

Hypothetical Soil Thresholds for Biological Effects of Rare Earth Elements

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Abstract

Objectives: Anthropogenic exposures to rare earth elements are poorly known and there is limited information on their toxicity and ecotoxicity. At the same time, world production of rare earth elements has doubled every 15 years over the last half-century, and high environmental concentrations of gadolinium and lanthanum have already been found. The current review aims to give some estimates of overall exposures and an initial in-depth appraisal of thresholds for effects on agricultural soil. The results are envisaged to be used in initial assessments of agricultural soil where the natural concentrations have been anthropogenically enhanced.

Methods: An extensive review has been made of available scientific literature. Criteria have been established for the selection and analysis of eligible research. For instance, only effects on soils with vegetation have been included in the assessment of biological effects. A species sensitivity distribution based on 25% inhibition of organism functions has been used to establish thresholds for effects on soil organisms.

Results: Around the year 2000, mean anthropogenic contributions of lanthanides in European soil regions were at most a few per cent of the total soil content. Since then, they should have increased considerably. The proposed hypothetical threshold for agricultural soils is 1125 mg total rare earth element per kg of soil. This threshold is about 8 times the natural soil concentration.

Conclusions: If this result holds up to scrutiny, it implies that general anthropogenic pollution by rare earth elements will not be a threat to agricultural sustainability for the coming generation. A preliminary assessment suggests that this threshold would also protect humans from adverse effects due to secondary exposure.

Keywords: natural elements, rare earth elements, lanthanides, soil threshold, concentration ratios, species sensitivity distribution

1. Emerging Contaminants With Little Toxicity Information

1.1 Rare Earth Elements Production Has Doubled Every 15 Years But Environmental Consequences Poorly Known

What are rare earth elements? The rare earth elements comprise 17 elements, all belonging to group 3 of the periodic system. They include Sc in period 4, Y in period 5, and 15 lanthanides in period 6.

Doubling every 15 years. Rare earth elements play a critical role in advanced technology, from smartphones to radar systems, from catalysts for the cracking of crude petroleum to electric cars. The world production of rare earth elements has doubled every 15 years over the last half-century (United States Geological Survey [USGS], 2021).

High concentrations found locally. Production is dominated by China where significant environmental damage has occurred in the areas surrounding mining and processing operations (United States Environment Protection Agency [USEPA], 2012). High environmental concentrations have also been found elsewhere for gadolinium, which has been extensively used as a contrast agent in magnetic resonance imaging. Even in Mediterranean bottom water far off the coast of Sicily, gadolinium has had anomalously high concentrations (Censi et al., 2010). High concentrations of lanthanum have been revealed near a production plant for fluid catalytic cracking catalysts on the Rhine river (Kulaksiz & Bau, 2011), and major contributions to atmospheric particles have been

found near optoelectronic industries (Yu et al., 2020). Several-fold increases have been found for many light rare earth elements in the water in the San Francisco Bay area (Hatje, Bruland, & Russel Flegal, 2016).

Poor knowledge of general anthropocentric contamination. However, the degree of anthropocentric contamination of the soil with rare earth elements is poorly known. This is contrary to the knowledge for some other metals, where for instance maps have been made of European contamination with heavy metals (Toth, Hermann, Da Silva, & Montanarella, 2016).

Poor knowledge of toxicity. The rare earth elements are poorly known with respect to toxicity and ecotoxicity, but there are concerns about adverse health effects to the respiratory tract (Rim, 2016), and environmental exposure has been associated with impaired intelligence in children (Zhu et al., 1996). In general, major databases such as those of IFA (2021), and Canadian Centre for Occupational Health and Safety (2021) lack occupational threshold limit values for rare earth elements except yttrium.

