

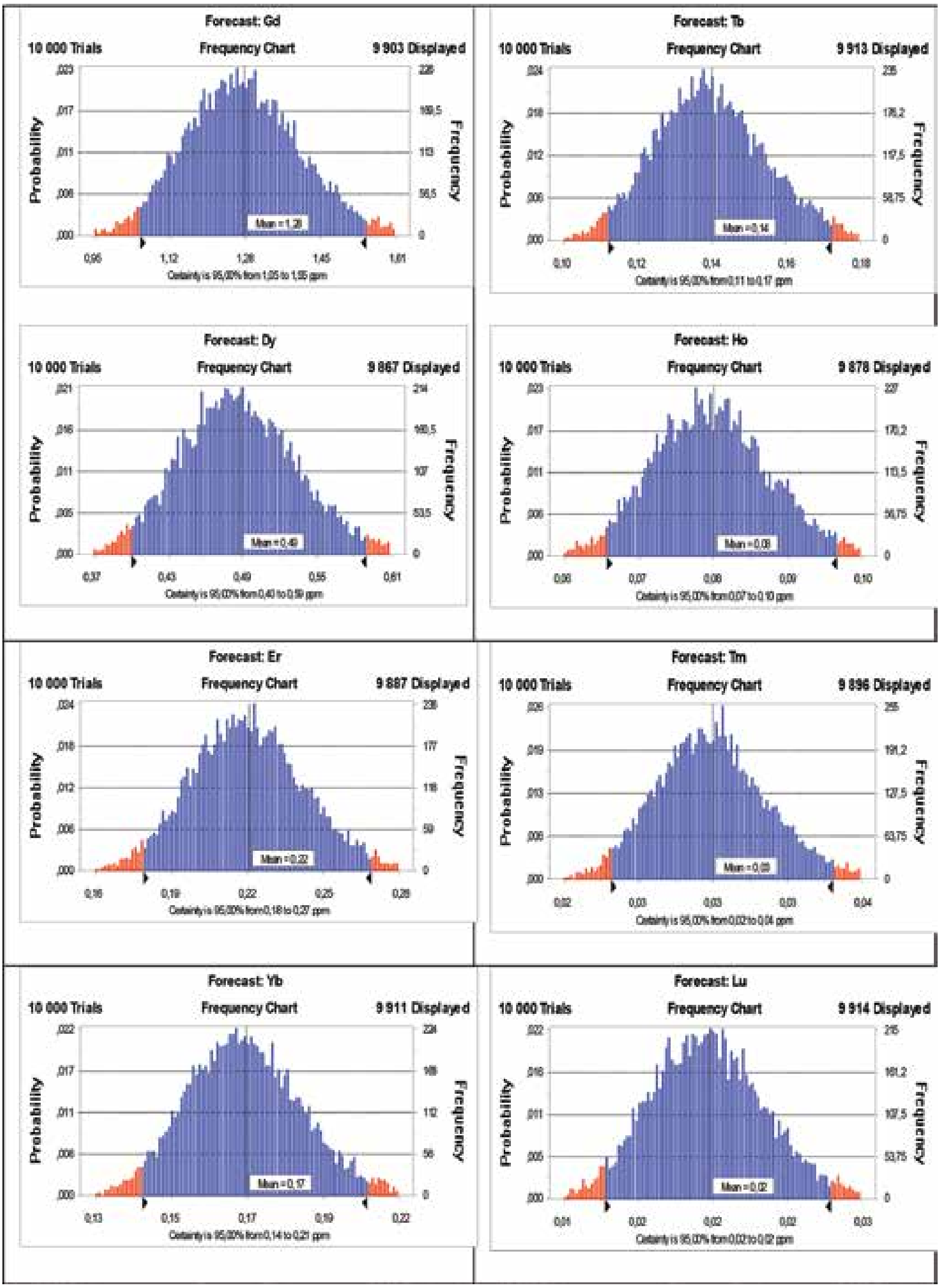


Figure 1. The frequency chart of the 16 analyzed REEs forecasted with 95% confidence level (source: own work).

Statistics	Total (ppm)
Trials	10,000
Mean	56.59
Median	56.49
Mode	—
Standard deviation	2.89
Variance	8.36
Skewness	0.21
Kurtosis	3.11
Coeff. of variability	0.05
Range maximum	45.78
Range minimum	69.17
Range width	23.38
Mean std. error	0.03

Table 2. Statistical report of outcomes from the simulation.

Percentile	Total (ppm)
0%	45.78
10%	53.00
20%	54.16
30%	55.01
40%	55.78
50%	56.49
60%	57.20
70%	58.02
80%	59.00
90%	60.34
100%	69.17

Table 3. Percentile report of outcomes from the simulation.

[23, 24], or in other words, positive coefficients indicate that an increase in the assumption is associated with an increase in the forecast; negative coefficients imply the reverse [19, 20]. The MC simulation results have then been used also to perform the SA, presented in the form of tornado charts (see **Figures 4** and **6**) and spider charts (see **Figures 5** and **7**). According to [72] the concentrate that contains a mix of phosphates (apatite and monazite) can be further enriched through magnetic separation thanks to the paramagnetic property of monazite (apatite is nonmagnetic). Magnetic separation leads to the production of a concentrate containing 17.5% of the initial phosphate content (monazite mainly) and the REE content from 170 ppm to 5,000 ppm for Ce (90 ppm to 2,800 ppm for La and 70 to 2,300 ppm for Nd).

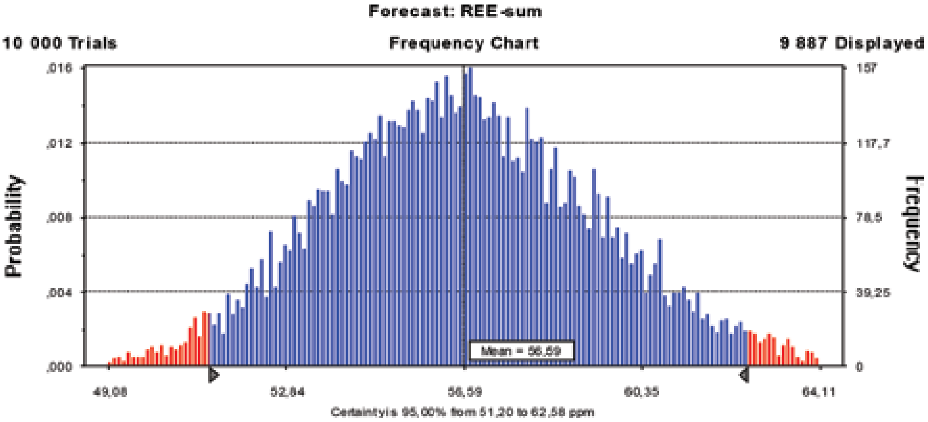


Figure 2. Frequency chart of the total REE forecast expression (95% confidence level), obtained from a MC simulation of 10,000 runs. Certainty range is from 51.20 pm to 62.58 ppm (source: own work).

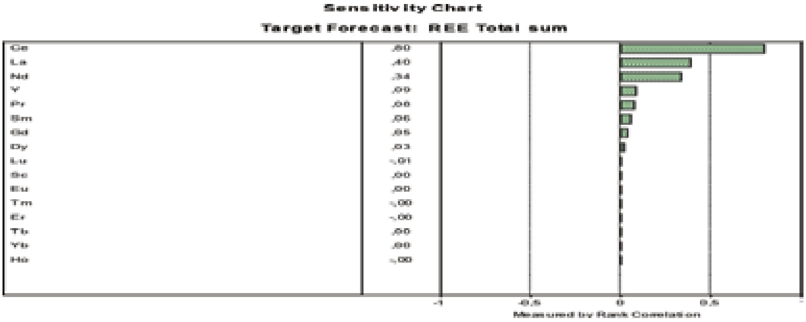


Figure 3. Sensitivity analysis with confidence levels of 95% (created by SRCC) (source: own work).

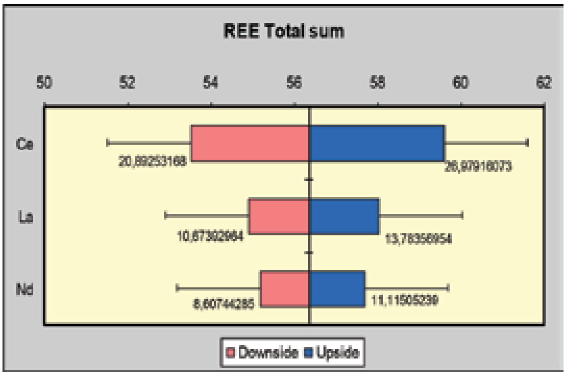


Figure 4. Tornado sensitivity chart of the Ce, La, and Ne scenario based on the percentiles of the variables, testing range of 10–90%. Error bars indicate mean standard errors (source: own work).

The sensitivity analysis demonstrates that Ce, La, and Ne are the most sensitive parameters and will be used for further analysis. The tornado and spider charts have been created on the basis of data included in the newly built tables, **Tables 4–7**, respectively. Tornado chart and spider

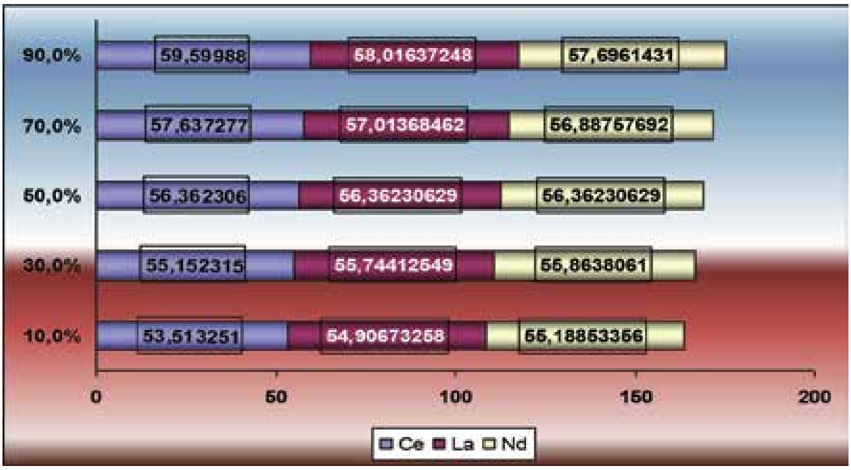


Figure 5. Spider sensitivity chart of the Ce, La, and Ne scenario based on the percentiles of the variables, testing range of 10–90%. Error bars indicate mean standard errors (source: own work).

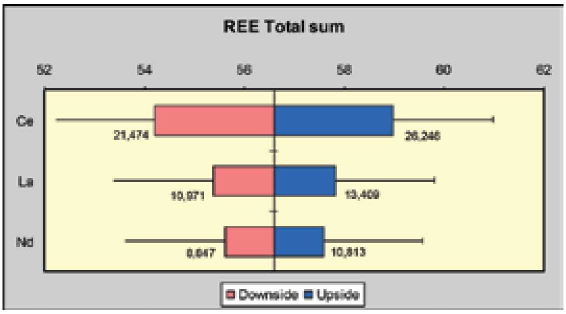


Figure 6. Tornado sensitivity chart of the Ce, La, and Ne scenario based on the percentage deviation from the base case method, testing range from −10% to +10%, using existing cell values (source: own work).

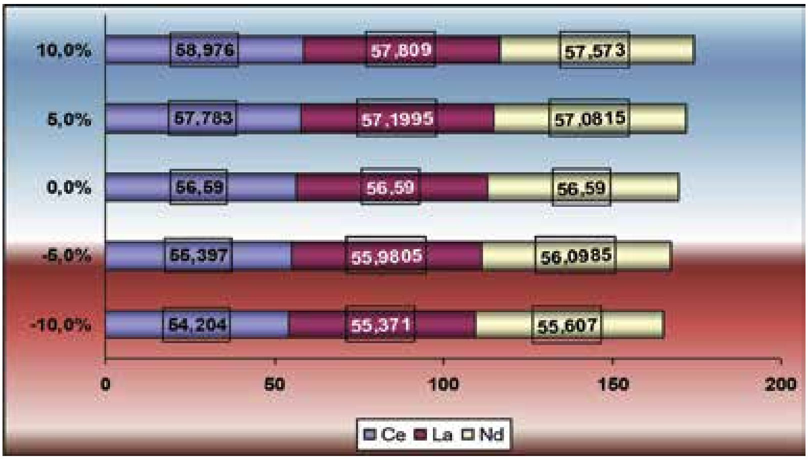


Figure 7. Spider sensitivity chart of the Ce, La, and Ne median value scenario based on the percentage deviation from the base case method, testing range from −10% to +10%, using existing cell values (source: own work).

	REE total sum			**Input**		
Variable	**Downside**	**Upside**	**Range**	**Downside**	**Upside**	**Base case**
Ce	53.51325061	59.59987966	6.086629053	20.89253168	26.97916073	23.74158736
La	54.90673258	58.01637248	3.109639906	10.67392964	13.78356954	12.12950335
Nd	55.18853356	57.6961431	2.507609539	8.60744285	11.11505239	9.78121558

Table 4. The MC simulation results, using CB for the tornado sensitivity analysis-sensitivity table.

