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Review article

Cryptic footprints of rare earth elements on natural resources and living organisms



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ABSTRACT

Background: Rare earth elements (REEs) are gaining attention due to rapid rise of modern industries and technological developments in their usage and residual fingerprinting. Cryptic entry of REEs in the natural resources and environment is significant; therefore, life on earth is prone to their nasty effects. Scientific sectors have expressed concerns over the entry of REEs into food chains, which ultimately influences their intake and metabolism in the living organisms.

Objectives: Extensive scientific collections and intensive look in to the latest explorations agglomerated in this document aim to depict the distribution of REEs in soil, sediments, surface waters and groundwater possibly around the globe. Furthermore, it draws attention towards potential risks of intensive industrialization and modern agriculture to the exposure of REEs, and their effects on living organisms. It also draws links of REEs usage and their footprints in natural resources with the major food chains involving plants, animals and humans.

Methods: Scientific literature preferably spanning over the last five years was obtained online from the MEDLINE and other sources publishing the latest studies on REEs distribution, properties, usage, cycling and intrusion in the environment and food-chains. Distribution of REEs in agricultural soils, sediments, surface and ground water was drawn on the global map, together with transport pathways of REEs and their cycling in the natural resources.

Results: Fourteen REEs (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Th and Yb) were plighted in this study. Wide range of their concentrations has been detected in agricultural soils ($< 15.9\text{--}249.1 \mu\text{g g}^{-1}$) and in groundwater ($< 3.1\text{--}146.2 \mu\text{g L}^{-1}$) at various sites worldwide. They have strong tendency to accumulate in the human body, and thus associated with kidney stones. The REEs could also perturb the animal physiology, especially affecting the reproductive development in both terrestrial and aquatic animals. In plants, REEs might affect the germination, root and shoot development and flowering at concentration ranging from 0.4 to 150 mg kg^{-1} .

Conclusions: This review article precisely narrates the current status, sources, and potential effects of REEs on plants, animals, humans health. There are also a few examples where REEs have been used to benefit human health. However, still there is scarce information about threshold levels of REEs in the soil, aquatic, and terrestrial resources as well as living entities. Therefore, an aggressive effort is required for global action to generate

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more data on REEs. This implies we prescribe an urgent need for inter-disciplinary studies about REEs in order to identify their toxic effects on both ecosystems and organisms.

1. Introduction

The periodic table elements from lanthanum (La: $Z = 57$) to lutetium (Lu: $Z = 71$) are usually referred to as rare earth elements (REEs). The REEs, also known as Lanthanides or 'Industrial vitamins', are a chemically uniform metallic group of elements having almost similar electronic configuration, including the same electronic layers but with small differences in their atomic number. There are seventeen elements in the group of REEs: cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), samarium (Sm), terbium (Tb), thulium (Th), ytterbium (Yb) (Khan et al., 2017). Mostly, the common valence for lanthanides in their dissolved state is (3^+), although some of them also show (2^+) and (4^+) when they are oxidized. Based on electronic configuration of these elements, generally lanthanides are classified into two groups, i.e., light rare earth element (LREEs) (La-Eu) and heavy rare earth element (HREEs) (Gd-Lu) (Gonzalez et al., 2014). According to Akimov et al. (2016), the LREEs are more soluble compared with HREEs, but overall lanthanides belonging to each group are not tightly defined.

The REEs are not as rare in geological abundance as other toxic metals (Kim et al., 2018). For example, the Earth's crust comprises 0.015% REEs, which are more than other heavy metals. China is the leading producer of rare earth oxides, followed by Australia, USA, Russia, Malaysia and Vietnam (Brown et al., 2017) (see the Supplementary Table 1).

Furthermore, in terms of international supply, China is the dominant country in both production and trade of these REEs (Haque et al., 2014). In 2010, China announced its intent to restrict REEs export to ensure their supply and usage on a domestic level (Gonzalez et al., 2014). Nowadays, REEs are indispensable for many sectors (Table 1) including phosphate fertilizers in agriculture, clean-energy, medicinal products, smartphones, permanent magnets, fluorescent bulbs, solar panels, hybrid engines, wind turbines, carbon arc lighting, iron and steel additives, glass polishing, ceramics, rechargeable batteries and car catalytic converters (Migaszewski and Galuszka, 2015). Ahead of geopolitical and economic considerations, environmental risks associated with these REEs have received little attention. Their increasing industrial usage is leading towards growing release points into the environment and raises the prospect of REEs as significant environmental pollutants.

REEs concentration in urban and agricultural soil is crucial. Plants bio accumulate these REEs from different anthropogenic activities such as REE mining and refining discharge of REE containing the industrial residues and agricultural practices (Wiche and Heilmeier, 2016). For example, REEs are also accumulating in lichens (2.08 mg kg^{-1}), vegetables ($3.58 \text{ } \mu\text{g g}^{-1}$) and soils ($243 \text{ } \mu\text{g g}^{-1}$) that surround mining areas (Anawar et al., 2012; Li et al., 2013). Thus, the presence of such excessive REE contents in soils can have serious consequences for the

surrounding environment including groundwater and agricultural products. Under these conditions, REEs present in soils and water can enter into the human body via multiple pathways, but especially by food ingestion. REEs elements were also detected in Chinese local vegetables markets ($0.281 \text{ } \mu\text{g g}^{-1}$, Jiang et al. (2012)) and in rice grain ($0.074 \text{ } \mu\text{g g}^{-1}$) (Šmuc et al., 2012). Consequently, the presence of anthropogenic La and Gd up to 18 ng L^{-1} in tap water but 52 mg kg^{-1} in effluent from production unit of fluid catalytic cracking catalysts (Kulaksız and Bau, 2011a, 2011b). During the health risk assessment study, Li et al. (2013) revealed that well water from local household of Fuzhou city contained 2850 ng L^{-1} and drinking water contain 54 ng L^{-1} of REEs elements.

REEs are very harmful over a wide, almost 1000-fold concentration range, and can affect the geo-environment, aquatic and human life. Higher dosages of lanthanide elements given to animals cause decreased growth and other negative impacts (Panichev, 2015). Cheng et al. (2014) added 20 mg kg^{-1} lanthanides to rat feed and observed subsequent damage to cyto architecture, impaired liver function, low levels of reticulocytes in blood and inhibited growth. These REEs are also being considered in risk assessments of human health (Wei et al., 2013). Although there is scarcity of data on the presence of REEs in the food chain, the potential concerns regarding human health are raised because these rare elements have been found accumulating in the brain from 0.1 to $19.4 \text{ } \mu\text{g g}^{-1}$ (McDonald et al., 2017) and in human rib bones from 0.4 to $22.0 \text{ } \mu\text{g kg}^{-1}$ (Zaichick et al., 2011).

Li et al. (2013) detected 425 to $1275 \text{ } \mu\text{g L}^{-1}$ and 0.06 to $1.89 \text{ } \mu\text{g g}^{-1}$ of REEs in human blood and hairs, respectively, and reported that these concentrations may have entered the human body through the food web after accumulating in plants growing in soils contaminated with REEs. Marzec-Wroblewska et al. (2015) detected La ($19.5 \text{ } \mu\text{g kg}^{-1}$), Ce ($41.9 \text{ } \mu\text{g kg}^{-1}$), Eu ($0.68 \text{ } \mu\text{g kg}^{-1}$) and Gd ($3.19 \text{ } \mu\text{g kg}^{-1}$) in men's sperm. Their impact on sperm quality varies from person to person and correlates with smoking and drinking. de-la-Iglesia-Iñigo et al. (2013) reported that REEs can induce abnormalities in red blood cells with the incidence of microcytosis up to 25%, anemia up to 10% and hemoglobinopathies up to 12%.

Our primary aim in this review article is to present a current snapshot of 14 REEs in soils, sediments and surface waters. We compile and present data on REEs from 35 countries and provide a comprehensive account of their impacts on eco-environmental health. Our review also provides an opportunity to summarize negative health effects of REEs on humans, animals and plants.

2. Sources of REEs in the environment

Asia is a major hub of REEs production compared with Europe and Africa. According to Chen (2011), Asia has fourteen rare earth elements producing countries including China, Vietnam, India, Mongolia, Kazakhstan and Kyrgyzstan; Europe has six including Greenland, Russia,

Table 1
Application of REEs in human activities.

Application	Principle REEs used	Examples of use
Magnets	Nd, Pr, Tb, Dy	Motors, disc drive, MRI, power generation, microphones and speakers and magnetic refrigeration.
Catalyst	La, Ce, Pr, Nd	Petroleum refining, catalytic converter, diesel additives, chemical processing and industrial pollution scrubbers.
Alloys	La, C Pr, Nd	Batteries, fuel cells steel, lighter flints, super alloys, aluminum, and magnesium
Glass and polishing	Ce, La, Pr, Nd, Gd, Er, Ho	Polishing compounds, decolorizers and colorizers, UV resistant glass and X-ray imaging
Phosphors	Eu, Tb, Nd, Er, Gd, Ce, Pr	Display phosphors CRT, LPD, LCD, fluorescent lighting, medical imaging, lasers and fiber optics
Other uses	All REEs	Nuclear, defense, water treatments, pigments (Ce), fertilizer and scientific research

[Sources were adapted from Long et al., 2010 and Charalampides et al., 2015].

Portugal and Germany; Australia has plenty of reserves but one of the producers, Lynas, was moved to Malaysia. The United States of America and Canada have many small-scale rare earth reserves. In South America, REEs production has been concentrated in Brazil since 1884; South Africa with the Steenkampskraal project has emerged as a relatively new potential site for REE extraction after North America and Australia (Jepson, 2012).