A hundred-fold range in earlier suggested thresholds for biological effects on soil organisms. A critical value of 30 mg rare earth element per kg of yellow cinnamon soil was early proposed by Tang, Sun, Xia, Wen, and Zhang (2004). Based on much more information, a threshold of 50 mg/kg was found for effects on soil organisms by Li, Verweij, and van Gestel (2018). This was based on 5% of organisms affected but did not account for aging of the elements in soil. In contrast, Li, Jiang, Chen, Zou, and Zhang (2006) reported on a three-year study in a bean field, where there was no effect on the number of species and the number of animals at rare earth element concentrations up through 3000 mg per kg of soil.

The vision: understanding consequences of anthropogenic contamination. Knowledge of the degree of anthropogenic contamination and the associated thresholds for effects may be important to assess hazards to the ecosystem, and to human health via food consumption. An example relating to the latter was provided by the work for heavy metals by Toth et al. (2016). They found that while most European agricultural land can be considered adequately safe for food production, an estimated 6.24% or 137,000 km² needs local assessment and eventual remediation action. A similar assessment for rare earth elements is needed. This would require further elucidation of anthropogenic exposures, and of thresholds for effects on soil organisms and human health.

1.2 Objectives

The main objective of the current work was to find thresholds for the biological effects of rare earth elements on soil organisms. These would meet needs for management of contaminated soils by providing general benchmarks for soil quality that will be protective of biota in soil systems, accounting for organisms and pathways. It should be seen as a first component, to be later followed by a similar assessment of effects on human health.

In the process, the goal is also to critically assess the existing data, find gaps in what is available, and identify research needs. Further, the degree of anthropocentric contamination of European soils will be explored.

Thresholds for environmental effects will be sought for all rare earth elements and put into the context of thresholds for other elements including nanomaterials. An initial hypothesis is that the effect of all rare earth elements, atom for atom, will be the same since they all belong to group 3 of the periodic system.

2. Methods

An extensive review has been made of available scientific literature to find data pertinent to anthropogenic exposures to rare earth elements, and to thresholds for their biological effects in soils. Three different subsets of data have been reviewed, concerning:

- (1) Concentrations in soil (Section 2.3). Natural concentrations define thresholds to which biota are adapted, and anthropogenic concentrations are a basis for estimates of risks from the emissions of rare earth elements.
- (2) Transfer from soil to biota (Section 2.4). Effect levels in soils might potentially be inferred from effect levels under laboratory feeding conditions using concentration ratios from soil to food.
- (3) Effects on biota (Section 2.5). Effects on many species are reviewed and used to establish species sensitivity distributions from which thresholds for effects on soil organisms can be derived.

Criteria have been established for the selection and analysis of such data. Many factors need to be considered for the setting of thresholds (Section 2.5.1). In the following, the criteria are discussed, and available data reviewed. The final selection of data is reported in the ensuing Section 3. Results. For brevity in the main text, details of the reviewed data are given in three appendices corresponding to items 1, 2, and 3 above.

2.1 Selection of Elements and Anticipation of Aberrant Properties

Of the lanthanides, Pm is radioactive. It is only seen extremely rarely in nature as a fission product with a dominant half-life for Pm-147 of 2.6 years; there are data on its pathways in nature but not on its effects. Information on the other 16 rare earth elements will be sought.

There are differences in atomic properties and relative soil concentrations between the elements, as detailed below. Because of these differences one might expect that Sc could be aberrant from the lanthanides with respect to environmentally relevant properties, Y lie somewhere in between, and properties of the lanthanides Pr, Tb, Dy, Ho Er, Tm, and Lu might be quite similar, with La, Ce, Nd, Sm, Eu, Gd, and Yb possibly showing different properties.