REE total sum					
Variable	**10.0%**	**30.0%**	**50.0%**	**70.0%**	**90.0%**
Ce	53.51325061	55.15231499	56.36230629	57.63727651	59.59987966
La	54.90673258	55.74412549	56.36230629	57.01368462	58.01637248
Nd	55.18853356	55.8638061	56.36230629	56.88757692	57.6961431

Table 5. The MC simulation results, using CB for the spider sensitivity analysis-sensitivity table.

	REE total sum		**Input**			
Variable	**Downside**	**Upside**	**Range**	**Downside**	**Upside**	**Base case**
Ce	54.204	58.976	4.772	21.474	26.246	23.86
La	55.371	57.809	2.438	10.971	13.409	12.19
Nd	55.607	57.573	1.966	8.847	10.813	9.83

Table 6. The MC simulation results, using CB for the tornado sensitivity analysis table.

REE total sum					
Variable	**−10.0%**	**−5.0%**	**0.0%**	**5.0%**	**10.0%**
Ce	54.204	55.397	56.59	57.783	58.976
La	55.371	55.9805	56.59	57.1995	57.809
Nd	55.607	56.0985	56.59	57.0815	57.573

Table 7. The MC simulation results, using CB for the spider sensitivity analysis-sensitivity table.

chart of the Ce, La, and Ne median-value base case model for input testing ranging from 10 to 90% that used percentiles of the variables method were presented in **Figures 4** and **5**, while tornado chart and spider chart of the Ce, La, and Ne based on the existing cell-value base case model for input testing ranging from −10% to +90% that used percentage deviation from the base case method were presented in **Figures 6** and **7**, respectively. Red bar indicates that the value was produced by the downside (lower bound), and a blue bar indicates that the value was produced by the upside (upper bound). Error bars indicate mean standard errors. The importance of the examined REEs is illustrated by the length of the associated bar. The rest 13

REEs were not included in the process of generating tornado and spider charts as other thirteen REEs are not in the field of ENVIRRE project research scope and interest.

Spider chart is obtained by perturbing Ce, La, and Nd median values (input variables) at consistent (testing) range from 10 to 90% from the base case, which used percentile of the variables from the base case method. The vertical y-axis maps the location measure of distribution expressed in percentages (percentile of the variables) ranging from 10 to 90% (see **Figure 6**). The variation of each input parameter (Ce, La, and Nd) (e.g., by 10, 50, and 90%) showed how much the output (REE Total sum) changes.

Spider chart is obtained by perturbing Ce, La, and Ne median values (input variables) at consistent (testing) range from 10 to 90% from the base case, which used percentile of the variables from the base case method. The vertical y-axis maps the location measure of distribution expressed in percentages (percentile of the variables) ranging from 10 to 90% (see **Figure 6**). The horizontal x-axis maps the sum of analyzed REEs (in ppm). As a result, the spider chart enables the possibility to simultaneously compare the examined REEs [23, 24].

5. Conclusions

This study refers to uncertainty in the input parameters used to create LCI of REE recovery processes from secondary sources performed according to ISO 14040 (2006). The focus of this study is defined in the goal and scope and was developed using the primary and secondary data.

Due to uncertainty analysis, a final result is obtained in the form of value range. The results from this study suggest that MC simulation is an effective method for quantifying parameter uncertainty in LCA studies.

The analyzed parameters are assigned with lognormal distribution. It is concluded that uncertainty analysis offers a well-defined procedure for LCI studies; early phase of LCA as the deterministic analysis does not include uncertainty in the input data.

The methodological approach regarding databases and boundaries was transparent and fully documented. Moreover, the results of this study can help to assess environmental impacts of rare earth mining, because production of REEs is associated with considerable environmental burdens. Additionally these result inventory data will be available for LCIA and, finally, for full LCA analysis. The obtained results may be also useful and interesting for further studies of REE recovery and could be used to other domestic and international LCA studies, and the study results demonstrate the utility of the MC simulation for a clear interpretation of LCA results. Moreover, they can also help scientist gain a cleaner understanding of the stochastic modeling in the environmental engineering and could be useful tool for decision support methods such as multi-criteria decision analysis.

And finally, consideration of uncertainty in LCA provides additional scientific information for decision-making, as discussed in the work of Romero-Gámez et al. [73].

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Compliance with ethical standards

Conflict of interest: the authors declare that they have no conflict of interest.

Research is not involving human participants and/or animals.

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Chapter 4

Lanthanide Soil Chemistry and Its Importance in Understanding Soil Pathways: Mobility, Plant Uptake, and Soil Health

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Additional information is available at the end of the chapter

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Abstract

The lanthanide elements or rare earth elements (REEs) are an active soil science research area, given their usage as micro-fertilizers, documented cases of environmental impact attributed to industry/mining, and their ability to identify lithologic discontinuities and reveal active soil processes. To fully understand REEs requires an understanding of their chemical reactivity, both for the individual elements and their behavior as a group of elements. The elements of the lanthanide series, including La and Y, may have subtle to very perceptible chemical differences that when viewed collectively reveal information that gives emphasis to soil processes that clarify soil behavior or soil genesis. This chapter concentrates on lanthanide soil chemistry and shows how the soil chemistry of REEs may support soil science investigations.

Keywords: rare earth elements, hydrolysis, complexation, adsorption, oxidation-reduction

1. The inorganic chemistry of the rare earth elements

In soil science the uniqueness and importance of the rare earth elements (REEs) arise because their respective concentrations as a function of atomic number have been employed to (i) assess soil genesis, (ii) augmenting soil fertility, (iii) evaluate anthropogenic impacts, and (iv) are sufficiently mobile to infer the intensity of key pedogenic processes. Soil mineralogy has documented that specific rare earth elements or collections of REE are present in specific minerals as a result of lattice isomorphic substitution or are unique minerals based on the presence of specific rare earth elements [1].

The rare earth elements (REE) are the 14 elements comprising the Lanthanide series: 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) [1, 2]. The Lanthanide series consists of unique elements characterized as having a ground state electronic configuration with at least one electron in the 4f electronic orbitals. Yttrium (Y) is frequently associated with the REEs because of its small ionic radius, approximately the same ionic radius as Ho. Lanthanum (La) is associated with the rare earth elements because of its Periodic Table position and its trivalent chemical affinity. Promethium undergoes rapid radioactive decay (half-life is 2.62 years) and its presence in the natural environment is virtually non-existent [1].

The lanthanide series is defined as elements having partially to filled 4f orbital ground state electronic configurations, with REE^{3+} species resulting from having three electrons removed from their d, s and f orbitals (**Table 1**). The number of f orbital electrons for each REE^{3+} species

	Atomic[1]		**Ionic Radius**[2]		**Ground State**
Element	**Number**	**Weight**	**CN6**	**CN8**	**Configuration**[1]
			10^{-12} meters		
Lanthanum (La)	57	138.9055	103.2	116	$[Xe]5d^1 6s^2$
Cerium (Ce)	58	140.12	101	114.3	$[Xe]4f^1 5d^1 6s^2$
Ce^{4+}			87	97	[Xe]
Praseodymium (Pr)	59	140.9077	99	112.6	$[Xe]4f^3 6s^2$
Neodymium (Nd)	60	144.24	98.3	110.9	$[Xe]4f^4 6s^2$
Promethium (Pm)	61	145	—	—	$[Xe]4f^5 6s^2$
Samarium (Sm)	62	150.36	95.8	107.9	$[Xe]4f^6 6s^2$
Europium (Eu)	63	151.96	94.7	106.6	$[Xe]4f^7 6s^2$
Eu^{2+}			117	125.0	[Xe]
Gadolinium (Gd)	64	157.25	93.8	105.3	$[Xe]4f^7 5d^1 6s^2$
Terbium (Tb)	65	158.9254	92.3	104.0	$[Xe]4f^9 6s^2$
Dysprosium (Dy)	66	162.50	91.2	102.7	$[Xe]4f^{10} 6s^2$
Holmium (Ho)	67	164.9304	90.1	101.5	$[Xe]4f^{11} 6s^2$
Erbium (Er)	68	167.26	89.0	100.4	$[Xe]4f^{12} 6s^2$
Thulium (Tm)	69	168.93	88.0	99.4	$[Xe]4f^{13} 6s^2$
Ytterbium (Yb)	70	173.04	86.8	98.5	$[Xe]4f^{14} 6s^2$
Lutetium (Lu)	71	174.967	86.1	97.7	$[Xe]4f^{14} 5d^1 6s^2$
Yttrium (Y^{3+})	39	88.9059	90.0	101.9	$[Kr]4d^1 5s^2$

[1] Greenwood and Earnshaw [1].

[2] Lee [2], Henderson [3].

CN6 is coordination number six and CN8 is coordination number eight.

Table 1. Chemical properties of the trivalent rare earth elements, including La and Y.

corresponds with their atomic number. Because the f-orbitals are mostly non-interactive, the REEs exhibit considerable ionic bonding character and are considered hard acids [1, 2].

Europium has a half-filled f-orbital, allowing stability for the Eu^{2+} species (**Table 1**); therefore, Eu is a lattice constituent in selected minerals important to igneous rook classification. Cerium exhibits oxidation-reduction behavior permitting either Ce^{3+} {[Xe]$4f^1$} or Ce^{4+} {[Xe]} to be present in the soil environment.

The influence of f-orbitals on the chemical attributes of the REEs observed by the regular decrease in the ionic radii on progression from La to Lu (**Table 1**). The so-called "Lanthanide Contraction" arises because of (i) the incomplete electric field shielding by the f-orbitals and (ii) unit increases in nuclear charge. The importance of the lanthanide contraction is revealed in greater chemical affinity for hydrolysis and greater stability of selected complexes on progression across the lanthanide series. The LREE are the light rare earth elements, comprised of the elements La to Eu, and the HREE are the heavy rare earth elements, comprised of the elements Gd to Lu.

The ionic radius is largely dependent on its atomic number, oxidation state, the coordination number (CN) and the radius of the anionic species. The ionic radii of REEs having octahedral coordination (CN 6) range from 103.2 pm for La to 86.1 pm for Lu (pm = picometer = 10^{-12} m) and the ionic radii of the REEs having cubic coordination (CN 8) range from 116.0 pm for La to 97.7 pm for Lu (**Table 1**).

2. Rare earth element rock and primary-secondary mineral abundances

Rock REE concentrations are predicated on rock type and source area. Most REE parent material compositions range from 0.1 to 100 mg/kg, thus REEs have moderate abundances. Typically, felsic's have greater REE concentrations than mafic's, with the LREE concentrations greater than the HREE concentrations. Similarly, argillaceous sediments have greater REE concentrations than limestones and sandstones.

The Oddo-Harkins rule states that an element with an even atomic number has a greater concentration than the next element in the Periodic Table. REEs typically obey the Oddo-Harkin rule. The PAAS, NASC, loess, and selected geochemical soil surveys usually reflect the Oddo-Harkin rule (**Table 2**).

Secondary minerals are (1) minerals formed after the rock enclosing the mineral was formed or (2) minerals that have chemically altered from primary minerals and have been transported. In some cases, REE are involved with isomorphic substitution or undergo adsorption reactions with phyllosilicates or oxyhydroxides. Precipitation reactions with fluoride, phosphate and carbonate may yield a variety of secondary REE minerals [6]. Cerianite (CeO_2) may form in oxic soil environments [7, 8].

Clark [6] provided a listing of important REE-bearing minerals, including (i) fluorite (CaF_2 where Y and Ce replace Ca), (ii) allanite [$(Ce,Ca,Y)_2(Al,Fe^{2+},Fe^{3+})_3(SO_4)_3OH$], (iii) sphene ($CaTiSiO_5$

Element	PAAS[1]	NASC[1]	Loess[1]	Soil[2]
	mg/kg			
La	38.2	32	35.4	26.1
Ce	79.6	73	78.6	48.7
Pr	8.83	7.9	8.46	7.6
Nd	33.9	33	33.9	19.5
Sm	5.55	5.7	6.38	4.8
Eu	1.08	1.24	1.18	1.2
Gd	4.66	5.2	4.61	6.0
Tb	0.774	0.85	0.81	0.7
Dy	4.68	5.8	4.82	3.7
Ho	0.991	1.04	1.01	1.1
Er	2.85	3.4	2.85	1.6
Tm	0.405	0.5	bdl	0.5
Yb	2.82	3.1	2.71	2.1
Lu	0.433	0.48	bdl	0.3
Y	27	27	25	

[1] Reported in McLennan [4].

PAAS is Post-Archean Australian Average Shale, NASC is North American Shale Composite.

[2] Reported in Kabata-Pendias [5].

(bdl) is below detection limit.

Table 2. Rare earth element abundances for various parent materials.

where Y and REE replace Ca), (iv) Zircon ($ZrSiO_4$ where Y and HREE replace Zr), (v) apatite (Ώ$_5$(XO_4)$_3$(F,OH,Cl); Ώ + =Ca,Be,Ce,Pb and Y and REE replace Ca), (vi) monazite ((CeLa)PO_4), (vii) xenotime (YPO_4 where REE replace Y), (viii) rhabdophane ((Ce,La)PO4 and REE replace La), and (ix) bastnaesite (LaREE fluorocarbonate).