2.1. Natural sources

The availability of REEs in the natural environment is highly dependent on the earth surface activities such as weathering of parental material from the earth's crust through hydrogeological, geochemical and biological processes; and movements on the surface of the earth's crust like volcanic activities, groundwater flow, and neomorphism (Guo et al., 2010; Hernández-Antonio et al., 2015; Migaszewski et al., 2016;

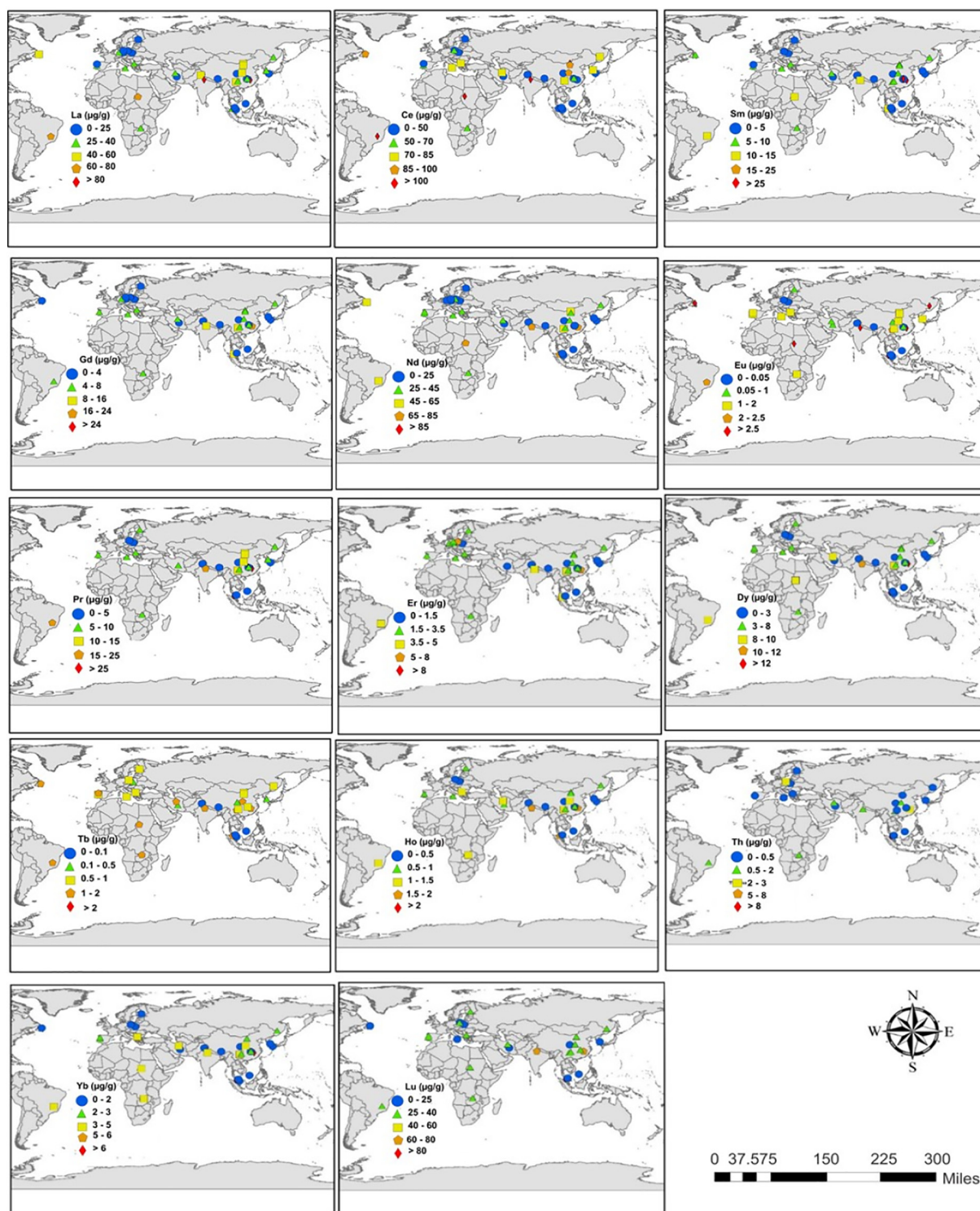


Fig. 1. Spatial difference of REEs in soils and sediments of several continents from 2008 to 2018. Data are compiled from the published literature for 35 countries. The baseline is developed by using the concept [Median + 2MAD ($\mu\text{g g}^{-1}$)/Finland surface soil] from Reimann and Caritat (2017) (see Supplementary Table 2).

Qing, 1998; Siebert et al., 2012; Sohrabi et al., 2017; Su et al., 2017; Tesmer et al., 2007; Vakh et al., 2017; Webb et al., 2009; Wulaningsih et al., 2013; Xu et al., 2015). Generally, REEs are present in mineral deposits such as ferromanganese oxide (stratiform) ores, parasite, synchysite, Ba-REE fluorocarbonates, xenotime, churchite fergusonite, loparite, phosphoric minerals, bastnaesite ore, monazite deposit and iodine mineral (Chakhmouradian and Wall, 2012; Lema et al., 2014; Mishra et al., 2007; Nikiforov et al., 2014; Zhou et al., 2017).

Natural weathering of black shale is a common cause of increasing REEs composition in water. The release of elements and substances such as phosphates, carbonates, sulphides, silicates and organic matter from the shales and parental materials corresponds to the weathering time (Abanda and Hannigan, 2007) and acidity of water (Atanasova and Baikusheva-Dimitrova, 2012). In the USA, Abanda and Hannigan (2007) report that high levels of REEs ranging from 0.011 ppb to 1.5 ppm are released with other elements such as phosphates, carbonates, sulphides, silicates and organic matter from the black shales into the water during the first 24 h of weathering time. The solubility product of the REE complexes is attributed to the acidity of water during the release of the unstable mineral species (Atanasova and Baikusheva-Dimitrova, 2012). However, carbonate causes the reduction of light weight REEs compared with heavy weight REEs (Kasper-Zubillaga et al., 2015). Higher enrichment of REE species especially for heavy rare earth elements (HREEs), (Tb, Dy, Ho, Er, Tm, Yb and Lu), in core marine sediment may be attributed to the presence of unstable mineral dominated by the presence of carriers of HREEs by wind and river transport (Ashraf et al., 2016).

2.2. Anthropogenic sources

Lanthanides are known as ‘industrial vitamins’ and ‘treasures’ of novel materials due to their deployment in the technical progress and the development of traditional industries. Application of REEs in various industrial fields includes non-nuclear energy production and energy utilizing products such as light bulbs, batteries and catalytic converters (Ault et al., 2015; Dutta et al., 2016; Li et al., 2008; Noack et al., 2014), anti-corrosive technique development (Li et al., 2010b; Niu et al., 2008), and magnet production. These applications have led to a high demand for REEs (refer to Table 1).

Active and abandoned mines are the primary anthropogenic factor, which significantly interferes with the natural flow of elements in ecosystem reservoirs and alter the physical and geochemical processes of the planet (Amyot et al., 2017; Balabanova et al., 2016; Chao et al., 2016; Delgado et al., 2012; Gwenzi et al., 2018; Humsa and Srivastava, 2015; Li et al., 2014; Meryem et al., 2016; Migaszewski et al., 2014). For example, the Baiyun Obo mine in Baotou, China is the most significant iron ore and REEs mining area in the world. The contamination of REEs in the Baiyun Obo area, especially in soils and water is increasing from year to year (Hao et al., 2015; He et al., 2010a; Inguaggiato et al., 2016; Wang and Liang, 2015; Wang et al., 2014; Xu et al., 2011). The processing of REEs is complex and requires various facilities. High leachability of REEs to the surrounding environment occurs during fractionation, extraction, and analysis, especially in mine tailings, which accounts for REEs in concentrations that are three-fold higher than the average background concentration in China (Tang et al., 2016).

REE ions in water have higher mobility from abiotic to biota, especially for plants such as *Citrus × limonia*, *Oryza sativa* L., *Solanum lycopersicum* L., *Triticum durum* L., *Vigna radiata* L. and *Zea mays* L. (Behbahaninia et al., 2009; D'aquino et al., 2009; Diatloff et al., 2008; Zeng et al., 2006; Zhang et al., 2013). Zaharescu et al. (2017) discovered that REEs were highly abundant in buffalo grass by presence of arbuscular mycorrhizal (ranging from 0.18 to 0.95 nmol g⁻¹) than water after abiotic dissolution. In China, Zhuang et al. (2017b) reported that the total REEs in vegetables from mining and control areas were 94.1 µg g⁻¹ and 38.7 µg g⁻¹, respectively, with a statistically

significant difference between them ($p < 0.05$). However, some farmers deploy REEs in fertilizers to promote the growth of crops (Saatz et al., 2015; Thomas et al., 2014; Wang et al., 2008). Wang et al. (2008) found that there is an increase of NH₄⁺-N resulting from urea hydrolysis from activated bacteria and as well as the induction of enzymes of nitrification and de-nitrification are consequences of REE addition to fertilizers. Therefore, farming practices that utilize REEs become a source of REE contamination in soils, surface runoff water, groundwater, and biota.

3. Occurrence of REEs in the environment

The study of heavy metals in the environment is widely established in terms of their toxicological effects. However, the high demand of REE in various industrial fields has led to uncontrolled exploitation. The construction of the mining area, transportation, processing and waste disposal stage of REEs has increased the risks of environmental pollution.