2.1.1 Atomic Properties of Rare Earth Elements

The atomic properties are cornerstones influencing concentrations of elements in soil and food, as well as health and environmental effects. Among the rare earth elements, atomic properties tend to be similar. Some properties are aberrant, however:

- Sc: the lowest ionic and covalent radii, smallest atomic volume, lowest density, and second-lowest elastic modulus, and the highest specific heat capacity and electronegativity among rare earth elements.
- Y: intermediate between Sc and the lanthanides for many properties
- Ce: has a cubic crystal structure (along with only Eu and Yb), the dominant oxidation states include 4 in addition to the common 3, and Ce has the lowest elastic modulus and the lowest melting point of all rare earth elements. Besides the Eu and possibly Yb anomalies (see Aberrations for Ce, Eu, and Yb in Section A2.3.1), a Ce anomaly is well-known in geology. Unlike the Eu and Yb anomalies, there is no trend anomaly for European soil concentrations, but a major anomaly for Moroccan apatite (Ramos et al., 2016).
- Sm: the only rare earth element with a rhombohedral crystal structure
- Eu and Yb: the dominant oxidation states include 2 in addition to the normal 3, the crystal structure is cubic rather than hexagonal, the boiling and melting points are rather low, the covalent radius and atomic volumes are rather high consistent with rather low density, the third ionization energy is high, and they have exceptionally low elastic moduli. In geology, a europium anomaly is well-known, and one can be seen in dietary concentrations (see Section A2.3.1). In chondrite normalized European soils, there are deviations from a smooth atomic number dependence of soil concentrations for Eu and Yb (Ramos et al., 2016). There are also large deviations in a sedimentary apatite from Morocco.
- Gd: there is a large drop in third ionization energy from the preceding Eu. This is compensated by rather high first and second ionization energies. Gd also has a high specific heat capacity.

Further, there are clear trends with the atomic number for electronegativity, elastic modulus and density (increasing), as well as covalent and ionic radii and specific heat capacity (decreasing). Such trends might be associated with trends in environmental properties of heavy versus light lanthanides. The following review will show to what extent data on soil and biota concentrations and effects on living organisms will reflect the differences in atomic properties.

2.1.2 Aberrations in Soil Concentration Over the Periodic System

The natural soil concentrations might also be important for biological effects. For instance, in the periodic system of elements, lanthanides are so related to the group 2 element calcium that they have been called “super-calcium” (Brown, Rathjen, Graham, & Tribe, 1990). Further, cerium plays a role similar to that of the other major group 2 element, magnesium (Guo, Nazim, Liang, & Yang, 2016). Interaction with phosphorus may also be important (Kovaříková, Tomášková, & Soudek, 2019). In the calcium case, the interaction is due to some trivalent lanthanides being similar in ionic radius to divalent calcium, which they can replace in enzymes and other functional proteins. The soil concentration for Ca in group 2 of period 4 (25 000 mg/kg for Europe) by far outweighs that of the sum of all rare earth elements (about 200 mg/kg), and of the sum of all other group 2 and 4 elements in periods 4-7 (4 400 mg/kg). Ca thus provides the dominant competition. The links to such competitions need further research.

2.2 Availability of Suitable Data

Data on exposures such as concentrations in soil or water or daily intakes can be found for almost all elements of interest.

Data on environmental effects are scarce and above all available for the more abundant elements Y, La, and Ce. Several sets of data on effects on single organisms are available. For the generalization of data to be meaningful, it should ideally start from a set of element data that has been derived coherently, preferably under the scrutiny of many different scientists. For the current analysis, this ideal cannot be realized with respect to thresholds for effects on soil organisms, and the conclusions are hypothetical.

2.3 Soil Concentrations of the Selected Elements

Thresholds for effects of natural elements on soil organisms are closely related to natural soil concentrations for elements in groups 5-12 of period 4, and some systematic dependence also appears to exist for periods 5 and 6 (Bengtsson, 2019). It is of interest to explore if similar relations might hold also for the rare earth elements in period 3, groups 4 (Sc), 5 (Y), and 6 (lanthanides). Little information has been found for effects on biota exposed in soils. Effect levels in soils might however potentially be inferred from effect levels under laboratory feeding conditions using concentration ratios from soil to food. Soil concentrations are reviewed in Appendix 1 and transfer from soil to biota in Appendix 2. In summary, the soil concentration of rare earth elements may vary by about a factor of 1000 between different locations. Higher soil concentrations of lanthanides are linked with several times lower relative concentrations of heavy lanthanides than lower soil concentrations. The mean rare earth concentration in European soils increased several-fold with the mean soil fractions of sand and total organic carbon, while no strong dependence on pH was found. Mean concentrations among different countries may vary by about a factor of 5. For elucidating health and environmental risks, a world mean sum lanthanide soil concentration of 133 mg/kg was selected. This can be compared with an average sum concentration of 126 mg element per kg dry soil for Europe and a sum concentration of 177 mg element per kg dry soil for China.