3. Rare earth element soil abundances

Rare earth element abundances in soils are influenced by (i) parent materials and organic matter contents, (ii) soil texture, (iii) pedogenic processes, and (iv) anthropogenic activities [5]. As with mineral assemblies, the soil LREE concentrations are generally greater than the soil HREE. Menfro soil series exists on uplands along the confluence of the Missouri and Mississippi Rivers (USA) and are developed in thick loess deposits. These well drained soils exhibit an A – E – Bt – C horizon sequence with acidification, Ca leaching and clay lessivage the dominant soil processes. The REE distribution shows that the light rare earth elements (La to Eu) are more abundant than the heavy REEs (Gd to Lu) and the distribution follows the Oddo-Harken rule. **Figures 1** and **2**

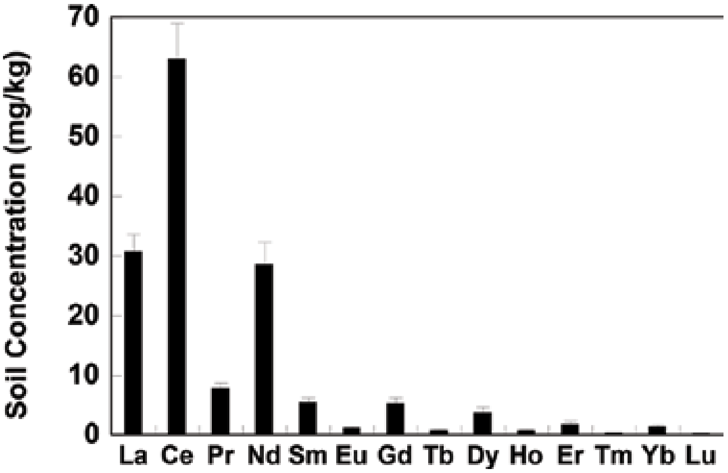

Figure 1. REE concentration distribution in two paired soil profiles of the Menfro series. (error bars are standard deviation). (Source: Data originally in [9]).

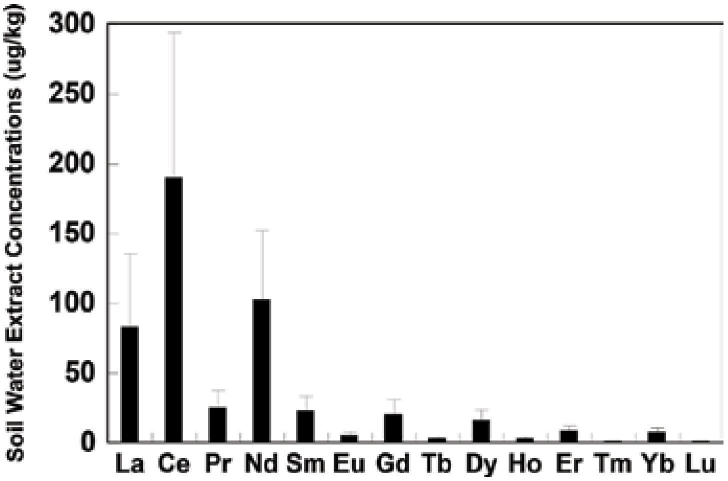

Figure 2. REE water extract concentration distribution in two paired soil profiles of the Menfro series (fine-silty, mixed, superactive, mesic Typic Hapludalfs). (error bars are standard deviation). (Source: Data originally in [9]).

The corresponding REE distribution from soil water extracts from the Menfro series closely correspond to the whole soil REE distribution.

4. Chemical reactivity of the rare earth elements in the soil environment

4.1. REE hydrolysis and complexation reactions

The hydrolysis of REE^{3+} species has been extensively investigated and numerous authors have published hydrolysis data [10–14]. For example, Eu^{3+} will undergo hydrolysis to produce $Eu(OH)^{2+}$, $Eu(OH)_2^+$, $Eu(OH)_3$ and $Eu(OH)_4^-$, having log K° constants log $K_{11}° = -7.64$, log $K_{12}° = -15.1$, log $K_{13}° = -23.7$, log $K_{14}° = -36.2$, respectively [13]. Nd and Yb hydrolysis speciation as a function of pH illustrates that the Nd^{3+} and Yb^{3+} species are the dominant species in acidic and near-neutral pH environments, whereas the Nd and Yb mono- and di-hydroxy species are the dominant species in alkaline and $Nd(OH)_3$, $Nd(OH)_4^-$ $Yb(OH)_3$, and $Yb(OH)_4^-$ are the dominant species in strongly alkaline pH environments (**Figures 3** and **4**). The hydrolysis speciation of any REE^{3+} species is like that of Eu^{3+}, with a necessary understanding that the relative stabilities of the various REE hydrolytic species are more stable on transition with increasing atomic number across the Lanthanide series (**Table 3**).

Complexation of the REE elements involves coordination with primarily anionic species and typically is expressed as:

$$REE^{3+} + yL^{n-} = REE - L_y^{(3-yn)},$$

where L^{n-} is an inorganic ligand with n ionic charge and y is the stoichiometric coefficient. Common inorganic complexing species with REE^{3+} include NO_3^-, Cl^-, F^-, SO_4^{2-}, CO_3^{2-}, and HPO_4^{2-}. Carbonate and dicarbonate complexes exist, with carbonate complexes more prevalent in the LREEs and dicarbonate complexes more prevalent in the HREE [11, 16, 17]. Luo and Byrne [18] documented the carbonate complexing behavior of the REE. Cantrell and Byrne [16] estimated that 86% of the La speciation existed as a dicarbonate complex, whereas 98% of the Lu speciation occurred as the dicarbonate complex. Thus, for the Lanthanide Series, the dicarbonate complex becomes increasingly more stable with increasing atomic number. For illustration purposes, the La speciation involving carbonate complexes of water in equilibrium

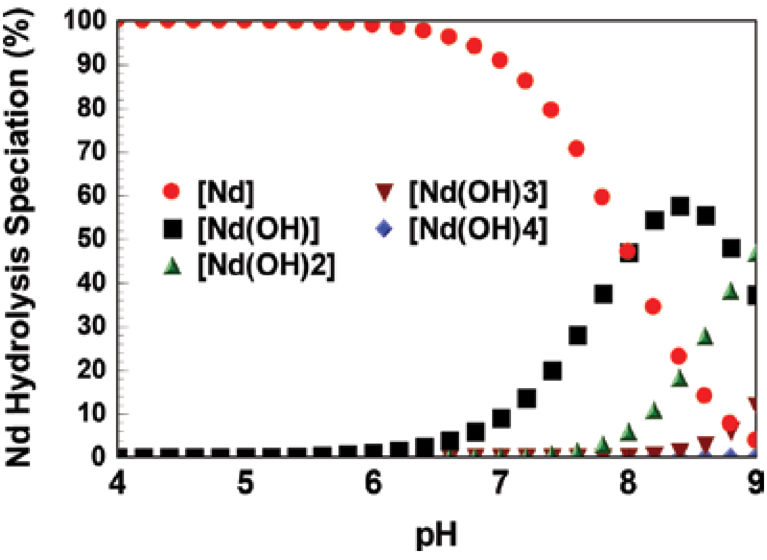

Figure 3. Aqueous hydroxyl speciation of Nd(III) over a pH interval. The Nd speciation involved concentrations without recourse to activity coefficients and overall formation quotients from Baes and Mesmer [10]. The total Nd concentration was 10^{-6} M.

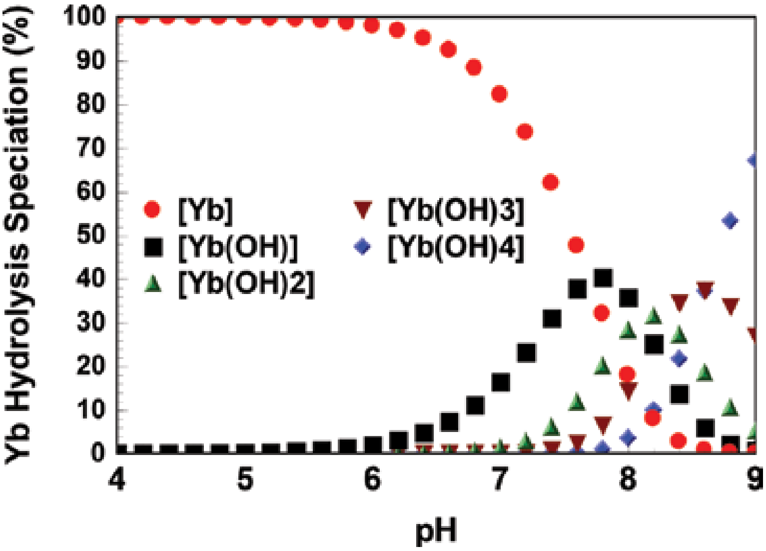

Figure 4. Aqueous hydroxyl speciation of Yb(III) over a pH interval. The Yb speciation involved concentrations without recourse to activity coefficients and overall formation quotients from Baes and Mesmer [10]. The total Yb concentration was 10^{-6} M.

Element	Log $Q_{1,1}$[1]	Infinite dilution stability constants			
		log CO_3	log $(CO_3)_2$	log Oxalate[3]	log HPO_4
La	−8.5	6.82	11.31	5.87	4.87
Ce	−8.3	6.95	11.50	5.97	4.98
Pr	−8.1	7.03	11.65	6.25	5.08
Nd	−8.0	7.13	11.80	6.31	5.18
Sm	−7.9	7.30	12.11	6.43	5.35
Eu	−7.8	7.37	12.24	6.52	5.42
Gd	−8.0	7.44	12.39	6.53	5.49
Tb	−7.9	7.50	12.52	6.63	5.54
Dy	−8.0	7.55	12.65	6.74	5.6
Ho	−8.0	7.59	12.77	6.77	5.64
Er	−7.9	7.63	12.88	6.83	5.68
Tm	−7.7	7.66	13.00	6.89	5.71
Yb	−7.7	7.67	13.08	6.95	5.73
Lu	−7.6	7.70	13.20	6.96	5.75
Y	−7.7			6.66	

[1] Q11 is the overall formation quotient for a hydrolysis product, $Ln(OH)^{2+}$.

[2] Baes and Mesmer [10].

[3] Carbonate-bicarbonate, phosphate, fluoride reported in Millero [11].

[4] Mono-oxalato complexation constants at infinite dilution from Schijf and Byrne [15].

Table 3. Hydrolysis and complexation constants for the La, REEs and Y.

with typical atmospheric concentrations of CO_2 are displayed in **Figure 5**. Similarly, the REE-Phosphate complex distribution as a pH function for La is displayed and shows that La^{3+} and $La(HPO_4)$ are the dominant species (**Figure 6**).

The hydrolysis, carbonate and EDTA ligand complex, and solubility products for La, Eu, and Lu (**Table 4**) show the expected trend of lanthanide contraction.

Millero [11] and Gramaccioli et al. [20] observed that REE-fluoride complexes obtained greater stability on transition from La to Lu. REE-phosphate precipitates have been implicated in limiting the mobility of the REE in soils and sediments [9].

4.2. Reactions involving organic complexation

Common organic complexes include: oxalic acid, malic acid and other low molecular weight organic acids and the semi-stable humus components fulvic and humic acids [15, 21–25]. Tyler and Olsson [26] reported that between 46 and 74% of the REEs extracted from the soil water of a Cambisol were associated with dissolved organic carbon. As with the inorganic REE complexes, organic REE complexes tend to show greater stability for the HREEs than the LREEs [15, 16].

Cteiner [27] observed monazite ($NdPO_4$) reactivity at low temperatures and low ionic strength to determine the influence of Cl^-, HCO_3^-, SO_4^{2-}, oxalate and acetate on solubility. At pH levels ranging from 6.0 to 6.5 Nd(oxalate) was the dominant species, followed by Nd^{3+} and $NdSO_4^+$. Gu et al. [21] independently proposed that organic materials may have multiple binding sites with a range of complexing bond strengths that strongly retain REE at low concentrations and provide non-specific REE retention at higher concentrations.