3.1. REEs in soils and sediments

The concentration of REEs in soils and sediment is higher than that of REEs in water resources due to pH and cationic exchange capacity (Chang et al., 2016; Ramos et al., 2016; Spencer et al., 2011; Welch et al., 2009; Xu et al., 2018). Typically, most REEs may adsorb to soils and sediments due to their dissolution and surface complexation reactions with inorganic and/or organic ligands (Gwenzi et al., 2018). Furthermore, higher weathering results in greater removal of more mobile cations (Silva et al., 2018). To evaluate the influence of REEs in polluting the environment on a global level, the occurrence of the REEs in soils and sediments, including urban and background global, we collected data from multiple database sources. In order to summarize the data collected, a spatial distribution of the rare earth elements was constructed according to the minima and maxima concentrations in soils and sediments (Fig. 1). The exercise was performed with mean and median concentrations of rare earth element from the data collected and analyzed with geographical information software (see Supplementary Table 2). LREEs are the highest detected in soils and sediments compared to HREEs. Meanwhile, soils in mining areas have higher REE abundance, followed by the urban and agricultural sectors.

The concentration of REEs in agricultural soils and in urban areas is important because of the bioaccumulation of REEs in plants from various anthropogenic input environments such as discharge of REEs residues into soils, application of REEs-enriched fertilizers or agriculture activities in land surrounding mining areas (Hu et al., 2004; Tyler, 2004). Due to their persistence in the environment, the risks, impacts and chronic toxicity of widespread REEs in soils and sediments are of concern. They accumulate in soils, bioaccumulate in crops, and ultimately enter the food chain (Charalampides et al., 2016).

The concentration of total REEs in agriculture soils was 83 to 9840 µg g⁻¹ (Fig. 1). The concentration of LREEs was higher than HREEs and Ce was most abundant, followed by La, Nd and Eu. Meanwhile, the concentration of HREEs in agricultural soils ranged from 0.039 to 37 µg g⁻¹, and Dy was found to be the highest accumulated REE in the soil. The total REEs in lake, river and marine sediment was 0.292–1430 µg g⁻¹ with the maximum levels being for Pr (682 µg g⁻¹) and Sm (468 µg g⁻¹). Meanwhile, the concentration of total REEs in wetland soil and sediment ranged between 377 and 47,565 µg g⁻¹ with the maximum concentration values being for La (47,028 µg g⁻¹) in Neogene Siwalik, Ravi River, Punjab re-entrant, India (Sinha et al., 2007). The development of anoxic conditions may induce the reduction of REEs oxide metals in waterlogged soil and sediment (Davranche et al., 2014). Presence of humid acid binding sites and potential competitive cations alter the complex stability and cause organic matter desorption and solubilization of REEs in the waterlogged area (Davranche et al., 2016). The increase with pH invokes the stronger

binding sites to participate in metal binding and possibly decreases ionic strength of REEs, and thus induces the fractionating the REEs at the earth surface (Sonke, 2006). Sonke (2006) found that La speciation is significant at acidic pH level, Lu speciation is dominated by humics at pH ranged 3–10, while the other REEs follow intermediate trends. REEs bioaccumulation in edible plants may result in health hazards directly or indirectly due to the changes of nutritional values. This may lead the population towards malnutrition problems or other chronic health disorders (Khan et al., 2015).

Many studies indicate that the REEs are widely influencing the soil fertility. China endures high REE pollution levels: Sm ($> 45 \mu\text{g g}^{-1}$),

Nd ($> 85 \mu\text{g g}^{-1}$), Ce ($> 100 \mu\text{g g}^{-1}$) and La ($> 80 \mu\text{g g}^{-1}$). These REE levels are considered as potentially high toxins compared with their occurrence in other countries. The rare earth industry has transformed China, especially in Baotou and the devastating environmental impacts are clear. Li et al. (2010a) reported the total REEs concentration (ΣREEs) in the five different Baotou croplands ranged from 225 to $658 \mu\text{g g}^{-1}$. Zhang et al. (2012) also reported that ΣREEs in Baotou Southern suburb farmlands was $189 \mu\text{g g}^{-1}$, which was 1.40 times that of background REEs in HeTao (Guo et al., 2010). Later, Wang and Liang (2015) also discovered the enrichment of REEs in surface soils where total concentrations ranged from 156 to $56,500 \mu\text{g g}^{-1}$ with an average

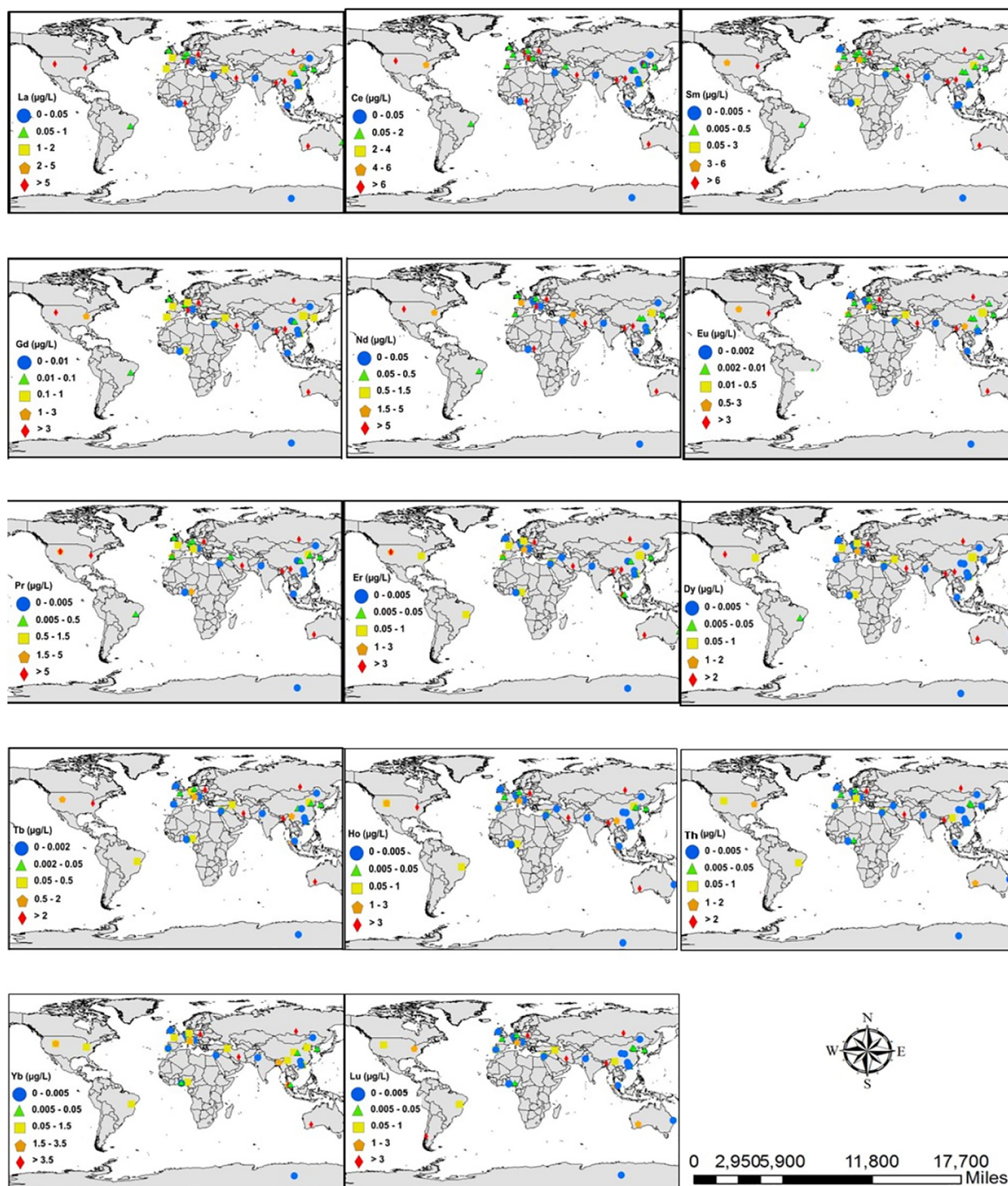


Fig. 2. Spatial difference of REEs in various water matrices in several continents from 2008 to 2018. Data are compiled from published literature for 35 countries. The baseline uses the concept [Median + 2MAD ($\mu\text{g L}^{-1}$)/lowest value surface water] from Reimann and Caritat (2017) (see Supplementary Table 3).

value of $4670 \mu\text{g g}^{-1}$ around mine tailings in Baotou, which is significantly greater than the average value in the rest of China ($181 \mu\text{g g}^{-1}$). Accumulation of REEs was also reported in Sanjiang Plain in the range of 138 to $226 \mu\text{g g}^{-1}$ due to both natural and anthropogenic activities along Heilongjiang (Cheng et al., 2012). Meryem et al. (2016) also reported that ΣREEs ranged from 455 to $502 \mu\text{g g}^{-1}$ in Hezhang agricultural soils (Supplementary Table 2).

Besides China, some of the developing countries and under-developing countries in Asia also face similar soil pollution caused by an abundance of REEs. From Fig. 1, most of these REEs concentrations are moderate compared to China. However, in some regions the presence of REEs is extremely high such as La at $47.28 \mu\text{g g}^{-1}$ in Neogene Siwalik, India. Khadijeh et al. (2009) reported that in east Malaysia, the ΣREEs in South China Sea marine sediments increased from $0.054 \mu\text{g g}^{-1}$ to $0.114 \mu\text{g g}^{-1}$. Sultan and Shazili (2009) also reported that from the Terengganu river basin, ΣREEs ranged from 0.746 to $60 \mu\text{g g}^{-1}$ with a mean ΣREEs of $23.7 \mu\text{g g}^{-1}$ in soils and sediments. They also reported that the river basin experienced a lutetium concentration of $> 2 \mu\text{g g}^{-1}$.