Around the year 2000, the anthropogenic contributions to rare earth concentrations in Europe at most amounted to a few per cent of the natural ones (Sections A1.2 and A1.3).

2.4 Transfer from Soil to Biota

Soil to biota transfer data is available for many parts of the transport from soil to food. Conceivably, they might be related to thresholds for effects on biota. The discussion in Appendix 2 starts with an elaboration of some uncertainties and defines the *concentration ratio* for soil to biota transfer, which is the ratio of the element concentration in the biota (mg/kg dry mass) to that in the soil. Appendix 2 continues with the differences among the elements and then discusses the extent of transfer from soil to biota. Finally, the transfer of Sc and Y is examined. The results on transfer are presented in Section 3.1.

2.5 Selection of Threshold Data

Recent reviews on effects in soils of rare earth elements include those of Gonzalez et al. (2015), Ramos et al. (2016), Adeel et al. (2019), and Blinova, Muna, Heinlaan, Lukjanova, and Kahru (2020). Conflicting results on sensitivities abound. One reason for this is that rare earths generally tend to enhance organism growth in the soil at low concentrations. Only at higher concentrations will the negative effects on growth and development dominate. Another difficulty has pertained to the study of aquatic species. The formation of insoluble species in some highly complexing media likely leads to changes in the soluble concentration of lanthanides during some tests (Gonzalez et al., 2015). Similar difficulties might also adhere to many studies of soil organisms made in nutrient or other solutions, and are further discussed by Blinova et al. (2020). To add to the complexity, rare earth elements may also enhance the taste and nutritional value of crops such as oranges (Cheng, Ding, Li, Zhang, & Wang, 2015).

The purpose of the analysis below in this Methods is to explore the extent to which effect concentrations vary among rare earth elements and discuss methods to establish soil thresholds. The lanthanides are treated separately from the other rare earth elements Sc and Y. Only exposures in real soil have been selected, thus no exposures in hydroponic solutions or the like; it is known that natural soils are far more heterogeneous and complex than homogeneous materials, and retention of engineered nanomaterials is always higher in natural materials (Cornelis, Hund-Rinke, Kuhlbusch, van den Brink, & Nickel, 2014).

For microorganisms, only experiments where soils have borne crops have been used. The intention is to establish thresholds for environmental effects of continuous exposures of the kind encountered in the environment after year-long emissions, and short-term experimental exposures should be corrected for insufficient aging.

2.5.1 Principles for Setting Soil Thresholds

General soil thresholds are often used in investigating and remediating contaminated sites (Gaudet, Bright, Adare, & Potter, 2002), and may have a role together with detailed site assessments in different stages of management, such as preliminary and detailed site investigations, as well as in site management planning and implementation

(Western Australia Department of Environment and Conservation, 2010). Many factors need to be considered when soil thresholds for the protection of the environment are set. Gaudet et al. 2002 provide an illustrative discussion of the issues at stake in the Canadian case. In the following, the parameters involved are the type of land use, the pathways of exposure, the desired degree of protection, the special attention needed for microorganism processes, the availability of data, and the aging phenomenon. In a more detailed assessment at later stage of management, additional factors need to be considered such as soil texture, organic matter content, and soil pH, as well as potential secondary poisoning of for instance birds and humans.