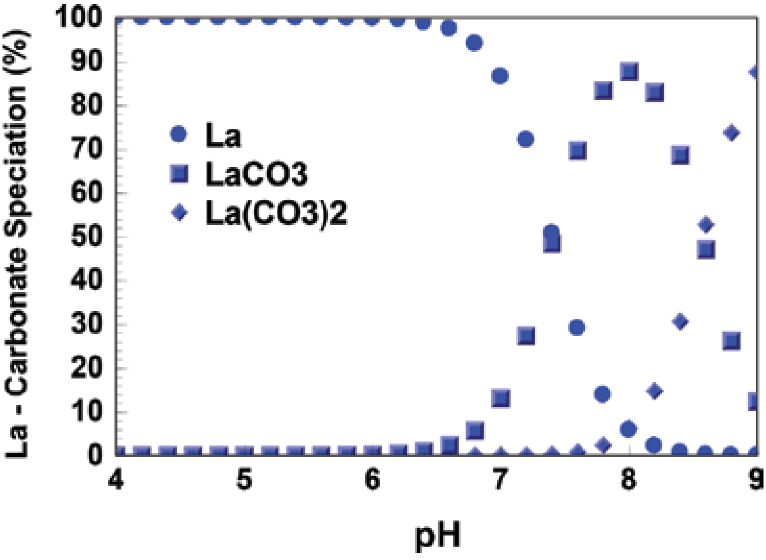

Figure 5. Aqueous hydroxyl and carbonate speciation of La(III). The La speciation involved concentrations with activity coefficients determined using by the Debye-Hückel equation. The carbonate complexation constants from Luo and Byrne [18] and acid dissociation constants for carbonic acid and bicarbonate from Essington [19].

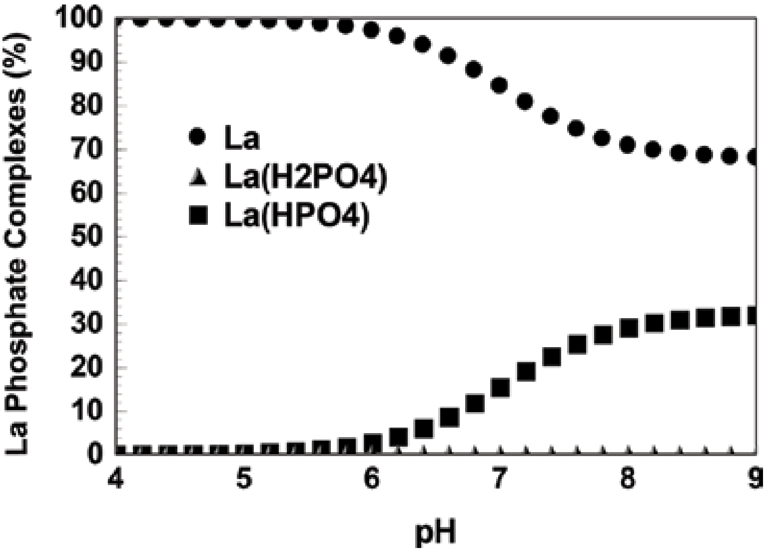

Figure 6. Aqueous carbonate speciation of La(III). The La speciation involved concentrations with activity coefficients determined using by the Debye-Hückel equation. The phosphate carbonate complexes are located in Millero [11].

The role of dissolved organic matter and element mobility is an active area of research. In a plot experiment, the release of La, Ce, Gd and Y decreased gradually as the pH of the soil was

Reaction	log β, Ksp, Log K
$La^{3+} + OH^- = La(OH)^{2+\backslash}$	−9.1
$La^{3+} + 2OH^- = La(OH)_2^+$	−17.9
$La(OH)_{3(s)} = La^{3+} + 3OH^-$	−20.3
$Eu^{3+} + OH^- = La(OH)^{2+}$	−8.4
$Eu^{3+} + 4OH^- = La(OH)_4^-$	−26.2
$Eu(OH)_{3(s)} = Eu^{3+} + 3OH^-$	−24.5
$Lu^{3+} + OH^- = Lu(OH)^{2+}$	−8.0
$La(OH)_{3(s)} = Lu^{3+} + 3OH^-$	−25.1
$La^{3+} + CO_3^{2-} = [La(CO_3)]^+$	5.00
$Eu^{3+} + CO_3^{2-} = [Eu(CO_3)]^+$	5.76
$Lu^{3+} + CO_3^{2-} = [Lu(CO_3)]^+$	6.02
$La^{3+} + EDTA^{4-} = [La(EDTA)$	]$^{-}$14.48
$Eu^{3+} + EDTA^{4-} = [Eu(EDTA)]$	$^{-}$16.23
$Lu^{3+} + EDTA^{4-} = [Lu(EDTA)]$	$^{-}$18.19

Source: Smith and Martell [14].

Table 4. Selected constants involving lanthanum, europium and lutetium with hydroxide, carbonate and EDTA (ethylenediaminetetraacetate).

raised from strongly acidic to alkaline pH ranges [28]. Davranche et al. [29] demonstrated that REEs and humic acid complexes frequently dominate soil aqueous systems, especially in near-neutral pH levels and at greater dissolved organic carbon concentrations. Pourret et al. [30] observed the strong competitive interaction between humic acids and carbonates for REE complexation, especially at increasing pH levels. Similarly, Wu et al. [24] described the strong competition from EDTA, humic and fulvic acids influencing lanthanum adsorption onto goethite as a pH function.

5. Exchange and adsorption reactions

Cation exchange and adsorption reactions involving cations and their hydrolytic products are dominant soil processes. Aide and Aide [9] reviewed REE reactions in the soil environment, including REE adsorption. Numerous studies cited in this review produced similar REE adsorption conclusions, including: (i) cation exchange reactions are largely associated with basal planar surfaces and pH-dependent silanol and aluminol reactions at edge positions, (ii) predominance of outer-sphere complexes occur at pH levels less than 4 and an increasing degree of inner sphere complexes at pH levels greater than 5, (iii) cation exchange was consistent with one electrostatic and non-specific site and one specific complexation site involving edge aluminol groups, (iv) REE affinity was reduced by increases in the ionic strength, (v) REE complexation affinity was greater at higher pH intervals. Conversely Tertre et al. [31] demonstrated the inner-sphere nature of aluminol sites on kaolinite and montmorillonite. Tang and Johannesson [32] noting that REE adsorption was more pronounced at greater pH intervals. At lower pH intervals, adsorption was attributed to REE^{3+} species whereas at greater pH intervals adsorption was attributed to REE^{3+} and REE-carbonate species. The adsorption constants increased regularly with an increase in REE atomic number.

6. Rare earth elements and soil availability

Tyler [33] reviewed the importance of REE in soils and plants in which he underscored the recent contributions of Chinese soil scientists in addressing REEs as plant promoting elements. Tyler acknowledged that the traditional definitions of plant essential nutrients may be challenged because of recent research involving the REEs and other elements. Pang et al. [34] documented the increasing use of REE-bearing fertilizers in China. More research needs to be performed to accurately assess whether any of the REEs are "plant essential" or simply supportive of plant growth and development.

Rare earth elements frequently have been shown to have greater concentrations in plant roots than leaves or above-ground woody tissue [35–37]. Li et al. [38] demonstrated that a 0.1 *M* HCl based extraction protocol effectively indicated REE plant availability. Lanthanum and to a lesser degree the other REEs exhibited root concentrations that were inversely proportional to the soil pH [36]. Using nutrient solutions, Gu et al. [39] demonstrated that sulfate inhibited REE uptake. Zhang et al. [40] reported that a mixture of malic acid and citric acid was effective in estimating REE plant availability. Cao et al. (200b) showed that water-soluble, exchangeable, and carbonate-organic fractions resulting from a selective-sequential extraction protocol were effective predictors of REE uptake in alfalfa (*Medicago sativa.* L). Wu et al. [25] isolated sap from xylem from non-hyperaccumulating REE plants to discover that aspartic acid, asparagine, histidine and glutamic acid were correlated with La and Y xylem transport.

Tyler and Olsson [41] showed that the majority of the REE were 40–50% removed from the A and E horizons of a Swedish Haplic Podzol. In a subsequent investigation Tyler [42] performed a *Fagus sylvatica* growth study and demonstrated only incidental REE uptake, except for Eu which was preferentially accumulated, mostly likely as Eu^{2+}. Soil liming has been shown to reduce REE concentrations in soil solution [43]. Tyler and Olsson [35] documented substantial REE plant uptake of grass grown in a Cambisol.

Aide (unpublished research) employed a 45 mμ filtered water leach extraction on a series of Endoaqualfs (poorly drained Alfisols) and Eutrochepts (somewhat poorly-drained Inceptisols) in southeastern Missouri to show REE availability (**Figure 7**). Cerium was consistently the most abundant REE leached from the soils, followed by La and Nd. The LREE had greater leachate concentrations than the HREE. REE compliance with the Oddo-Harkin's rule was consistently observed.

Loell et al. [44] employed total and EDTA extractions to infer bioavailability and reported that Ce had the greatest total concentration and the lowest bioavailability, whereas Y had the highest availability expression. Using regression analysis, the REE bioavailability was a function of pH, clay content, organic carbon and the total REE concentration. Mihajlovic et al. [45] observed the vertical distribution of REE in marshland soils using selective sequential extractions and documented that the residual fraction exhibited the largest REE abundance, followed by the reducible fraction. They also reported that the LREE were more abundant than the HREE, that the HREE exhibited the greater tendency to leach because of complex formation and the HREE were relatively more abundant in the exchangeable/available fractions.

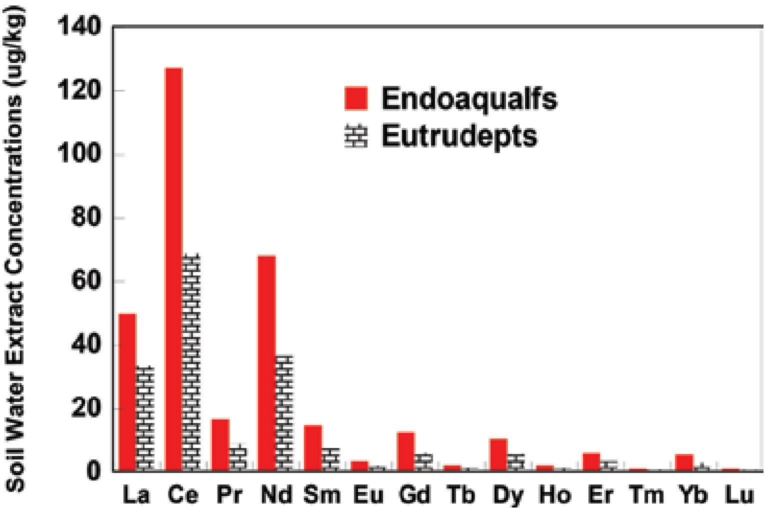

Figure 7. Soil water extract concentrations from two great groups in Missouri. The Endoaqualfs represent 27 observations, whereas the Eutrudepts represent 24 observations.

Selective, sequential extractions have been used to estimate REE plant uptake potential [40, 46–48]. Brantley et al. [49] reinforced the microbial component for REE availability, an area of research that is largely missing within the literature.

7. Rare earth elements and soil development

The importance of the REEs rests with their "signature", which may be defined as either the actual REE concentrations, when displayed by atomic number. Analysis of the REE signatures typically involves identifying evidence of fractionation, i.e., LREE and HREE ratios, La/Yb ratios, Nd/Sm ratios, and the presence of Ce or Eu anomalies. REE signatures have been compared to reveal (i) lithologic discontinuities [9], (ii) the presence of eolian or anthropogenic additions [50], (iii) estimates of the weathering intensities and elemental loss rates of soils [33], and (4) oxidation–reduction conditions in soil [9, 51]. Wang et al. [52] observed that greater soil water contents supported greater overland water flow, in which greater quantities of REE and P were transported. Similarly, Wu et al. [48] observed that apatite and calcium phosphate fertilizers altered the speciation and availability of selected REEs.

In a review of literature, Aide and Aide [9] reiterated numerous studies indicating REE migration in soil profiles. A summarization of the key REE soil transformations are (i) CO_2 and organic matter displace REEs as carbonate complexes and chelates in near surface horizons to support their accumulation in deeper soil horizons because of exchangeable, adsorption or precipitation reactions, (ii) HREE were enriched in the deeper soil horizons to a greater degree than the LREE, whereas other studies have indicated that the LREE were more readily transported to deeper soil horizons, (iii) apatite weathering supports the relatively rapid mobilization of the LREEs, whereas the weathering resistance mineral 'zircon' limits the mobilization of HREEs, (iv) similarities involving the REE signatures among the soil horizons and the host rock have been used to support arguments for parent material uniformity, whereas differences involving the REE signatures among the soil horizons and the host rock have been used to infer lithologic discontinuities (v) argillic (illuvial) horizons may have greater concentrations of LREE than the near-surface horizons (eluvial) inferring that phyllosilicate adsorption is an important soil process, (vi) crystalline Fe-oxyhydroxide and labile organic fractions accumulated HREEs than the LREEs, whereas the soil organic matter fraction representing humic acids and fulvic acids preferentially accumulated LREEs.

As an example, recent unpolished data from the authors of this manuscript follow. The Alred soil series (Loamy-skeletal over clayey, siliceous, semiactive, mesic Typic Paleudalfs) demonstrates differences in the rare earth element signatures to isolate lithologic discontinuities. The Alred series is a deep, well-drained collection of soils formed in cherty hillslope sediments (loess) and the underlying clayey limestone residuum. The eluvial (overlying loess mantle) and the illuvial (hill slope sediments derived from limestone residuum) differ significantly in their respective rare earth element concentrations, suggesting the REE differences are inherited (**Figure 8**).