Production of REEs in North America is mainly focused in Mountain Pass (USA) and Ontario, Québec and Labrador (Canada) (Desbarats et al., 2016). The concentration of REEs in soils and sediments in Canada is moderately high when compared to those in China due to > 200 REE exploration projects under development, including 11 at an advanced stage (Macmillan et al., 2017). Recent studies indicated that REEs as soil pollutants in the Mountain Pass in the USA were relatively small when compared to that in Asian countries and occurs in relatively isolated unpopulated area away from residential areas. Thus, there is much less public interest regarding environmental and social impact assessment of the operation in the Mountain Pass mine (Ali, 2014).

Europe shows the second highest REE pollution signatures after Asian countries. In a case study conducted on paddy soil contaminated by Pb-Zn in Kocani Field, Macedonia, the ΣREEs ranged between 105 and $250 \mu\text{g g}^{-1}$ with a mean value $174 \mu\text{g g}^{-1}$ (Dolenec et al., 2007). Wiche et al. (2017) reported that ΣREEs in surrounding post-mining area of Freiberg, Germany ranged from 97 to $402 \mu\text{g g}^{-1}$, and they also discovered that Ge is the highest accumulated REE species in herb plants (e.g. *Phalaris arundinacea*: 449 ng g^{-1}). Brazil is the main and the oldest REE production area in South America (Chen, 2011). REEs are adequate tracers of phosphogypsum contamination in the Santos estuary with a mean ΣREEs of $299 \mu\text{g g}^{-1}$ (De Oliveira et al., 2007). de Sá Paye et al. (2016) also reported a mean ΣREEs of $32.2 \mu\text{g g}^{-1}$ in the Minas Gerais soil bank, Brazil, in which the concentration was exceeding its threshold concentration of $2.28 \mu\text{g g}^{-1}$. Africa is growing as a major REE producer after China and Europe (Jepson, 2012). The mining areas are mainly focus in South Africa like the Savannah District (northern Côte d'Ivoire), Western and Eastern Cape. Several studies showed that African soils are severely contaminated with REEs: Zwartwater soil ΣREE $177.8 \mu\text{g g}^{-1}$ (Compton et al., 2003), Slangkap soil ΣREE $154 \mu\text{g g}^{-1}$ (Compton et al., 2003), Katanga soil ΣREE $162 \mu\text{g g}^{-1}$ (Atibu et al., 2016) and Tongon soil ΣREE $253 \mu\text{g g}^{-1}$ (Sako et al., 2018).

Overall, China faces the biggest challenge in terms of soils and sediments pollution from REEs as compared to other countries. Alarmingly, the cases of REEs occurrence in soils and sediments are increasing from year to year. The consequences of REE pollution in soils and sediments such as bio-concentration and bioaccumulation of biota may not be predictable due to the encounter of REEs in the food chain. The implementation of a regulatory system on controlling REEs concentration in soils and sediments should be introduced and enforced.

3.2. REEs in surface water and groundwater

Similar exercise was performed with mean and median concentrations of rare earth element in water including urban water, lake water, river water and groundwater were collected from several countries and analyzed with geographical information software (see Supplementary

Table 2). A spatial distribution of the rare earth elements was illustrated to summarize the information of REEs concentration in water collected from various resources according to the minima and maxima concentrations in Fig. 2. Because there is an absence of a regulatory standard on REE concentrations in water from international organizations such as WHO, the risk toxicity levels have rarely been addressed. The results indicate that there is a spatial difference in the REEs concentrations.

The information about REEs in water, especially on background concentration, is crucial for ecological and human health risk assessments. According to the regional studies, the Asian continent experiences the most critical risk of REE pollution level, especially in China. Ce and La are the most abundant elements found in water, followed with other LREEs and HREEs. Europe is the second, at the most risk of REE pollution, followed by Africa, USA and Australia.

Mining activities are the primary input for the discharge of REEs into water systems. A study reported that the total suspended REEs in 33 major Eastern China rivers was about $1,712,000 \mu\text{g L}^{-1}$ with the average concentration level of suspended REEs in each tributary of $5188 \mu\text{g L}^{-1}$. Pearl River is an extensive river system across several provinces that producing REE such as Guangdong, Guizhou and Hunan. An investigation was found that the concentration of REE had increased from $1 \mu\text{g L}^{-1}$ (Ouyang et al., 2006) to $3007 \mu\text{g L}^{-1}$ (He et al., 2010a). Another study was performed in the Sarcheshmeh mine area of Kerman, Iran. The stream water surrounding that area was contaminated with REEs ($\Sigma\text{REEs} = 934 \mu\text{g L}^{-1}$) due to a leakage and improper management (Sharifi et al., 2013). The mining pit in Ipoh, Perak, Malaysia also experienced a similar phenomenon: La ($17.8 \mu\text{g L}^{-1}$), Ce ($46.5 \mu\text{g L}^{-1}$), Pr ($8.96 \mu\text{g L}^{-1}$), Nd ($10.8 \mu\text{g L}^{-1}$), Eu ($3.03 \mu\text{g L}^{-1}$), Gd ($6.83 \mu\text{g L}^{-1}$), Tb ($2.42 \mu\text{g L}^{-1}$), Dy ($12.1 \mu\text{g L}^{-1}$), Ho ($3.8 \mu\text{g L}^{-1}$), Er ($12.7 \mu\text{g L}^{-1}$), Tm ($15.6 \mu\text{g L}^{-1}$), Yb ($18.2 \mu\text{g L}^{-1}$) and Lu ($3.72 \mu\text{g L}^{-1}$). These values were traced in the surface water of the ex-mining pit lake (Khan et al., 2016). A mining pit in Wisniowka, Poland was also found to be polluted with: La ($116 \mu\text{g L}^{-1}$), Ce ($371 \mu\text{g L}^{-1}$), Pr ($59.6 \mu\text{g L}^{-1}$), Nd ($317 \mu\text{g L}^{-1}$), Eu ($128 \mu\text{g L}^{-1}$), Gd ($33.9 \mu\text{g L}^{-1}$), Tb ($168 \mu\text{g L}^{-1}$), Dy ($24.2 \mu\text{g L}^{-1}$), Ho ($21.8 \mu\text{g L}^{-1}$), Er ($55.5 \mu\text{g L}^{-1}$), Tm ($7.02 \mu\text{g L}^{-1}$), Yb $9.31 \mu\text{g L}^{-1}$ and Lu $6.51 \mu\text{g L}^{-1}$ (Migaszewski et al., 2016) (see the Supplementary Table 3).

Active anthropogenic Gd and La were found to be partitioned between dissolved and suspended particulate phases in the Rhine river (Klaver et al., 2014). It was believed that this phenomenon was caused by effluent discharged from the industrial areas of Plume and Worm, which was previously reported to contain La ($2478 \mu\text{g L}^{-1}$) and Ge ($44.8 \mu\text{g L}^{-1}$) (Kulaksız and Bau, 2013). Similarly, in the Herault watershed in France, a REE pattern showed that anthropogenic Gd increased from upstream to downstream with a value nearly zero upstream and increasing up to $52.9 \mu\text{g L}^{-1}$ downstream (Rabiet et al., 2009). Meanwhile, Ito et al. (2017) also discovered that heavy metal processing, including REEs, is anthropogenically influencing the Kinta river water with a ΣREE of $1580 \mu\text{g L}^{-1}$. Therefore, treatment of the REE influenced wastewater is required before the water can be discharged into the water stream.

The concentration level of REE in groundwater is lower than in surface water. Sun et al. (2011) found a ΣREE of $0.103 \mu\text{g L}^{-1}$ in Renlou coal mine groundwater in northern Anhui Province, China. Meanwhile, the concentration of REE in the groundwater from the Hetao Basin of Inner Mongolia, ranged from 0.0092 to $0.0177 \mu\text{g L}^{-1}$ (Guo et al., 2010). However, acidic conditions such as acid mine drainage result in releasing various REEs species due to the stability constant such as REE oxalate-complexes (Schuf and Byrne, 2001) and REE sulphate-complexes (Gammons et al., 2003). Li and Wu (2017) reported that REEs from coal and bedrocks are released into acid mine drainage due to the acid dissolution of coal and bedrocks caused by the oxidation of pyrite. Lei et al. (2008) reported that there was contamination by REEs discharged from the BS nickel mine in western Australia: ΣREE of $515 \mu\text{g L}^{-1}$ in groundwater and $0.477 \mu\text{g L}^{-1}$ in the run-off surface

water. Sahoo et al. (2012) also reported an average ΣREE of $715 \mu\text{g L}^{-1}$ discharged from the Jaintia Hills coalfield that was released into the drainage and caused groundwater contamination. Globally, safety and quality of drinking water are strictly controlled and enforced with various guidelines, criteria, acts, and regulations. However, these standards may not apply to rare earth elements. A study on REEs concentration in tap water was conducted in Croatia and a ΣREE of $0.15 \mu\text{g L}^{-1}$ was reported with Ce as the highest abundant REE species ($0.051 \mu\text{g L}^{-1}$) (Fiket et al., 2015). In Southern France, large anthropogenic gadolinium (Gd) anomalies were found in wastewater treatment plant effluents and in the aquatic environment up to $2.42 \mu\text{g L}^{-1}$ (Rabiet et al., 2009). Similarly in Germany, Kulaksiz and Bau (2011a) reported that large Gd anomalies were found in the tap water from the western district of Berlin, indicating the presence of up to 18ng L^{-1} of anthropogenic Gd on top of a geogenic background of 0.54ng L^{-1} ; the abundance is predicted to be increased from year to year (Tepe et al., 2014). There was a similar anthropogenic Gd phenomenon in San Francisco Bay (Hatje et al., 2016), Australia (Lawrence et al., 2009), Switzerland (Vriens et al., 2017), and the UK (Thomsen, 2017).