(1) Type of Land Use

Land can be used for different purposes, *e.g.*, agricultural, residential, and industrial. In the current discussion, the use of agricultural land has been chosen. Common policy is that the level of protection for commercial and industrial land use does not need to be as stringent as for agricultural or residential/parkland land uses.

As an example, the widely used Finnish set of soil thresholds (Ministry of the Environment, Finland, 2007) encompasses three levels of contamination:

- Threshold: triggers assessment of soil contamination and remediation needs.
- Lower guideline: defines the area as contaminated for general areas.
- Upper guideline: defines industrial, storage, or transport areas as contaminated.

On average, the lower guideline concentration is 4 times the threshold concentration, and the upper guideline is 10 times the threshold concentration.

(2) Pathways of Exposure

Exposures may occur through different pathways, *e.g.*, soil contact for invertebrates or food ingestion for animals. For the discussion below, soil contact tends to be the most limiting. In the Canadian case for agricultural soil (Gaudet et al., 2002), consideration is given to no-effects and effects on soil nutrient cycling processes, invertebrates, crops/plants, and livestock/wildlife.

(3) Degree of Protection Aimed For

For the Canadian case, the desired degree of protection is discussed in detail in a protocol of some 200 pages (Canadian Council of Ministers of the Environment, 2006). The overall objective is to achieve a level of ecological functioning that sustains the primary activities associated with the chosen land use. Adverse effects are identified that undermine a species' ability to survive and reproduce under normal living conditions. Selected endpoints normally include those considered critical to the maintenance of soil-associated plants and animals, such as mortality, reproduction, and growth (Gaudet et al., 2002). The procedure for deriving soil quality guidelines contains several options. One of these, pertaining to soil contact, involves finding the concentration below which 25% of the species concerned are protected. If necessary, a safety factor can be applied before this option is used as the threshold effects concentration. Other options can have a starting point in the lowest observed effect concentrations or lethal concentrations. It is important to note that the protection aimed for is not total protection against all kinds of effects on all organisms.

For the current discussion, the lowest observed effect concentrations *per se* are not useful as policy thresholds, besides their weaknesses on statistical grounds (Laskowski, 1995). The Benchmark Dose concept for assessment of human health risks (European Food Safety Agency [EFSA] Scientific Committee, 2016) has gained increased recognition, and is a more interesting model. It is commonly applied to a Benchmark Dose-Response of 25%. In the current evaluation, effects at 25% have been sought to provide the basis for the assessment of ecological effects. Validation studies show that the ranking involved in species sensitivity distributions reflects expected relative ecological impacts (Posthuma & De Zwart, 2014).

(4) Separation of Species and Functions for Microorganisms

When it comes to microorganisms, the species approach will not give useful results. Microorganisms play a major role among soil organisms. They are extremely versatile and the composition among thousands of species is constantly changing. Effects on microorganisms in themselves may therefore not be an indication of harmful effects on the functioning of the soil ecosystem. As an example, lanthanum additions stimulated the growth of actinomycetes, fungi, and cellulolytic bacteria at different rates at different concentrations (Tang, Sun, Xia, Wen, & Zhang, 2004). Only when the overall functions of the microorganisms in the soil ecosystem are affected, however, may the functioning of the soil ecosystem be threatened. Indicators of such overall function effects have been used in threshold assessments, and effects on species and functions have been treated separately. Examples of such indicators include a total number of bacteria, bacterial biomass, and dehydrogenase activity.

The term function sensitivity distribution has been used to describe the management of effects on soil process functioning (Suter II, Traas, & Posthuma, 2002).