The overcup series consists very deep, poorly drained, very slowly permeable soils that formed in alluvium (Fine, smectitic, thermic Vertic Albaqualfs). Aide (unpublished data) separated the

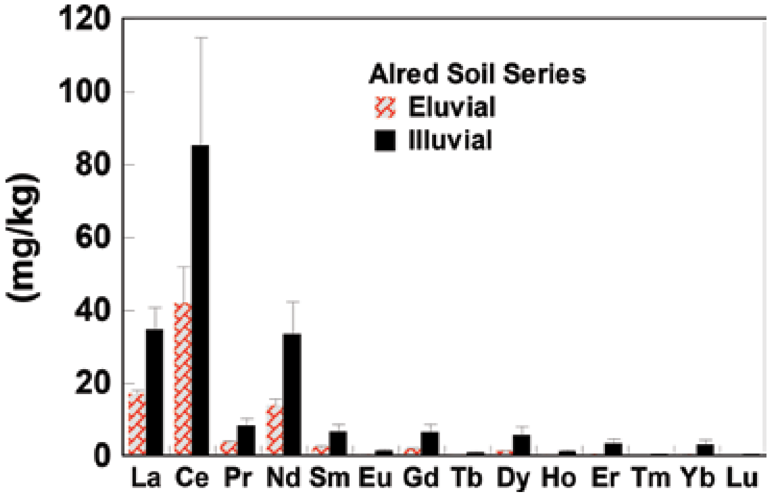

Figure 8. The rare earth element distributions for the eluvial and illuvial horizons of the Alred soil series (Cape Girardeau County, Missouri, USA). Error bars are the standard deviation).

soil horizons into their sand, silt and clay fractions, then determined the REE distribution using aqua regia digestion with ICP-MS. Selecting La for presentation, the La concentrations for the Ap through Btg2 horizons are rather evenly partitioned among the textural separates, with the clay separate showing slightly greater La abundance (**Figure 9**). The other REE elements show similar patterns. The Btg3 and Btg4 separates have greater La expression, especially for the sand separate. The Btg3 horizons are marked by a significant increase in sand-sized glabules

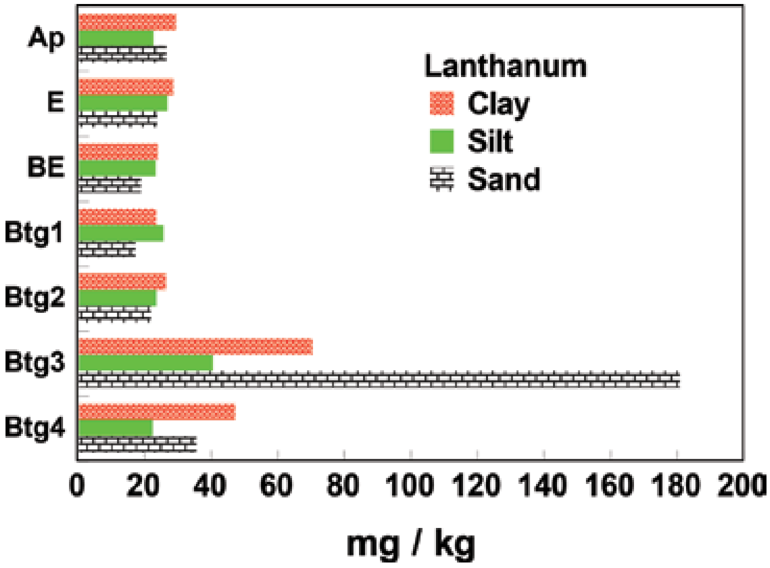

Figure 9. Rare earth element distribution by particle size for the Overcup soil series.

(nodules of Fe- and Mn-oxyhydroxides) and an abrupt increase in pH from an acidic to alkaline regime. Thus, oxidation-reduction and pH appear to be the controlling variables.

8. Future research needs

Future research needs include; (i) understanding of the REE-microbiological interactions, especially in the rhizosphere, (ii) are the REE elements plant essential elements or growth promoting entities, (iii) more complex models (along with thermodynamic data) to better simulate the soil environment, and (iv) anticipate REE impacts to the soil environment because of increasing industrial REE utilization.

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Chapter 5

Lanthanides in Soils of the Cherepovets Steel Mill

Dmitry V. Ladonin

Additional information is available at the end of the chapter

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Abstract

Content of forms of the lanthanides in soddy-calcareous soils at a different distance from the Cherepovets steel mill (Vologda region, Russia) has been studied. In soils near the steel mill, an increased content of Pr and Tb was found, while the content of other light lanthanides (from La to Gd inclusive) is less increased. In addition to increasing of the total content, technogenic pollution leads to increasing the amount and the degree of extraction of acid-soluble forms of the lanthanides from soils. About 80–95% of Ln is located in the residual fraction strongly bound to aluminosilicates. As a result of the processes in the soil, 5–18% of the total content of lanthanides is bound to organic matter and 0.1–5% to Fe and Mn (hydr)oxides. The lanthanides' individual properties are manifested in this interaction: medium lanthanides are mostly bound to organic matter and whole heavy lanthanides to Fe and Mn (hydr)oxides.

Keywords: soddy-calcareous soils, soil pollution, lanthanides, forms of compounds, sequential fractionation, soil organic matter, Fe and Mn (hydr)oxides

1. Introduction

The lanthanides (Ln) comprise a group of 15 elements of which only 1, promethium (Pm), does not occur naturally in the Earth's crust. The lanthanides are placed in the sixth period of the periodic table, the secondary subgroup of the third group. Together with scandium (Sc) and yttrium (Y), the lanthanides are commonly referred to as the rare-earth elements (REE). Due to their special chemical properties, content and peculiarities of accumulation in soils, and the use of methods of determination in natural objects, the lanthanides are usually considered as a group of elements isolated from other TM.

The use of REE in industry, and as a consequence, contamination of the biosphere, has become noticeable only in recent decades, which is related to the development of new technologies and materials on their basis [1, 2]. The lanthanides are generally considered to be of low toxicity for living organisms. Moreover, the efficiency of lanthanide-containing fertilizers, widely used in agriculture in China, is proved [3]. However, environmental risks related to changes in the lanthanide content, mobility, and proportions in soils, caused by enhanced technogenic pollution of soils, are still unknown.

Objective: to study the lanthanides in soils under anthropogenic impact of the Cherepovets steel mill (CSM), Vologda region, Russia

Tasks: (1). To study the total and acid-soluble form content of the lanthanides in soils. (2). To study the forms of the lanthanide compounds in soils using the sequential fractionation

2. Chemical properties of the lanthanides and their distribution

The REE are extremely similar to each other in electron shell structures and, accordingly, in chemical properties. Scandium and yttrium have one *d* and two *s* electrons on their outer electron levels. The lanthanides have also 4f sublevel, gradually filled from Ce to Lu. This structure of electron shells is the reason that 3+ is the main oxidation state for the REE. Although 4+ oxidation state is known for Ce, Pr, and Tb, and 2+ for Sm, Eu, and Yb, in natural conditions only Ce and Eu have oxidation state different from 3+ [4, 5].

La, Ce, Tb, and Er were isolated in pure form in the first half of the nineteenth century and the remaining lanthanides a bit later [6]. The difficulties in isolation of individual elements from rocks, containing their mixture, led to the formation of a sustainable opinion that these elements have similar chemical properties and geochemical behavior [7]. Investigations, carried out later, showed that in the lanthanide series, there are regular changes in chemical properties, associated with structural features of their electron shells. Unlike other heavy metals (HM), whose variation in chemical properties from element to element is not always obvious, in the lanthanide series, there are some interesting regularities.

In the La-Lu series, there is a gradual decrease in ionic radii (so-called lanthanoid compression). This is a consequence of the filling of the 4f level by electrons [5]. As a result, the stability of complex compounds increases, and the pH of the beginning of precipitation of lanthanide hydroxides decreases [4, 8, 9].

Since there are no cases of formation of own solid phases of the lanthanides under soil conditions, it can be assumed that the redistribution of the lanthanides between soil components during soil-forming processes and technogenic pollution is proceeding mainly due to ion exchange, sorption interactions, and complexation. The regularities of sorption of the lanthanides by the main soil components influencing the behavior of heavy metals—(hydr) oxides of iron and manganese, clay minerals, and organic matter—were studied [10–12]. The adsorption of the lanthanides increases significantly with increasing of pH of the soil liquid phase [13–15].

Investigations of lanthanide adsorption by various soil components showed the dependence of the amount of absorbed element on the ionic strength of the solution. In addition, under adsorption from solutions with high ionic strength, the amount of absorbed element increases with increasing atomic number of the element, corresponding to a change in ionic radii. This regularity is absent in adsorption from solutions with low ionic strength [13, 16].

It can be assumed that the differences in individual chemical properties of lanthanides will have a great effect on formation of their compounds in soils, both in background conditions and under technogenic pollution [10–12].

The average content of lanthanides in different rocks depends on their origin and is described in detail in [17]. The most rich in lanthanides are acid magmatic and clay sedimentary rocks.

Another specific distribution feature of the lanthanides in the Earth crust and its individual components is the "sawtoothness" of the graphs, where the atomic number is plotted on x-axis and its content on y-axis (so-called geochemical spectra) (**Figure 1**). This kind of graphs clearly demonstrates one of the basic rules of geochemistry: the Oddo-Harkins rule states that an element with an even atomic number is more abundant than adjacent elements with odd atomic numbers.

Differences in the abundance of even and odd elements, as well as significantly higher abundance of light lanthanides, make difficult to compare characteristics of their behavior and location in natural objects, including soils. To exclude the influence of these differences, in geochemistry, it was suggested to normalize the content of elements in the studied objects to their content in standard objects.

Data on the content of lanthanides in geological rocks are usually to be normalized on composition of chondrites or shales [17–24]. However, chondrites are not suitable for studying lanthanides in soils of different compositions and origins.

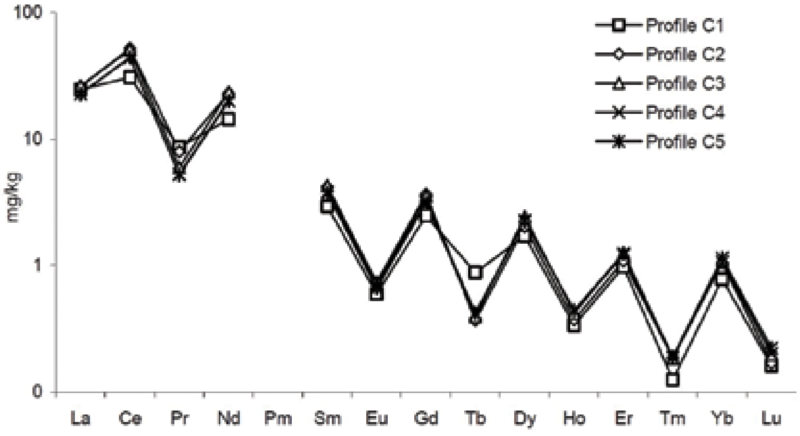

Figure 1. Total content of the lanthanides in the surface horizons of soils in the CSM impact zone, mg/kg.

The clay of the Russian platform [19] is the best object for normalization of the content of lanthanides in the soils studied. The soils of the taiga-forest zone of the European part of Russia, formed on quaternary sediments as a result of the glacier activity, have similar elemental ratio for most of HM. These rocks were formed as a result of processing of the same source material by glaciers [25]. The main differences in the elemental composition of the sediments are related to their granulometric composition. They depend on the ratio of clay minerals with the maximum content of HM and quartz depleted by them.

3. Objects and methods

We've studied the content of lanthanides in the soils of the impact zone of the Cherepovets steel mill. CSM is one of the most powerful sources of technogenic impact on the European territory of Russia. Pollution with heavy metals on the investigated territory has been monitored since 1955 [26, 27]. We selected soil samples from five soil profiles at different distances from the CSM. Profile C1 is located near the CSM boundary, and profiles C2–C5 are at a distance of 2, 5, 12, and 30 km to the north from it.

The soil of profile C1 is represented by an industrizem—strongly technogenic-transformed soil. The top layer of this soil contains a large number of fallout particles, containing heavy metals, which adhere the soil mass, making it difficult to take samples from deeper layers (only one sample from 0 to 20 cm layer was selected).

The soils in other profiles are represented by soddy-carbonate leached (Rendzic Leptosols) also formed on light cover loam and underlain by carbonate calcareous moraine. The profiles of these soils include humus-accumulative A horizons with thickness from 10 to 25 cm, gray color, of medium granular structure, transitional B horizons from 15 to 30 cm, and calcareous C horizons of parent rock. Samples for chemical analysis have been taken from these horizons.

According to their chemical properties (**Table 1**), the investigated soils are quite typical representatives of soddy-carbonate leached soils.

The upper humus-accumulative horizon is characterized by a rather high content of organic carbon (in comparison with the underlying horizons) and weakly acid reaction, which becomes weakly alkaline down the profile. Near the source of pollution, weakly alkaline reaction is observed throughout the profile because of the input of a large number of technogenic compounds on the soil surface. The content of exchangeable cations is typical for light loamy soils.