de Boer et al. (1996) and Sohrabi et al. (2017) have proposed that the indicative admissible of drinking water concentrations for rare earth La, Ce, Tb, and Yb can be regulated at $2 \mu\text{g L}^{-1}$, for Gd and Tm, $10.5 \mu\text{g L}^{-1}$ and for Pr, Nd, Sm, Eu, Dy, Ho, Er and Lu, $1050 \mu\text{g L}^{-1}$. However, there is no any action and measure taken and enforced. The continuity of exploitation and processing of REEs will result in unpredictable amount of REEs released into water. The increasing abundance of REEs in water may contribute to water insecurity associated with risks driven by inadequate water sanitation. Therefore, a regulatory standard should be framed and introduced to control the occurrence of REEs in water systems. Mining strategies and monitoring strategies into water require upgrading and optimizing to reduce REEs accidentally released.

4. REEs associated with human, and animal health

4.1. Humans

The REEs pose multifaceted problems regarding human health and

the environment, but there are examples where REEs have been used to benefit human health. For example, these elements possess antioxidant properties that positively influence human organs and are used for the treatment of various diseases (Rim, 2016). The concentrations of REEs in human blood and hair have been reported as 424.76 to $1274.80 \mu\text{g L}^{-1}$ and 0.06 to $1.89 \mu\text{g g}^{-1}$, respectively. However, sometimes even the lower levels of REEs cause human health problems by accumulating in bones and brain of the human body (Li et al., 2013). Different REEs including Y, La, Ce, Nd, Gd, Tb and Yb result in oxidative stresses and cause toxicity to human cells. Liver, lungs and blood are the primary organs to be affected by REEs (Pagano et al., 2015a; Pagano et al., 2015b). The distribution of REEs near smelting and mining areas of Hezhang, China indicates a positive correlation between agricultural soils and human scalp hair and urine (Meryem et al., 2016). The impacts of REEs on different organs of human body are clearly indicated in Fig. 3.

Nowadays, many fatal diseases can be cured by radiation therapy. However, sometimes healthy cells found in vicinity of abnormal cells can be killed by means of radiation treatments. In this context, the use of CeO_2 nanoparticles protects healthy cells from the harmful effects of radiation. CeO_2 nanoparticles have been found to prevent pneumonitis along with positive impacts in radiotherapy (Colon et al., 2009). Moreover, Marzec-Wroblewska et al. (2015) determined the presence of REEs in human sperm and calculated the association of these elements with the quality of semen. The concentrations of La (19.5), Ce (41.9), Eu (0.68) and Gd ($3.19 \mu\text{g kg}^{-1}$) were estimated in human semen to be large enough to increase sperm motility and enhance the percentage of normal spermatozoa. The detected levels of these REEs show no harmful effect for the sperm quality.

Excessive accumulation of REEs by ingestion or inhalation causes many health problems that can lead to mortality. Intake of minor doses of REEs may contribute to a rise of blood cholesterol interfering with the production of high density lipoproteins ultimately leading to arteriosclerosis in residents of REEs mining areas (Migaszewski and Galuszka, 2015). Moreover, REEs exposure to photoengravers, glass polishers and movie projectionists can affect respiratory systems (Pagano et al., 2015a).

Gd and Lu in high concentrations cause brain tumors. Neurotoxicity

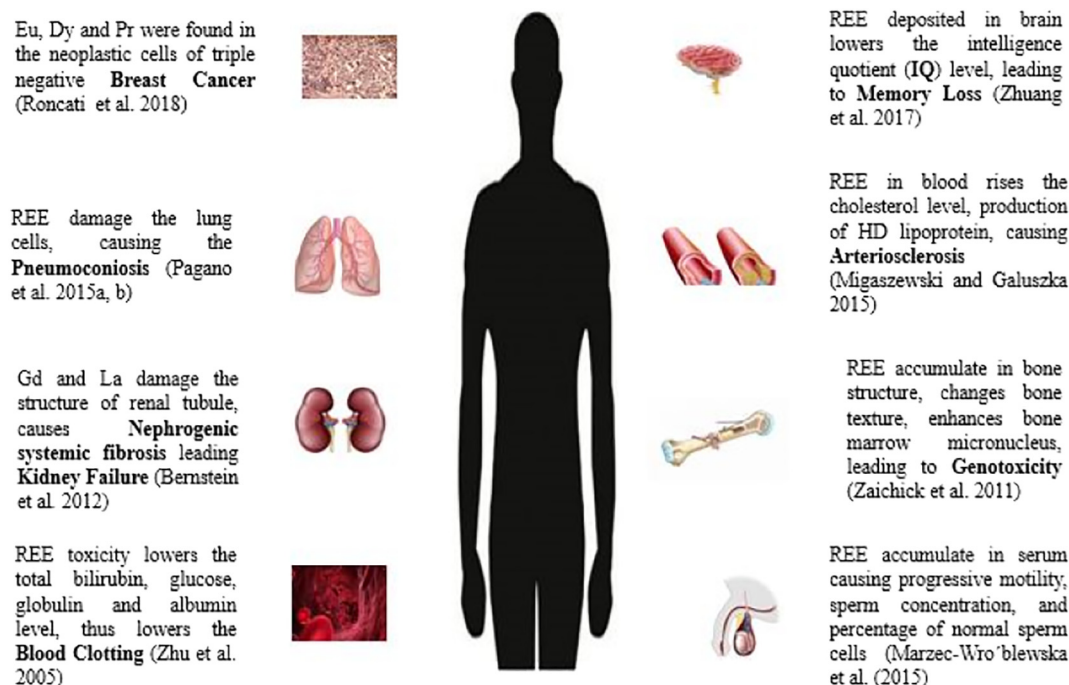


Fig. 3. Effects of REEs on human health.

of the brain has been reported as a result of accumulation of REEs like Ga and Lu. Gd also causes toxicity in humans by disturbing the Ca^{2+} homeostasis and human nervous system (Kulaksiz and Bau, 2011b). REEs can lower the intelligence level of the brain, ultimately causing loss of memory (Zhuang et al., 2017a). Rib bones get damaged because of toxicity to REEs (Zaichick et al., 2011). Lung disease associated with leukemia can be caused by inhalation of high amounts of REEs present in mine dust ultimately leading to myocardial infarction. Gd is reported to cause nephrogenic systemic fibrosis (Bernstein et al., 2012; Chang et al., 2013). Trivalent Gd^{3+} ion releases due to de-chelation of less stable chelates of Gd may ultimately lead to nephrogenic systematic fibrosis, leading to kidney failure in humans (Bernstein et al., 2012). REEs are also capable of crossing the placenta and blood barrier; hence the fetus can accumulate large quantities of REEs leading to birth defects (Liang et al., 2014).

The intake of REEs into the human food chain occurs through plants and animals by adopting various routes leading to human health hazards (Naczynski et al., 2013). Various case studies performed on humans have been well-explained in Table 2. These studies represent the negligible effect of different concentrations of REEs on human health caused by their daily intake through respective food samples. For example, a health risk assessment that was performed in the Shandong area estimated the daily intake of total REEs for vegetable consumption was $0.69 \mu\text{g kg}^{-1} \text{day}^{-1}$ in a mining area and $0.28 \mu\text{g kg}^{-1} \text{day}^{-1}$ in a control area (Zhuang et al., 2017b). Meanwhile, Yang et al. (2016) reported that the estimated daily intake of total REE by a consumption group in Shandong Province was $0.0076\text{--}0.0921 \mu\text{g kg}^{-1} \text{day}^{-1}$ for fresh water fish consumption and $0.0029\text{--}0.0913 \mu\text{g kg}^{-1} \text{day}^{-1}$ for marine fish consumption. However, these studies did not include long-term REEs exposure to humans. The outcome of these studies point out potential hazardous effects of REEs on children in comparison to adults, hence more studies are required on young persons having long-term exposure to REEs.

Hollriegel et al. (2010) studied the relationship between Ce content in the breast milk and blood serum/plasma of humans. The breast milk and blood plasma were taken from lactation mothers of Germany and Spain. Acid cleaned breast milk pumps were used for collection of milk samples. Instrumental analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS). No correlation was found between Ce concentrations of Spanish breast milk samples and serum. The content of Ce in the milk doesn't depend upon its amount in the blood serum. The Ce intake in Madrid, Spanish mothers was higher than the Munich, German mothers. The amount of Ce in breast milk is not an indicator of environmental Ce while Ce concentration in blood plasma/serum indicates Ce contaminated environment.

The study of impact of heavy metals on human breast carcinogenesis is recently an active area of research. Roncati et al. (2018) reported the presence of three REEs, i.e., Eu, Dy and Pr in the neoplastic cells of triple negative breast cancer demonstrated by elemental microanalysis. They evaluated an in vivo uptake of heavy metals for the first time in neoplastic cells from single female breast cancer patient out of total 113 that worked for the whole life in ceramic industry; a rich source of

heavy metals. Hence, more research in this domain is required to elucidate possible therapeutic measures of this highly toxic form of cancer.