(5) Availability of Data and Ranking

Data is often scarce and disparate. In the current application, a species sensitivity distribution is used. A species sensitivity distribution for a chemical is commonly based on the logarithm of a measure of an ecotoxicity endpoint, for instance, the concentration at which 50% of the organisms die. The species sensitivity distribution curve is fitted to the cumulative frequency distribution of these logarithms across organisms for which data is available. The minimum size of the data set that can be employed for establishing such a distribution and the minimum quality of eligible studies is disputed (Posthuma, van Gils, Zijp, van de Meent, & de Zwart, 2019), and further elaborated in Section 2.5.1(7). For lanthanides, marginally enough data is available for the aquatic toxicity of several La and Ce compounds to enable environmental risk assessment using species sensitivity distributions (Posthuma et al., 2019, Supplemental data), but no corresponding major data compilation has been found for terrestrial organisms. A toolbox has recently been made available for the calculation of species sensitivity distributions (Center for Computational Toxicology and Exposure, EPA's, 2021).

Note that microorganisms are treated separately from other species (Section 2.5.1(4)).

(6) Aging and Long Exposures

As mentioned in Section 2.5.1(3), the overall objective is to achieve a level of ecological functioning that sustains the primary activities associated with the chosen land use. The length of exposure involved is in most found studies a few weeks, in some cases months, and very rarely years. For interpretation of study results, the duration of exposure must be related to the objective of sustaining activities, in the current case for agricultural purposes. Two different occurrences are involved:

- Aging of compounds added to the soil, which are moved to soil matrices where they become less available for organisms. The aging phenomenon is well known (Section A.2.1). As a crude hypothetical correction for lack of aging, sensitivities have been reduced by a factor of 1-3.4 if the equilibration time has been less than 6 months.
- Exposure of organisms through their life cycle. If the mean residence time in organisms is short compared to the life span, element concentration in the organism will reach equilibrium before the life span is attained. The most relevant studies should be the ones where exposure occurs during periods that are approximating to or beyond the mean residence time for the element in critical organs of the organism.
 - For *microorganisms* with their short life cycles, equilibrium concentrations are generally attained.
 - For *short-lived plants*, the found studies often comprise the period from seed to plant maturity, and the later decay and withering is less significant from the perspective of sustaining soil activities. For *long-lived plants* such as trees, results from study periods of a few weeks may underestimate the adverse effect of a continuous exposure.
 - For *invertebrates*, the studies of interest mainly concern arthropods with life cycles of a few months to a few years. Results from study periods of a few weeks must be discussed in the light of the short fraction of the lifetime of arthropods that is involved. Little and conflicting information has been found on turnover times.

According to a review of earthworm metal concentrations (Richardson, Görres, & Sizmur, 2020), earthworms exposed less than 2 weeks generally had lower concentration ratios to soil than those exposed their entire life. For exposures 3-20 weeks, however, concentration ratios could vary a factor of 100 up or down those of lifelong exposures. Factors like aging, toxicity, and essential element interaction were given as potentially contributing to the variations. The review comprised only one element, uranium, in periodic system group 3, with a concentration ratio near 1 for lifelong exposures.

This scarce information does not give grounds for assuming continued enhancement of rare earth element concentrations in arthropods after 4 weeks of exposure.

- For *mice, rats, pigs, and rabbits* there may be significant losses of ingested rare earth elements over the lifetime.

Scarce evidence suggests that a large fraction is lost from 5 to 8 weeks after ingestion for rats (Cao et al., 2020). A general retention time of 45 days was given by Nakamura, Tsumura, Tonogai, Shibata, and Ito (1997). When the exposure time was increased by a factor of 6 from 25 to 150 days, the

concentration of Yb in the liver increased by a factor of 3 and in the femur by a factor of a 9 (Feng et al., 2007). The mean residence time in rats and rat liver of injected Ce was about a month (Norris, Lisco, & Brues, 1956), and this also applied for the retention of Y between 16 and 64 days (Hamilton, 1944).

In humans, rare earth elements tend to concentrate in bones, about 100 times more than in the liver, kidneys, lungs and testes (El Ramady, 2010). The residence time of Gd in the human bone may be of the order of 8 years (Darrah et al., 2009), consistent with the accumulation in the rat femur.