To determine the total content of the lanthanides, soil samples were treated with a mixture of hydrofluoric, hydrochloric, and nitric acids in medium-pressure autoclaves in the laboratory microwave Ethos One (Milestone) according to [28].

Acid-soluble forms of the lanthanides were extracted from soils by the treatment with 1M HNO_3 with a ratio of soil:solution equal to 1:10 [29].

Profile	Horizon, depth, cm	pH_{H_2O}	Total organic carbon, %	Sum of exchangeable cations, $cmole_c$/kg
C1	U, 0–20	7.60	Not determined	
C2	A, 0–20	7.14	2.65	18.79
	B, 20–35	7.05	0.68	15.05
	C, 35–65	7.25	0.15	12.31
C3	A, 0–23	6.89	3.17	21.10
	B, 23–41	6.92	0.51	16.32
	C, 41–70	7.12	0.12	13.58
C4	A, 0–21	6.77	2.95	19.21
	B, 21–38	6.89	0.57	14.39
	C, 38–70	7.10	0.14	11.06
C5	A, 0–23	6.85	2.86	20.36
	B, 23–45	6.93	0.49	16.54
	C, 45–75	7.14	0.17	11.88

Table 1. Some chemical properties of soils in the CSM impact zone.

The sequential fractionation of the lanthanides in soils was carried out by using the McLaren and Crawford scheme [29]. The following fractions were separated: exchangeable cations, fraction of specifically sorbed ions, fraction bound to organic matter, fraction bound to (hydr) oxides of iron and manganese, and residual (strongly bound to aluminosilicates) fraction.

The quantitative determination of the lanthanides in the obtained extracts was carried out by the inductively coupled plasma mass spectrometry on 7500a ICP-MS (Agilent Technologies), according to [28]. The lower determination limit of measured concentrations of the lanthanides does not exceed 0.001 mg/L, which corresponds to a total metal content equal to 0.05 mg/kg or forms of compound content of 0.01 mg/kg. The relative error of determination did not exceed 20%.

4. Results and discussion

4.1. Total content of the lanthanides

Total content of the lanthanides in soils is given in **Table 2**.

The analysis of the results shows that changes in total content of the lanthanides are observed in profiles C1 and C2 located in close vicinity to the pollution source. We observe either a significant increase or some decrease in the total content of the lanthanides (primarily Pr and Tb) compared to soils, located at a considerable distance from the CSM.

Profile	**Horizon**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**
C1	U	24.76	30.88	8.65	14.39	2.95	0.60	2.49
C2	A	26.15	52.10	7.98	23.02	4.20	0.74	3.66
	B	28.52	55.45	6.42	24.46	4.44	0.77	3.92
	C	29.57	56.25	6.48	25.22	4.76	0.89	4.74
C3	A	26.40	51.09	5.98	23.55	4.31	0.71	3.55
	B	27.79	52.17	6.12	25.47	4.74	0.81	3.90
	C	28.64	55.48	6.63	26.21	5.32	0.87	4.51
C4	A	22.98	44.28	5.31	20.36	3.85	0.70	3.22
	B	24.15	48.95	5.80	22.61	4.26	0.76	3.66
	C	27.30	52.78	6.63	26.20	5.15	0.98	4.52
C5	A	22.86	44.38	5.23	20.05	3.74	0.66	3.13
	B	27.10	52.68	6.16	23.48	4.31	0.74	3.64
	C	27.90	54.46	6.41	24.08	5.29	0.84	4.29
Profile	Horizon	Tb	Dy	Ho	Er	Tm	Yb	Lu
C1	U	0.88	1.72	0.34	0.98	0.13	0.78	0.16
C2	A	0.37	2.04	0.37	1.09	0.19	1.06	0.17
	B	0.40	2.50	0.47	1.27	0.20	1.18	0.21
	C	0.46	2.69	0.49	1.39	0.25	1.96	0.21
C3	A	0.40	2.43	0.42	1.27	0.19	1.12	0.20
	B	0.49	2.44	0.46	1.29	0.21	1.34	0.20
	C	0.56	2.76	0.51	1.48	0.22	1.64	0.23
C4	A	0.42	2.29	0.44	1.22	0.19	1.07	0.20
	B	0.49	2.53	0.48	1.30	0.20	1.10	0.20
	C	0.53	3.31	0.63	1.83	0.27	1.62	0.29
C5	A	0.42	2.24	0.44	1.24	0.19	1.15	0.22
	B	0.49	2.55	0.48	1.40	0.21	1.24	0.23
	C	0.51	2.78	0.57	1.75	0.24	1.41	0.26

Table 2. Total content of the lanthanides in soils of the CSM impact zone, mg/kg.

Content of the lanthanides in the upper horizons of the investigated soils is given in **Figure 1**. The different levels of elemental content in soils and sawtooth character of the distribution of elements in the figure make it difficult to identify the similarities and differences in the behavior of studied elements in the soil and the effect of the CSM emissions on their content in the soil.

When normalizing data to the clay of the Russian platform, the graphs of the content of the lanthanides in unpolluted soils are gently sloping, almost horizontal, without clear maxima or minima (**Figures 3** and **4**). Thus, a high content of quartz and other minerals with low content of rare-earth elements in light loamy deposits affects equally the level of all lanthanides in the soils.

Normalized content of the lanthanides in the surface horizons of industrizem (profile C1) and soddy-calcareous soil (profile C5), which are the most contrast in chemical composition and technogenic impact, is given in **Figures 2** and **3**. The results of normalization show that the studied soils are strongly enriched with the lanthanides compared to chondrites and the degree of enrichment gradually decreases with increasing of atomic numbers of elements.

In the background soil C5 (**Figure 3**), europium stands out, whose point lies below the general trend line, as well as lutetium, a bit above it. This feature manifests at the normalization of all objects and is typical for all investigated soils (**Figure 4**).

The potential effect of technogenic pollution is of greater interest than the changes in the content of the lanthanides in soils on the geological time scale (which can be estimated by normalization to chondrites); therefore, rocks, whose composition is most similar to that of the studied soils, were used as objects for normalization. The normalization to the content of the lanthanides in the world shale and, especially, to clay of the Russian platform shows good correspondence with these objects in uncontaminated soils. Since the investigated soils are formed on light loamy sediments, the content of many chemical elements will be deliberately underestimated compared to shales or clays because of dilution with quarts.

Soil contamination by CSM emissions strongly changes the elemental relationships in contaminated soils (**Figures 2** and **4**). A noticeable increase in the content of Pr and Tb is observed at normalization to all abovementioned objects. The maximum increase in Tb content is registered in profile. Pr content is slightly lower in C1 profile, but this element is also found in

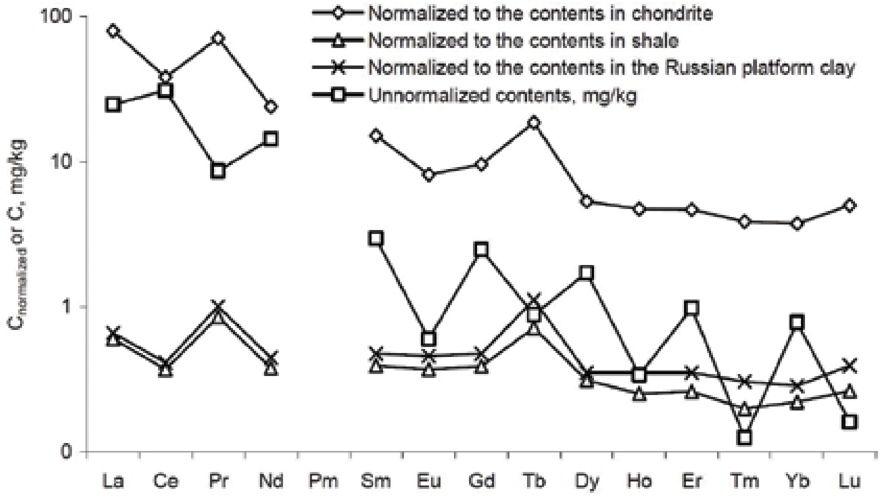

Figure 2. Total content of the lanthanides in the surface horizons of profile C1.

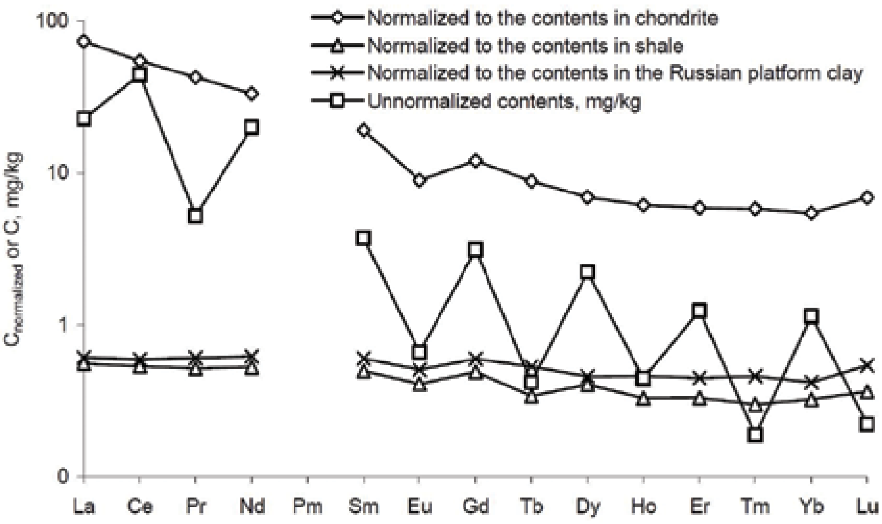

Figure 3. Total content of the lanthanide in the surface horizons of profile C5.

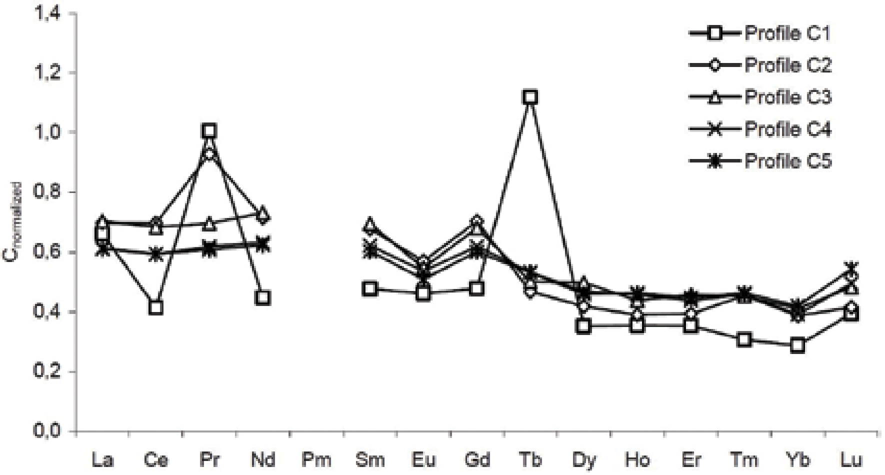

Figure 4. Total content of the lanthanides in the surface horizons of soils in the CSM impact zone, normalized to the content in the Russian platform clay.

profile C2. This may indicate significant changes in the elemental composition of atmospheric fallout with the distance from the pollution source. Along with Pr, a tendency of content increasing of other light lanthanides, from La to Gd, is observed in soils in profiles C2 and C3.

4.2. Content of acid-soluble forms of the lanthanides

Content of acid-soluble lanthanides in the surface horizons in the studied soils is given in **Table 3**. It can be seen that the main trend of the lanthanide distribution soils regulated by the Oddo-Harkins rule basically is saved at transition from total content to acid-soluble forms of elements.

Profile	Horizon	La	Ce	Pr	Nd	Sm	Eu	Gd
C1	U	5.19	11.58	1.27	4.98	1.03	0.28	0.97
C2	A	4.20	8.89	1.11	4.26	0.78	0.18	0.77
C3	A	1.63	5.64	0.66	2.47	0.54	0.11	0.57
C4	A	1.67	5.07	0.58	2.57	0.50	0.10	0.51
C5	A	1.45	4.83	0.51	2.48	0.49	0.12	0.45
Profile	Horizon	Tb	Dy	Ho	Er	Tm	Yb	Lu
C1	U	0.15	0.72	0.13	0.35	0.05	0.27	0.04
C2	A	0.11	0.56	0.10	0.25	0.03	0.17	0.02
C3	A	0.09	0.36	0.07	0.15	0.02	0.12	0.02
C4	A	0.09	0.48	0.09	0.23	0.03	0.18	0.03
C5	A	0.09	0.45	0.08	0.18	0.03	0.13	0.02

Table 3. Content of acid-soluble forms of the lanthanides in the surface horizons of soils in the CSM impact zone, mg/kg.

The content of acid-soluble forms of the lanthanides in soddy-calcareous soils (profiles C1 and C2) is higher than in other profiles. Obviously, this is a consequence of their fallout near the CSM, their presence in ore, and their use in technological process of steel production.

Not only technogenic pollution but also the original contents of elements in rocks, their chemical properties, and their affinity to soil components affect the amount of acid-soluble HMs in soils; thus, it is necessary to conduct more detailed analysis of acid-soluble forms of lanthanides in the investigated soils. For this purpose, the extraction degree of acid-soluble lanthanides from soils was calculated, and their contents were normalized using data for the Russian platform clays.