Huo et al. (2017) performed a pilot study on the possible relationship between the risk of neural tube defects (NTDs) in offsprings and REEs in maternal hair of pregnant women. The REEs analyzed in maternal hair were Ce, La, Pr and Nd. Out of these four REEs, the median concentration of Ce and Pr were found to be higher in the NTDs group as compared to the control group. However, no association between concentrations of REEs in maternal hair and NTDs was observed.

4.2. Terrestrial animals

REEs have been used as natural feed supplements in livestock production for > 40 years. Several studies indicated that adequate concentrations of REEs supplements in the diet can improve body weight (BW) in cattle, pigs, chicken and rabbits, as well as milk production in dairy cattle and egg production in laying hens (He et al., 2010b; Thacker, 2013). Dietary REEs improved nutrient digestibility via increasing gut motility and permeability, therefore improving the absorption of various nutrients (Thacker, 2013). In addition, the optimum supplementation of REEs, $200 \text{ mg kg}^{-1} \text{ DM}$, enhanced rumen fermentation and feed digestion in sheep (Xun et al., 2014).

One study indicated that body weight gain and feed consumption ratio (FCR) was improved by 5 to 23% and 4 to 19%, respectively, by addition of REEs in the pig diet (Thacker, 2013). There were fewer chances of residues forming in the tissue of animals supplemented with REEs as compared to a commercial diet. Furthermore, bacterial resistance was not reported via exposure of REEs in animal nutrition (Thacker, 2013). REEs as feed additives for swine were mainly composed of lanthanum, cerium and praseodymium (Han and Thacker, 2010).

Another study by Cai et al. (2015) in broiler chickens showed that feed consumption ratio (FCR) was reduced in the REE-enriched yeast (RY) group. The RY product was obtained through a fermentation process. *Pichia kudriavzevii* LA30 (KCCM 11262P) was cultured at 30°C in an incubator ($250 \times \text{g}$) for 2 days. The culture (2%) was inoculated into an YM broth containing 320 mg kg^{-1} of La and 480 mg kg^{-1} of Ce at 30°C for 5 days in the fermenter. The culture broth was centrifuged at $15,800 \times \text{g}$ to separate the cultured cells and supernatant. The collected cells were washed, crushed and mixed with distillers dried grains (DDGS) as an excipient. The resulting mixture was air-dried. The final product of RY containing 2.82% La, 4.71% Ce, 40.3% DDGS, and 52.17% yeast was used in this study (Cai et al., 2015). Diets containing 70 mg kg^{-1} (La-citrate, 14.7 mg kg^{-1} ; Ce-citrate, 46.9 mg kg^{-1} Pr-citrate, 12.0 mg kg^{-1}) and 100 mg kg^{-1} of REE-citrate (La-citrate, 21 mg kg^{-1} ; Ce-citrate, 67 mg kg^{-1} ; Pr-citrate, 8.4 mg kg^{-1}) can significantly reduce the FCR in broilers compared to controls. However, FCR in broiler chickens cannot be affected by an addition of 70 mg kg^{-1} of REE-citrate (He et al., 2010b). The real phenomenon is still unclear, but the different responses may be due to REEs composition, experimental species, low biochemical rate, environment and physiological status of the animal. Conversely, a trial

Table 2

Studies encompassing REEs daily intake through various food samples and the impact on human health.

Sample Source	RCS ($\mu\text{g kg}^{-1}$)	EDI ($\mu\text{g kg}^{-1} \text{day}^{-1}$)	ADI ($\mu\text{g kg}^{-1} \text{day}^{-1}$)	HHR	Reference
Seafood	0.013	0.0005	0.015	Low	Liu et al.(2018)
Vegetables	37-984	0.69	70	Low	Zhuang et al. (2017b)
Vegetables	0.0008-0.003	0.017	70	Low	Jin et al.(2015)
Vegetables	70-64420	0.02-11.7	100-110	Low	Li et al.(2013)
Flower Herb Tea	95-7492	0.31-5.7	4200	Low	Ni et al.(2017)
Wheat	109	18-65	70	Low	Zhuang et al., (2017a)
Maize	43	18-65	70	Low	
Legume	95	18-65	70	Low	

RCS: REEs concentration in sample, EDI: Estimated daily intake, ADI: Allowable daily intake, HHR: Human health risks.

revealed that chicks fed diets containing 15,000 mg kg⁻¹ of yeast had a higher BW and FCR compared to the control group (Li et al., 2016). The RY might be considered as a safe additive without deleterious effects in broiler chickens. But the exact effect of RY in broiler chickens is still unknown, and further research is needed.

Elevated fortification of REEs (300 mg kg⁻¹ DM) in diets has a detrimental effect on the growth of rumen bacteria, which reduces the ammonia N utilization in sheep. REE Mixture was mainly comprised of lanthanum (35.0%), cerium (56.8%), and praseodymium (6.5%). REEs supplements reduced the ratio of acetate to propionate with increasing REEs in sheep diets. Moreover, the decrease in feed of acetate to propionate and increase of total volatile fatty acid (VFA) concentration were mostly caused by the increase in content of propionate. The reaction of ruminal pH to REEs supplementation increased the total ruminal VFA concentration. Previous studies stated that ruminal bacteria are dose-dependent and are affected by REEs supplementation (Adua et al., 2015). Lanthanides toxicity depends on chemical composition of Ln, the route of administration and the experimental animals. A study has showed that toxicity mechanisms such as phosphate deficiency (due to precipitation of phosphate-Ln), lipid-peroxidation (for lanthanide that can exist in more than one oxidation state), and competition between Ca/Mg and La disrupt bone integrity and cellular signaling (Zielhuis, 2006).

Several studies have been reported on impact of LREEs on animals (Pagano et al., 2015b). However, heavy REEs associated favorable effects are mostly unknown. Numerous data revealed REEs toxicity in lab animals (Table 3). There are few data on REEs about mutagenicity and carcinogenicity. However, these reports provide some data on Ce and Ho as mutagenic and Y as a carcinogenic. Notably, the United States Environmental Protection Agency (USEPA) still has not categorized any of the REEs as carcinogens. In addition, studies of long duration exposures of REEs are still deficient.

4.3. Aquatic organisms

Zebrafish (*Dania rerio*), a small and fast growing vertebrate species, can be easily bred and maintained in the laboratory for experiments. Zebrafish eggs are translucent and grow very fast, which provides clear observations of toxic effects on their internal organs. REEs at low concentration have positive effects on fish, but a comparatively high dose of REEs cause toxicity (Tang et al., 2009). REEs cause acute

toxicity in the growth of zebrafish embryos. However, this is probably due to the homeostasis of Ca²⁺ in zebrafish embryo. Zebrafish cells have high calcium contents. Due to similar ionic radius (9.6–11.5 nm) as the calcium ion (9.9 nm), it has been proposed that REEs might attach in place of calcium and affect physiological functions by regulating Ca²⁺ levels in zebrafish embryos (Cui et al., 2012).

Cui et al. (2012) found that zebrafish embryos exposed to La³⁺ or Yb³⁺ at concentrations from 0.01 to 1.0 mmol L⁻¹ resulted in delayed larval and embryo development, reduced hatching and survival rates, and induced tail deformities. These adverse effects were concentration-dependent and observed at low concentrations 0.1 mmol L⁻¹. La³⁺ interacts with calcium homeostasis and produces toxic effects in the zebrafish embryo. The toxic effects of the light REE La³⁺ were more acute than the heavy REE Yb³⁺. They concluded that the effect was due to the greater stability of Yb³⁺ complexes with biological molecules relative to La³⁺. Liver is more sensitive to stress and antioxidant enzyme plays key role in defense mechanism. If these enzymes reduce it may cause the reduction of fish immunity. For example, in *Carassius auratus* (goldfish), Ytterbium (Yb³⁺) had deleterious effects on liver and antioxidant enzymes (Damian, 2014). Goldfish were exposed to 0.01 to 1 mg L⁻¹ Yb³⁺, and catalase (CAT) activity was clearly reduced at all given concentrations compared with controls, while CAT was not concentration-dependent. Superoxide dismutase (SOD) was higher at Yb³⁺ concentrations of 0.05 or more. Glutathione peroxidase and glutathione S-transferase variations were not concentration-related. This suggests that liver CAT activity might be a good marker to evaluate the effect of REEs in aquatic organisms.

Marine organisms are very sensitive to several kinds of stressors and are able to activate different defense strategies. Ecotoxicity Testing Techniques (ETT) is mainly suitable for determining toxic effects on organisms in the aquatic environment (Fig. 4). ETT is crucial to estimate the innate properties of the substances and also has a potential role in the classification of chemicals. The sea urchin embryo is one of the most important marine invertebrates used as a bio-indicator of heavy metal pollution and an important toxicological model organism in developmental biology (Lewis et al., 2016). Sea urchin embryos (*Paracentrotus lividus*) exposed to 10⁻⁵ M Cerium (Ce⁴⁺) experienced entire mortality with an EC₅₀ of 1.9 10⁻⁶ M (Oral et al., 2010). Mitotic aberrations and developmental arrest were observed at concentrations from 10⁻⁶–10⁻⁵ M Ce⁴⁺. Exposure of Ce⁴⁺ 10⁻⁵ M to sperm of the sea urchin resulted in decreased fertility and 100% developmental

Table 3
REEs effects on domestic animals.