In piglets daily fed a commercial additive containing rare earth elements, the only major accumulation of rare earth elements after 126 days occurred in bone and not in heart, liver, kidney, muscle, or skin + subcutaneous fat (EFSA, 2019). Similarly, for pigs, the accumulation rate of La and Ce in the muscle, liver, and kidneys was very low after feeding the rare earth element diet for 3 months (He, Ranz, & Rambeck, 2001).

Thus, while bones may serve as accumulators of rare-earth metals, the concentrations in other organs influencing growth, survival, and reproduction might be reaching semi-equilibrium within a few months, suggesting that exposures of such length may not grossly underestimate these effects. This should be considered a hypothesis until further research can give better information.

o For *ruminants* such as sheep, goats, and cows, the found study periods of a couple of months are far shorter than the typical life span of 10-20 years. The significance of such short exposures in the sustainability context must be discussed. Little relevant information has been found.

This limited information suggests that the study periods of a couple of months are too short to entail a full scale of effects from sustained exposures over ruminant lifetimes, and that effective concentrations may be overestimated.

(7) Number of Studies

Concerning the number of studies required, the principles enumerated by the Canadian soil guideline protocol (Canadian Council of Ministers of the Environment, 2006) have been consulted for guidance. According to this protocol:

- Data for plants and invertebrates should, where possible, be evaluated separately.
- At least ten data points from at least three studies are required.
- A minimum of two soil invertebrates and two crop/plant data points must be represented. Single studies reporting data for multiple species and/or multiple endpoints will be considered as separate data entries.
- Data points for the same species that are redundant should be combined into a single composite response concentration calculated as the geometric mean of the individual values.
- For data points with the same concentration, it is recommended that these be assigned separate, sequential ranks.

All requirements could be met in the current assessment.

2.5.2 Assumption of Little Variation in Effects Among Lanthanides and Rare Earth Metals

Different lanthanides are similar in many respects as discussed in Section 2.1.1. One might expect rather similar thresholds for effects with possibly significant deviations for Ce (Section 2.1.2). Most studies reviewed by Blinova et al. (2020) support the similarity hypothesis. There are, however, signs of atomic number dependencies. For aquatic toxicity, heavy lanthanides have been predicted to be more toxic than light ones. For instance, Blinova et al. (2020) quote the example of the marine bacterium *V. fischeri*, the sensitivity of which to Gd was 7-fold higher than that to La. Blaise, Gagné, Harwood, Quinn, and Hanana (2018) studied the freshwater invertebrate cnidarian *Hydra attenuata*. Lethality to 11 lanthanides varied within about a factor of 2 and morphological changes occurred at concentrations between one-fifth and 2.7 of the mean. A detailed discussion of variations in effects among rare earth elements is given in Appendix 3.

Nonetheless, many experimental results are contradictory. There may be flaws in the chemical speciation in ecotoxicological test media that might entail marked underestimation of lanthanide ecotoxicity (Gonzalez et al., 2015). Another difficulty is related to the failure of certain fibroblasts to respond to lanthanide induced growth stimulation which may reflect the physiological state of the cells in question rather than a unique response to the lanthanides (Jenkins et al., 2011). More studies are needed to elucidate the possible existence of common

mechanisms or modes of action across the lanthanide series. Pending more convincing information, the similarity hypothesis is applied for the setting of thresholds (Section 3.5.2).

2.5.3 Examples of Lanthanide Effects on Organisms Exposed in Soils

Major reviews concerning adverse effects on soil organisms include those of Hu, Shen, and Zhao (2006), Redling (2006), El-Ramady (2010), Rim (2016), Kovaříková, Tomášková, and Soudek (2019), and Agathokleous, Kitao, and Calabrese (2019). Examples of adverse effects for major classes of organisms are given in Appendix 3.