The extraction degree of acid-soluble lanthanides expressed in percentage to their total content is shown in **Figure 5**. There is a significant increase in the extraction degree for all lanthanides (except Pr and Tb) in the soil of profile C1 and a less significant for a set of elements from La to Er in the soil of profile C2. The results of determination of the content of acid-soluble forms clearly show a tendency to increase the degree of extraction from the soil of medium lanthanides, from neodymium to erbium. Primarily, this is due to stronger hardening of heavy lanthanides by the soil (due to increase in adsorption that corresponds to published data [9, 13–15]). This leads to the worst extraction of heavy lanthanides from the soil by nitric acid. On the other hand, this may be a result of a decrease in lanthanide distribution in soils as the number of the element increases.

Based on the results of determining the extraction degree of acid-soluble forms, we can divide lanthanides into three groups, depending on extraction degree of acid-soluble forms from the soils of the CSM impact zone (**Figure 5**). The first group included praseodymium and terbium, which, despite a strong increase in the total content in the most polluted soil C1 (**Table 2**), is characterized by the lowest degree of extraction of acid-soluble forms (less than 16%). The

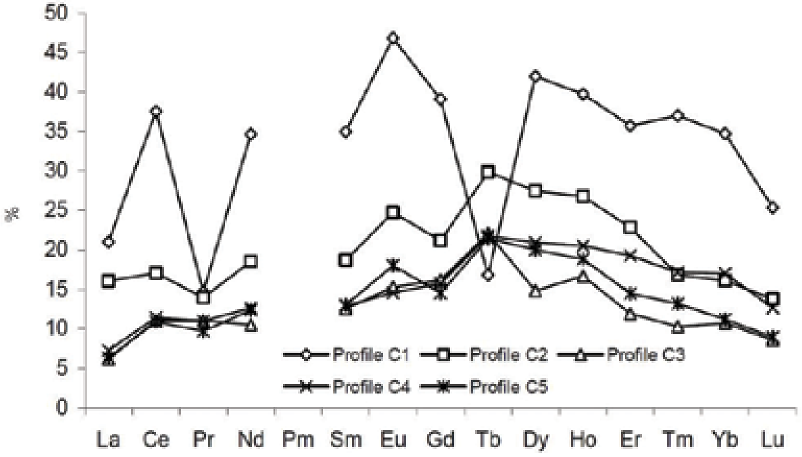

Figure 5. Content of acid-soluble forms of the lanthanides in the surface horizons of soils in the CSM impact zone, share in the total content.

majority of lanthanides—La, Ce, Nd, Sm, Eu, Gd, Dy, Ho, and Er—belong to the second group, and the extraction degree of acid-soluble forms increases in the first two most polluted soils. The third group of elements consists of three heavy lanthanides—Tm, Yb, and Lu—with the lowest changes in the extraction degree of acid-soluble forms, determined only in the most polluted soil C1.

Based on grouping of the lanthanides, we suggested that praseodymium and terbium of technogenic origin in soils in near the CSM are found in poorly soluble acid-technogenic particles of a large size. The lanthanides' content in finer and lighter technogenic particles is more homogeneous, and they are spread to a longer distance from the pollution source and are extracted by acid better. As the atomic number of lanthanides increases, their involvement in technogenic emission flows in the CSM impact zone gradually decreases.

Additional information on the lanthanides' redistribution in the studied soils can be obtained by normalizing the contents of acid-soluble forms to the contents of elements in the Russian platform clay (**Figure 6**). The comparison of the content of total and acid-soluble forms of the lanthanides has shown that almost horizontal curves are typical for the distribution of the total content of the lanthanides, and more complicated with clear maximum—for acid-soluble forms of medium lanthanides (Eu, Gd, and Tb).

As the content of acid-soluble lanthanides (**Figure 6**) is not related to their total content in the studied soils, then it is difficult to estimate soil contamination with the lanthanides using these data. So, the minima for Pr and Tb in **Figure 5** are absent in **Figure 6**.

Nevertheless, with this exception, the general shape in **Figures 5** and **6** is similar, which confirms our assumptions about changes in the extraction degree of acid-soluble forms of the lanthanides depending on their atomic number, with the maximum for medium lanthanides.

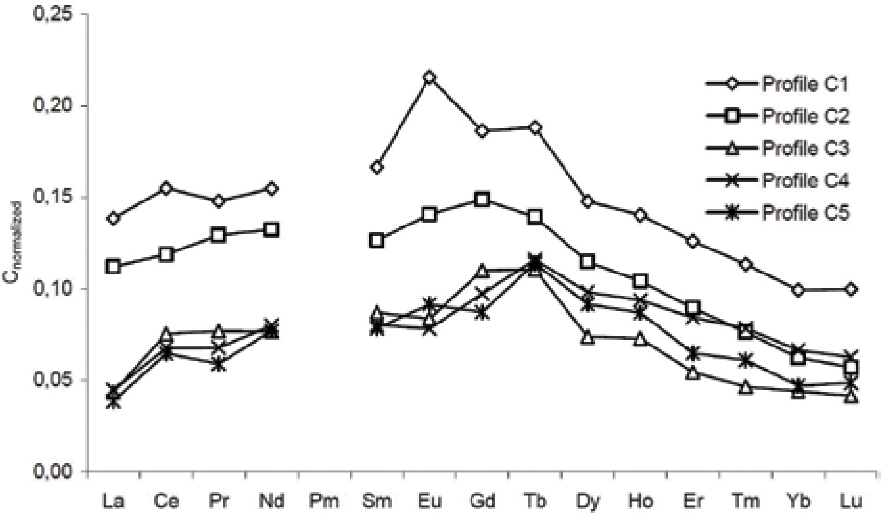

Figure 6. Content of acid-soluble forms of the lanthanides in the surface horizons of soils in the CSM impact zone, normalized to the content in the Russian platform clay.

4.3. Fractional composition of the lanthanide compounds

For all lanthanides in all studied soils, regardless of a distance from the source of pollution, a significant predominance of the residual (strongly bound to aluminosilicates) fraction (80–95% of the sum of fractions) is typical. This indicates that the main soil components determining the background level of the lanthanides in soils are aluminosilicate minerals, which strongly fix lanthanides in their structure, and lanthanide compounds, fallen into the soil under the impact of the CSM, are also chemically stable. As a result, most of the technogenic lanthanides are detected in the residual fraction. This corresponds to the data available in the literature [10–12].

Soil-forming processes have no significant influence (compared to the share of residual fraction and many other HMs in the studied soils) on redistribution of lanthanides among soil components [30–32]. The highest effect of pedogenesis on the fractional composition of lanthanides has been determined in the fraction bound to organic matter (**Figure 7**).

This fraction is reached from 5 to 18% of the sum of all fractions, depending on the element. The largest content of the fraction, associated with organic matter, is typical for the middle lanthanides. This is similar to the regularity observed for acid-soluble forms of lanthanides (**Figures 5** and **6**). Both light and heavy lanthanides have low affinity to soil organic matter. This, certainly, requires further study.

The content of the fraction associated with (hydr)oxides of Fe and Mn is much lower than the fraction considered above and amounts to only 0.1–5% of the sum of all fractions (**Figure 8**). The maximum part of this fraction in contaminated soils C1 and C2 corresponds to heavy lanthanides. In soil C1 the maximum of this fraction was detected for ytterbium and in soil C2 for dysprosium and holmium.

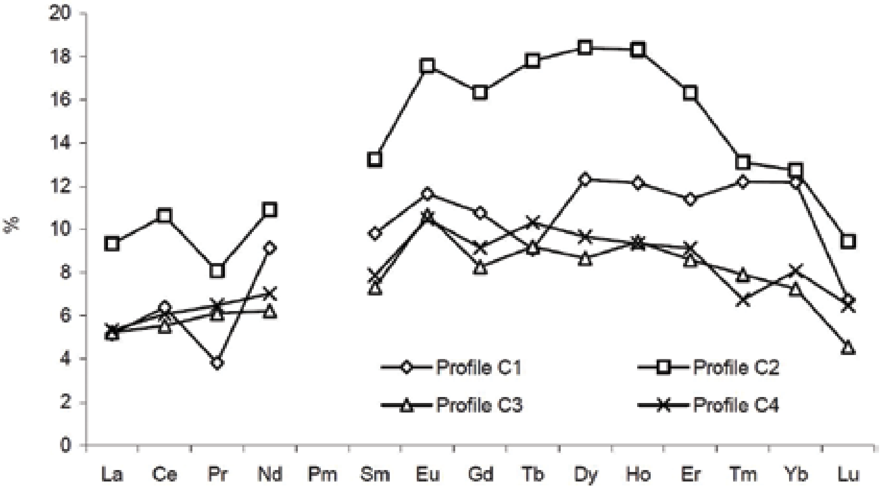

Figure 7. Fraction of the lanthanides, bound to organic matter, percentage of the sum of fractions.

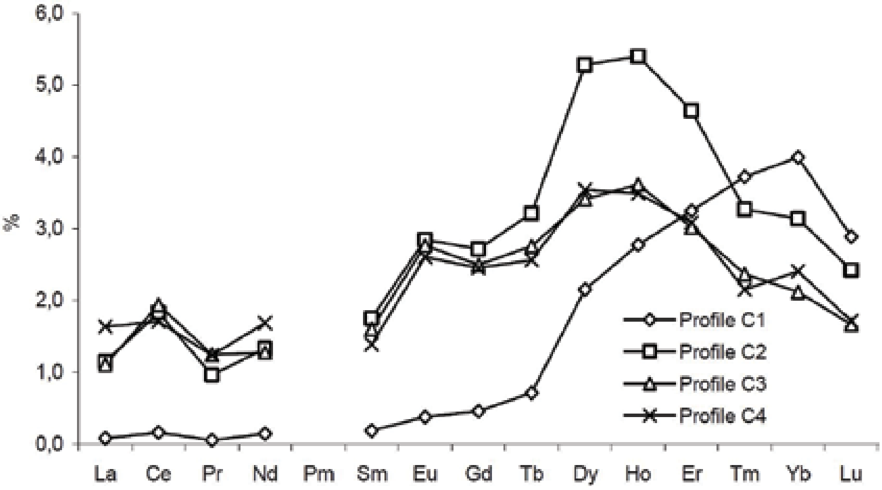

Figure 8. Fraction of the lanthanides, bound to Fe and Mn (hydr)oxides, percentage of the sum of fractions.

The obtained regularities reflect an increase in the affinity of lanthanides to iron oxides, which are the main component of the CMP emission substance, according to the number of the element raising. The decrease in the fraction share for heavy lanthanides in weakly contaminated soils of profiles C2–C4 is more significant than in profile C1. This is related to the lower technogenic input of these elements into the soil, as well as an increase in the strength of fixation of the lanthanides on the surface of ferruginous minerals as their number increases, that is corresponds to generally accepted understanding of chemical properties of the lanthanides [4, 8, 33].

The amount and share of the specifically sorbed fraction of the lanthanides are expectedly low because of their low mobility in the studied soils and moderate level of pollution. There are only two cases when the content of this fraction reaches significant values. The first case is the high content of this fraction of europium in soil C1 (4% of the sum of extracted fractions). This may be due to the peculiarities of this element and its entry into the soil with contamination, as in this soil we observe the maximum extraction degree of acid-soluble forms of europium (**Figures 5** and **6**).

The second case is a high content of a specifically sorbed terbium fraction in all soils (4–7% of the sum of all fractions). This is a consequence of technogenic contamination of soils, as it is terbium that falls down in the largest of all lanthanide quantities into the soils near the CSM (**Figure 4**). It must also be remembered that both europium and terbium can exist in two different states—Eu(II)/Eu(III) and Tb(III)/Tb(IV) [4]. The changes in redox conditions during the smelting of metal may have an effect on the state of lanthanides entering the soil during contamination.

The content of the exchange fraction of lanthanides in the investigated soils is very low and is at the level of the detection limit of the ICP-MS method that confirms the extremely low mobility of these elements in the soils.

The largest part of the sum of fractions is the residual fraction of lanthanides that corresponds to the literature data [10, 11]. There are no significant differences between soils located at different distances from CSM. Because of the absence of extractive solutions in the fractionation schemes to extract stable technogenic TM compounds from the soil, this method is inapplicable to adequate estimating of soil pollution without additional investigations.

In this context, the comparison of the total extraction capacity of sequential fractionation and 1M HNO_3 is of great interest. The shares of acid-soluble lanthanides in the total lanthanide content in all fractions separated from the soil (except the residual fraction) are shown in **Figure 9**.