Element	Test Species	Findings	References
Lanthanum (La)	Rat (liver)	↑ GPx, GSH and MDA in mitochondria; ↓ SOD and CAT	Xia et al. (2011)
Gadolinium (Gd)	Rats Rat (cortical neurons) Four cell lines	↑ WBC count, alanine aminotransferase, aspartate aminotransferase, lactate dehydrogenase, prothrombin time, cholesterol and triglycerides ↓ platelet numbers, albumin and blood glucose ↑ Ferritin, transferrin oversaturation; and lipid peroxidation N-acetylcysteine (NAC) protection ↑ ROS formation; NAC protection ↑ Ferritin increased iron import	Ramalho et al. (2016) Pereira et al. (2012) Xia et al. (2011) Ghio et al. (2011)
Cerium (Ce)	Mice	Pulmonary hemorrhage and hepatic congestion, thickened alveolar septa, liver necrosis, neutrophil infiltrations; ↑ ROS and lipid peroxidation; ↓ antioxidant capacity; ↑ Proinflammatory cytokines, cyclooxygenase-2 ↑ Lipid peroxidation; ↓ antioxidant capacity; ↓ SOD and CAT	Kawagoe et al. (2008) Jie et al. (2014) Ma et al. (2011) Li et al. (2010c)
Neodymium (Nd)	Rat (liver) Mice	Accumulation in hepatocyte nuclei and mitochondria; ↓ SOD and CAT; ↑ GPx, GSH and MDA ↑ Lipid peroxidation; ↓ antioxidant capacity; ↓ SOD and CAT	Rim et al. (2013) Ma et al. (2011) Li et al. (2010c)
Terbium (Tb)	Mice	↑ lipid peroxidation; ↓ SOD, CAT and GPx < 0.1% Tb absorbed from the GIT	Damian (2014)
Yttrium (Y)	Rats	↑ calcium concentration in spleen and liver, ↑ glutamic-oxaloacetic transaminase and glutamic-pyruvate transaminase Poorly excreted in the urine < 0.5%	Damian (2014) Kitamura et al. (2012)

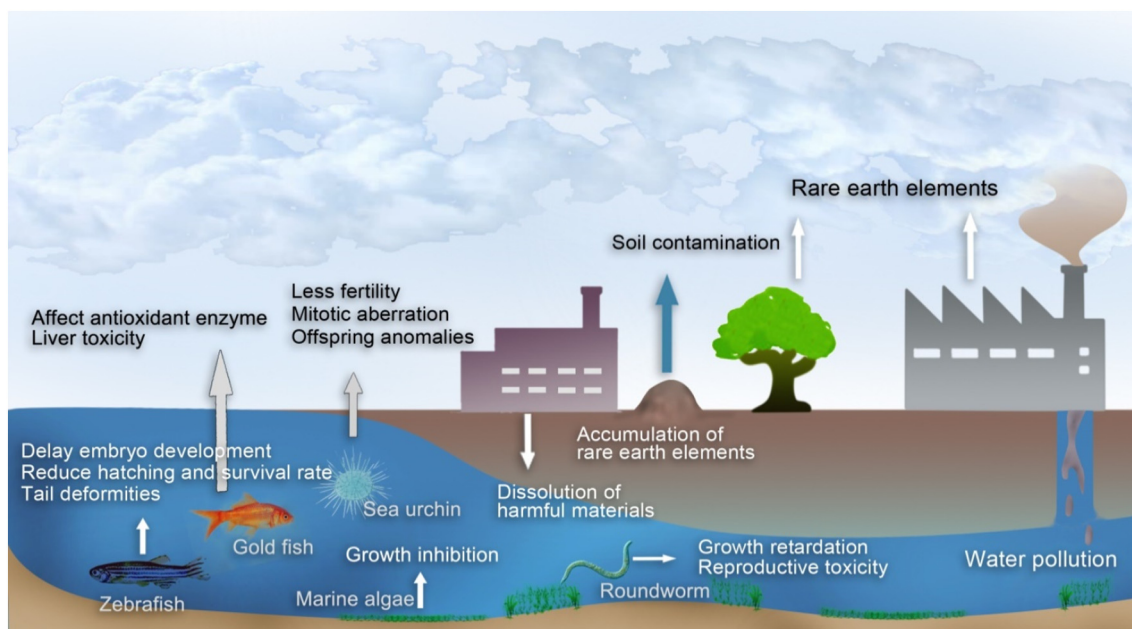


Fig. 4. REEs associated risks in aquatic species; Zebrafish (Cui et al., 2012), goldfish (Guo et al., 2002), sea urchin (Oral et al., 2010) and nematode (Zhang et al., 2010).

anomalies in offspring.

The findings of a study showed the diverse REEs sensitivities of the three sea urchin species. *Sphaerchinus granularis* showed higher

embryo and sperm exposures sensitivity compared to *Arbacia lixula* and *P. lividus*. Recently, four different sea urchin species showed variant sensitivities to Gd (III) (Martino et al., 2017). The results confirmed that

REEs	mg/kg	Germination %	Photosynthesis	Shoot growth	Root growth	Oxidative Stress	Plant Species	Reference
Tb	23.25-819						<i>A. syriaca</i>	Carpenter et al., 2015
La	0.4-150						<i>O. Sativa, S. lycopersicum, T. aestivum, C. limonia</i>	L. d'Aquino et al., 2009; Zeng et al., 2006
Pr	10-592						<i>R. Sativas</i>	Carpenter et al., 2015
Li	1-25						<i>H. annuus</i>	Hawrylak et al., 2012
Y	0.09-102.8						<i>Z. Mays, A. syriaca</i>	Maksimovic et al., 2014; Thomas et al., 2014
Te	16.8-66.7						<i>A. syriaca</i>	Kovacik et al., 2016
Er	5-1065						<i>S. lycopersicum</i>	Carpenter et al., 2015
Ce	0.21-1						<i>V. radiata, O. Sativa, S. oleracea</i>	Liu et al., 2012; Hong et al., 2002
Sm	26.5-317						<i>R. sativus</i>	Carpenter et al., 2015
Nd	0.5-1545						<i>Z. mays, T. aestivum, O. Sativa, R. sativus, S. lycopersicum</i>	Basu et al., 2016
Dy	1.20-78.25						<i>A. syriaca</i>	Carpenter et al., 2015

+ Effect (Green) - Effect (Red) ± Effect (Yellow) × Effect (Blue) Not Known (White)

Fig. 5. Effects of REEs in plants, the matrix has been created utilizing different plant responses under REEs exposure reported in the literature. Contradictory reports have been detected but effects of each REEs might be different depending on the specific concentration and the plant species.

P. lividus showed the greatest embryo sensitivity to Gd (III), while presenting minor effects on *A. lixula* and *S. granularis* embryos. Another study showed that *S. granularis* and *A. lixula* seemed more sensitive than *P. lividus*. The detected enhanced sensitivity of *S. granularis* to REEs might be an indication of a more general sensitivity of this species to environmental pollution.

5. Effects on plant growth and development

The REEs found in mineral rocks could be successfully used as phosphate fertilizers in the agricultural sector (Val'kov et al., 2010). They can be used in the form of leaf sprays, seed treatments or additions to solid or liquid root fertilizer formulations, as micronutrients or plant growth stimulators in the agricultural industry (Sabiha-Javied et al., 2010). However, still, there is a controversy between the risk of uptake capacity of beneficial vs. toxic concentrations, and its mechanism in plants. Taking these previous studies into account, there is a great need for further information on whether REEs can be used as an alternative crop nutrition option in protected and open field agricultural conditions.

Generally, plants with high REEs concentrations show reduced biomass, inhibited root growth, leaf chlorosis and morphological alterations, which most of the time lead to plant death (Straif et al., 2009). A decrease in the growth of wheat and rice plants were observed when concentration of 10 and 25 mg L⁻¹ of Nd were applied (Basu et al., 2016). Moreover, no significant reductions in biomass of pasture grasses were observed when these plants accumulated concentrations of 500–1000 mg kg⁻¹ Li in their leaf tissues, but tissue concentrations of > 1000 mg kg⁻¹ in lettuce plants resulted in necrosis of the older leaves and reduced biomass (Kalinowska et al., 2013). Additions of La and Ce at higher concentrations (> 51M) significantly effect the growth of *Zea mays* and *Vigna radiata* grown under hydroponic conditions (Behbahaninia et al., 2009; Diatloff et al., 2008; Zhang et al., 2013). The Tb concentration at 23–819 mg kg⁻¹ and Dy at 1–78 mg kg⁻¹ can inhibit root and shoot growth of *A. syriaca* while Pr (10–592 mg kg⁻¹) and Sm (26–317 mg kg⁻¹) also negatively affect the root and shoot growth of *R. sativas* (Fig. 5) (Carpenter et al., 2015). REEs can significantly affect plant growth parameters like seed germination, seedling, root and shoot growth (Thomas et al., 2014). In plants, the range of total content of REEs vary between 4 and 168 mg g⁻¹, but these values may fluctuate from species to species and REEs speciation in soils which broadly affects plant growth and development (Zeng et al., 2006). There are no long-term studies available regarding the use of REEs in both controlled and open field conditions. Such future long-term studies could be very helpful to reveal the potential impacts of REEs in agriculture.