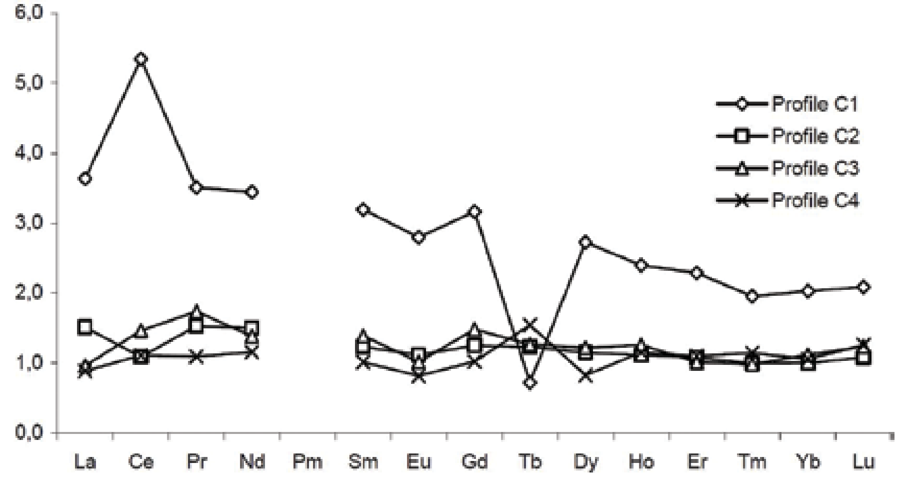

Figure 9. Ratios between the content of acid-soluble forms of the lanthanides and the sum of fractions (without the residual fraction).

It is clearly shown in **Figure 9** that the content of lanthanides in nitric acid extract from the most contaminated soil C1 significantly exceeds the sum of isolated fractions. In other less polluted soils, both these indices are practically equal. Terbium and cerium are out of the general trend in soil C1, and the differences in the behavior of cerium hadn't been noticed earlier and can be associated not with soil contamination by this element but its variable valency and its variation when forms are extracted from the soil. The extraction of lanthanides by nitric acid from the soil of C1 is higher than the amount of other fractions; the inflow of chemically resistant technogenic compounds of lanthanides (presumably oxides) into the soil that could not be extracted under sequential fractionation is clearly indicated.

5. Conclusions

1. Because of different natural abundances of lanthanides, their comparative study in soils is impossible without techniques that allow eliminating this factor: the normalization of the content of elements by a standard object similar to the investigated soils in terms of composition and conditions of formation and determination of extraction degree of various forms of lanthanide compounds. Comparison of distribution diagrams of lanthanides constructed with these indicators allows deriving both qualitative and sometimes quantitative differences in the behavior of these elements and in the technogenic contamination of soils with lanthanides.

2. The soils of the investigated territory are contaminated with the lanthanides due to CSM activities. The lanthanides are characterized by a high degree of extraction of acid-soluble forms (5–40% of the total content).

3. A significantly increased content of praseodymium and terbium was found in soils near CSM. In these soils a less increase in the content of other light lanthanides, from lanthanum to gadolinium inclusive, was also determined. Technogenic contamination also leads to an increase in the amount and to changes in extraction degree of acid-soluble forms of lanthanides from soils.

4. About 80–95% of the total content of lanthanides in the soils of the impact zone of CSM is concentrated in the residual fraction; thus, they are represented by extremely chemically stable compounds. The main soil components determining the background level of the lanthanides in investigated soils are aluminosilicate minerals, strongly fixing the lanthanides in their structure, and the compounds fallen into the soils as a result of the CSM impact are also chemically stable.

5. As a result of soil processes, a part of the lanthanides is bound to organic matter and Fe and Mn (hydr)oxides (5–18% and 0.1–5% of the total content correspondingly). The individual properties of the lanthanides are clearly manifested in their interaction with these soil components. The largest part of the fraction, bound to organic matter, contains medium lanthanides; the part bound to Fe and Mn (hydr)oxides contains heavy lanthanides.

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Section 2

Lanthanides and Algae

Lanthanides and Algae

Milada Vítová, Mária Čížková and Vilém Zachleder

Additional information is available at the end of the chapter

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Abstract

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

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

1. Introduction

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

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

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

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

2. Lanthanides in algae

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

3. Beneficial effects of lanthanides

The probable biological effect of lanthanides is related to similarities between their ionic radii and coordination numbers with elements such as Ca, Mn, Mg, Fe, or Zn. Another aspect is their ability to form stable complexes with organic molecules [30]. Substitution of essential metal ions involves, for example, changes in enzyme activity, protein conformation, or polymerization. Also, changes in the use or allocation of ion channels affects specific membrane permeability and the cellular ion ratio.

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

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

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

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

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

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

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

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

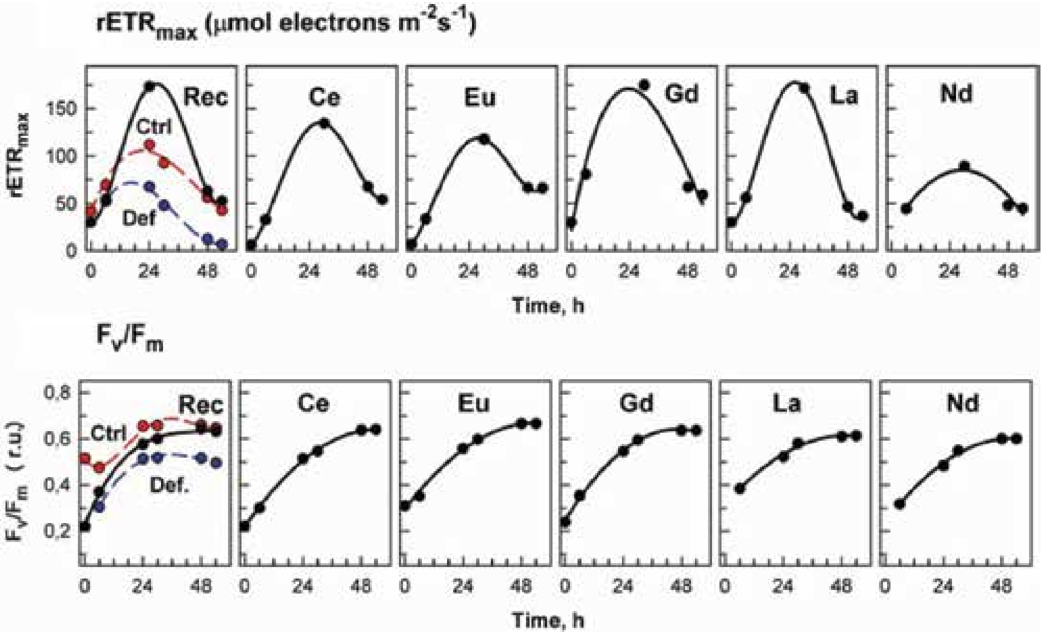

Figure 1. Photosynthetic parameters expressed as maximum relative electron transport rates (rETRmax), and the maximal quantum yield (*Fv/Fm*), in cultures of the alga *Desmodesmus quadricauda,* grown either in complete mineral medium (Ctrl, *red* symbols, *dashed* curve) or in calcium-deficient mineral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

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

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

4. Toxicity of lanthanides

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

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

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

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

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

5. Bioaccumulation of metals in algae

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

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

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

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

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

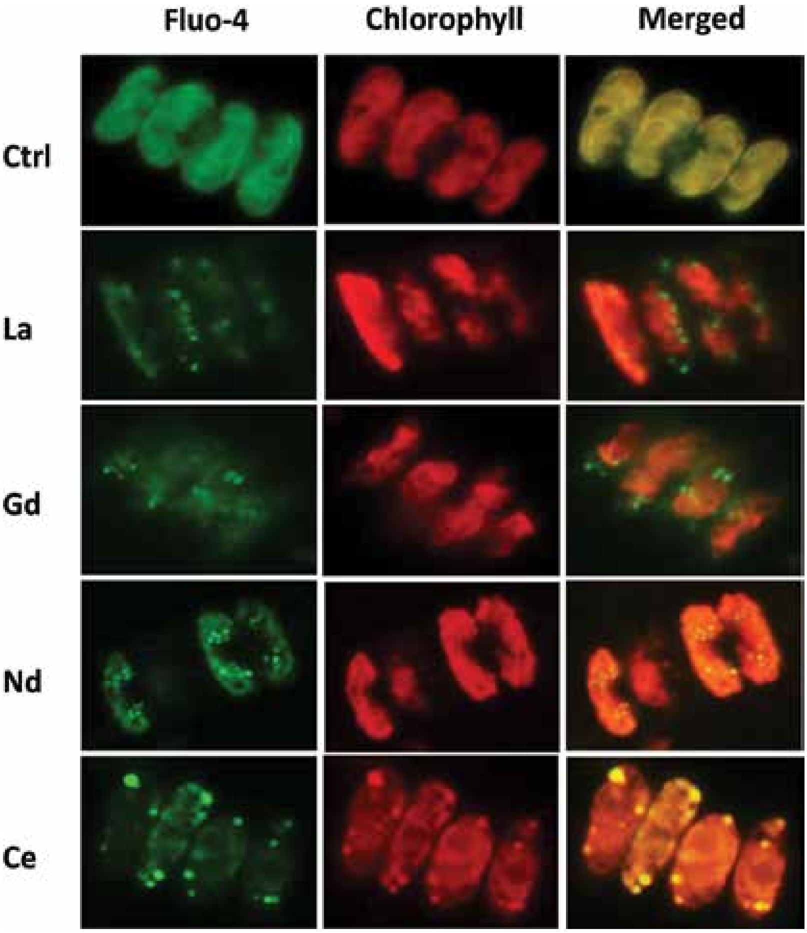

Figure 2. Intracellular localization of different lanthanides in *Desmodesmus quadricauda*. The absorbed lanthanides (horizontal rows) were visualized in cells stained with the fluorescent dye Fluo-4 (left column). Chloroplasts are visualized by autofluorescence of chlorophyll (middle column). In merged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

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

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

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

6. Biological applications of lanthanides

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

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

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

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

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

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

7. Remediation of lanthanide waste and their recovery

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

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

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

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

7.1. Chemical recycling

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

7.2. Biosorption

As a biotechnological approach, biosorption is considered to be a more efficient and cheaper alternative to conventional chemical methods of recycling lanthanides [133, 145, 146]. Various different organic residues of animal or plant origin, including resin, activated charcoal, or biomass of various organisms (algae, fungi, and bacteria), have been shown to adsorb different lanthanides and have been tested as biosorbents [95, 98, 132, 147]. The development of effective biological methods for lanthanide regeneration from these materials was proven in the aerobic, genetically modified bacterium, *Caulobacter crescentus* [148]. The use of various other biosorbents, including algae, bacteria, fungi, and yeasts, has also been evaluated [149]. Seaweeds, especially brown seaweeds, have been identified as strong biosorbents due to the presence of binding sites for chemical moieties such as carboxyl, amine, and hydroxyl groups [86]. Marine macroalgae are particularly important [150, 151]. For example, Oliveira et al. and Oliveira and Garcia [97, 152] evaluated the potential of *Sargassum* sp. biomass for biosorption of Eu, Gd, La, Nd, Pr, and Sm. They observed the rapid and efficient recovery of these metals, even though they were unable to separate them. The authors suggested that carboxyl groups present in alginates (the main component of the cellular brown algal wall) are the major reactive functional groups. Similar results were obtained with other brown seaweed such as *Sargassum* spp. [16, 96, 102, 135] and *Turbinaria conoides* [98]. Some unicellular algae such as *Chlorella* spp. and *Nannochloropsis* spp. and cyanobacteria *Microcystis* spp. were also shown to be active biosorbents of lanthanides (La^{3+} and Ce^{3+}) [19, 153]. The disadvantage of adsorption methods, including biosorption, is the generation of secondary wastes similar to chemical approaches although at a considerably lower rate, the subsequent processing of which is often financially demanding [154].

7.3. Accumulation in living cells

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

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

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

8. Conclusions

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

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This edited book *Lanthanides* is a collection of research chapters, offering an excellent review of recent applications in our lives. It consists of a number of interesting chapters by scientists and researchers from different parts of the world.

The book is divided into six chapters. The first chapter is a short introduction that explains the nature and purpose of the book and the logic and significance of its contents. In the second chapter, Katarzyna Kiegiel et al. introduce novel apparatus solutions, for example membrane contactors in the extraction stage and different types of matrices (uranium ore, phosphorites, etc.). The third chapter by Dariusz Sala and Bogusław Bieda from AGH University of Science and Technology, Management Department, Poland, describes the development of the life cycle inventory to rare earth elements (REEs) based on secondary sources, conducted according to ISO 14040 (2006) guidelines. Chapter 4 concentrates on lanthanide soil chemistry and shows how the soil chemistry of REEs may support soil science investigations. Dmitry V. Ladonin in Chapter 5 studies the content of forms of lanthanides in soddy-calcareous soils at different distances from the Cherepovets steel mill (Vologda region, Russia). The author concludes that the individual properties of lanthanides are clearly manifested in their interaction with soil components. The largest part of the fraction, bound to organic matter, contains medium lanthanides, while the heavy lanthanides are bound to Fe and Mn (hydr)oxides. The last chapter discusses ecological and physiological impacts of lanthanides on algae as primary producers in aquatic environments. This book will definitely encourage readers, researchers, and scientists to look further into the frontier topics of lanthanides and opens new possible research paths for further novel development.

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