These elements can be very beneficial when used in small dosage (approximately 0.5–1 mg L⁻¹) in agricultural plants (Thomas et al., 2014). Zeng et al. (2006) and d'Aquino et al. (2009) reported positive effects of La (0.4–150 mg kg⁻¹) on seed germination in crops like *O. sativa*, *S. lycopersicum*, *T. aestivum*, *C. limonia* as presented in Fig. 5. A positive effect of REEs was observed on the shoot development of maize

and spinach by Chaturvedi et al. (2014) by using small concentrations (1–10 mg kg⁻¹). A positive increase in seed germination and oxidative stress defense system was reported by Liu et al. (2012) when Ce (0.21–1 mg kg⁻¹) was applied in *V. radiata*, *O. sativa*, *S. olerace*. Different REEs had single or combined effects on different plant growth parameters, which make chelates and other specific interactions beneficial to plants for specific metabolism and biochemical reactions (Funes-Collado et al., 2015). Most plants absorb REEs by the uptake system for essential ions, and REEs with lower molecular mass are actively secreted out and act as chelators (Babula et al., 2008).

A small dosage of La³⁺ is suitable for stimulating root vigour as compared to higher dosages of the same element, which indicates a decreasing effect with amount. In a case study, cerous nitrate Ce³⁺ enhanced the formation of the seedling root tissue of *Dioscorea zingiberensis* at a concentration range of 1–15 mg L⁻¹, with a rapid propagation at 5 mg L⁻¹ (Wang et al., 2010). However, in *Eriobotrya japonica* (loquat) Eu and La at concentrations of 1.0–3.0 mM augmented root growth and enzyme activities like POD and (EC) nitrate reductase (Zhang et al., 2013). Both root growth and biochemical reactions exhibited by plants depend on the specific medium used for plant growth, because soils can interact with REEs and make it very sensitive to the crops at high concentrations. However, effects of La at concentrations of 5 to 50 μM on the growth of *Zea mays*, *Vigna radiata* and *Vigna mungo* were 100% positive (Chaturvedi et al., 2014).

Pre-soaking of seeds at concentrations of 1 and 10 mM of La³⁺ and REEs nitrate solution up to 2 to 4 h inhibited the seed germination of many crops (D'Aquino et al., 2009). Carpenter et al. (2015) demonstrated that applications of REEs to soils did not have a negative effect on seed germination rate of most agricultural crop plants; however, higher concentrations (1545 and 1065 mg kg⁻¹) of Nd and Er into the seeds of *R. sativus* and *S. lycopersicum*, respectively, were found to reduce seed germination rates (Carpenter et al., 2015). Thomas et al. (2014) also reported that Yt at higher concentrations (1052 and 2000 mg kg⁻¹ soil) has a negative impact on germination of *S. lycopersicum*, and Ce also has a harmful influence on seed germination of *R. sativus* and *S. lycopersicum* at 978 mg kg⁻¹ soil. At high pH, La⁺ does not have any influence on seed germination for *S. lycopersicum* and *R. sativus*.

Many studies are available to explore the relationship between seed germination and REEs, but still, it is not yet clear which REEs elements have positive and negative effects on specific plants at different concentrations as consumption of food can affect human health with serious health problems by excessive accumulation of REEs in human body by food ingestion in daily diet. Most studies reported that low concentrations of REEs are beneficial for seed germination in most of the agricultural plants investigated.

5.1. Effects on antioxidative defense system

Oxidative stress develops due to inflation and accumulation of reactive oxygen species (ROS). It controls the physiological and chemical phenomenon that carries out roughly all of the biotic and abiotic

Table 4
Effect of various concentrations of REEs on crop growth.

REEs Elements	Crop	REE (mg L ⁻¹)	Effect	Reference
Nd	<i>T. aestivum</i> , <i>O. sativa</i>	5	↑ enzyme activity	Basu et al., 2016
La	<i>T. aestivum</i>	0.4-1.4	↓ Mitotic index, ↑ Ascorbate content, total glutathione	L. d'Aquino et al. 2009
La	<i>S. lycopersicum</i>	0.007-0.14	↓ MDA	Ippolito et al., 2011
La	<i>S. lycopersicum</i>	0.07-1.4	↑ H ₂ O ₂	Ippolito et al., 2011
La	<i>O. sativa</i>	0.007-0.14	↑ MDA, SOA, POD, CAT and H ₂ O ₂ ,	Liu et al. 2016
Ce	<i>O. sativa</i>	0.14-0.21	↑ MDA, H ₂ O ₂ , SOD, POD	Liu et al., 2012
Li	<i>H. annuus</i>	25	↑ Carotenoids, malondialdehyde	Hawrylak-Nowak et al., 2012
Yt	<i>Z. mays</i>	0.88	↓ Proline	Maksimovic et al. 2014

stresses in agricultural plants. According to the most advanced research, due to oxidative stress in plants, ROS are developed from NADPH peroxidases and oxidases rather than from the classical chloroplast, peroxisome sources and mitochondria (Demidchik, 2015). Biotic and abiotic stresses both affect considerably the levels of secondary metabolites in plants, which are synthesized metabolites normally involved in many defense responses of plants (Montanari et al., 2008).

Different plant species were subjected to different doses of REEs, but the results from field and laboratory experiments were inconsistent. REEs applications play a crucial role as anti-oxidative agents, which may improve antioxidant enzymes such as glutathione S-transferase, glutathione reductase (GR), ascorbic acid peroxidase (APOX), catalase, CAT, POD and SOD activities (El-Ramady, 2011; Emmanuel et al., 2010). These above-mentioned enzymes play a vital role in decreasing ROS, helping to avoid oxidative stress. La^{3+} stimulate *Oryza sativa* plants to be resistant to environmental stresses by promoting catalase (CAT), superoxide dismutase (SOD) and peroxidase (POD) activity (D'aquino et al., 2009). A significant increase in the activities of enzyme content was observed when Nd was applied at 5 mg L^{-1} as in Table 4 (Basu et al., 2016).

Ippolito et al. (2010) reported that enzymatic and non-enzymatic antioxidants are differently affected by La^{3+} and REEs nitrate, and their behavior vary from one parameter to another depending on the plant organ. For example, in roots, La^{3+} (1 mM) and REEs nitrate solution (3 mM) treatments stimulate the ascorbate (ASC) and glutathione (GSH) contents while in shoots only La^{3+} nitrate caused an increase in ASC content. Moreover, GSH was lowered following both La^{3+} and REEs nitrate treatments. An increase in ASC peroxidase activity in shoots and roots whereas catalase does not show any difference in roots and little reduction in shoots.

If the concentration of REEs is too high, plants adopt different strategies to cope with metal induces of stress. One of the molecular strategies to cope with a high concentration of REEs and heavy metals is called metal homeostasis. It regulates the metal-induced ROS signaling pathway (Lin and Aarts, 2012). This is one of the natural strategy systems inside of the plants to cope with Ce and La toxicity. Wang et al. (2007) reported accumulations of proline in the plants treated with La and Ce. Proline interacts with ROS scavenger, which helps in reduction of protein stabilizer and lipid peroxidation. In *H. verticillata*, by decreasing the SOD and CAT activities and stimulating ROS production, these REEs like La and Ce prompt oxidative stresses that result in lipid peroxidation and lower chlorophyll and protein contents. La and Ce act like heavy metals and may be considered a new type of pollutant causing oxidative damage in plants.

6. Conclusions and future directions

Mainly, this monograph draws attention towards potential risks of intensive industrialization and modern agriculture on the release of REEs and their effects on plants, animals and humans health. Finally, it establishes that, REEs in spite of having a few biological benefits, they render innumerable harmful effects on plants, animals and humans. Occurrences of REEs in surface water and groundwater are caused by three main factors; weathering of deposits, leachate of mining areas, and discharges of industrial waste. Justifiable concern has been expressed in the published literature from Europe and U.S.A concerning the possible presence of REEs especially Gd in drinking water and their consequent effects on human health. The REEs hamper the metabolic system of brain, breasts, lungs, kidneys, bones and testes in humans. They cause shortness of breath, cyanosis, pneumoconiosis, coughing, skin lesions, itching, heat sensitivity and chest pain. Considering these human health issues associated with REEs, it is necessary to investigate toxicological and beneficial mechanisms to improve the basic knowledge about REEs in the healthcare field. The REEs may also be used to increase the animal's body weight via food supplements. However, they are not considered secure as feed supplements for all animals due to

insufficient scientific data. Metabolic system of aquatic organisms might be disrupted by high levels of REEs due to interference in calcium homeostasis. Cultivated lands in the vicinity of mining sites are rich in different REEs, and the REEs derived from mining processes could actually accumulate in agricultural soils and crops. Although, application of REEs could stimulate and promote plant growth and development at low concentrations. However, at higher concentrations REEs may cause serious adverse effects on plants at both physiological (germination, root and shoot length and biomass), and cellular (photosynthesis, senescence) levels.

In the context of above mentioned facts, following specific points are foreseen for developments in this field:

- Regulatory standards are required to establish the safe threshold concentrations of REEs for soil, environment and living organisms.
- Due to an unprecedented boost in environmental contamination, epidemiologic investigations with extensive inclusion of participants are warranted to determine the subsequent health effects of exposure to REEs.
- Domestic and aquatic species sensitive to high doses of REEs should be categorized to avoid life threatening effects.
- Each lanthanoid element should be analyzed to clarify its comprehensive toxicity to an organism. Further, there is a dire need to investigate the REEs associated with beneficial or harmful effects in domestic and aquatic animals to avoid economic losses and to support a profitable animal industry.
- Due to different levels of REEs in agricultural crops, scientists are still unable to classify them as toxic or beneficial. Thus, more studies should be performed to unveil the gainful effects of REEs on crops at molecular level.
- When using REEs via phosphate fertilizer, their long-term effects on soils, plants, water resources, animals, and human health should be considered carefully.

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Appendix A. Supplementary data

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