It should be noted that many studies encompass the influence of rare earth exposures on microorganisms in soil without vegetation. Such effects may be quite different from those where the microorganisms have a vegetation environment. For instance

- The dehydrogenase activity was up to 15 times higher in soil bearing maize or oilseed rape compared with that for soil without vegetation (El-Ramady, 2008);
- Nano-CeO₂ did not affect soil bacterial communities in unplanted soils, but 100 mg/kg nano-CeO₂ altered soil bacterial communities in planted soils, indicating that plants interactively promote nano-CeO₂ effects in soil (Ge et al., 2014).

Studies on microorganisms without vegetation were deselected and for the current assessment, only studies on soil with vegetation were used for the evaluation of thresholds.

For rare earth elements, no thresholds have been found relating to mammals in a soil environment. However, many effect thresholds for intakes of rare earth elements by mammals are available. These might be translated to soil concentration thresholds if the concentration ratio soil-mammal-diet can be determined, as discussed in Section 3.4. There are, however, large uncertainties in the concentration ratios (Section 3.2).

Even less information has been found for birds.

2.5.4 Examples of Effects of Sc and Y on Soil Organisms

Little information may be found on the effects of scandium and yttrium. For instance, in compiling data for a major review, Gwenzi et al. (2018) could not obtain any literature on the toxicity of Y in humans, and information on biological effects was scarce in the eChemPortal (Organisation for Economic Co-operation and Development [OECD], 2021). Because of this, the selection criteria applied for lanthanides could not be upheld for Sc and Y.

Judging from atomic properties (Section 2.1.1), Y can be expected to be intermediate between Sc and the lanthanides for many properties. Concentration ratios might also give some clues (Table A2.1); the concentration ratios are not significantly different between Sc, Y, and lanthanides but the variation is large.

There is some information on the effective concentrations for Sc and Y relative to those for lanthanides (Section A3.3.2). This points in the direction of the same effect concentrations for Sc and Y as for lanthanides per mol, within a factor of 2. The limited information on the effects of Sc and Y suggests that soil concentrations of about 1000 mg/kg might not be harmful to plants or to rodents living in the soil environment.

3. Results

As mentioned in the introduction to Section 2. Methods, the data reviewed concern:

- Concentrations in soil,
- Transfer from soil to biota, and
- Effect concentrations for soil organisms. A special assessment has been made for mammals since there is no information of effect concentrations for mammals in a terrestrial habitat.

The information is summarized below while details are given in the respective appendices. The information is used to derive hypothetical thresholds for initial assessments of the status of agricultural soil where the natural concentrations have been anthropogenically enhanced.

3.1 Concentrations in Soil

Under geological conditions, the relative concentrations of the different lanthanides in soil may be very changeable. The emphasis could be on light, intermediate, or heavy elements (Section A1.5). Similar variations occur in the aquatic environment (Section A2.3.3). Light lanthanides tend to be clearly enhanced at high total lanthanide concentrations (illustrated in Figure A1.1 of Section A.1.5).

Anthropogenic depositions were explored in appendix A.1.2. From that discussion, it appears that soil properties are the main factors behind relatively high topsoil concentrations, rather than unusually high depositions. It should be noted that the underlying soil measurements are about two decades old. In the years between 2000 and 2020, the world production of rare earth elements has increased 2.6 times (USGS, 2021), and this should have resulted in more significant anthropogenic contributions to topsoil concentrations.

3.2 *Transfer From Soil to Biota*

The transfer from soil to biota is discussed in detail in Appendix 2. There, the potential to relate soil-to-biota transfer data to the threshold for effects on biota was elaborated for lanthanides, Sc, and Y. The concentration ratios for lanthanides from soil to biota vary about 100 000-fold, with a range from 0.000 002 to 0.2 (Section A.2.4). Section A2.1 gives examples of extremely high local concentrations in a few biota samples, e.g., for Dy and Er. An extreme case concerns a food sample with 20 000 times higher Er concentration than the 90th percentile.

The concentration ratios biota/soil are enhanced for light lanthanides in human hair and wheat seeds, maize seeds, and legumes (Section A2.3.3). In contrast, the concentration ratio tends to vary among lanthanides less than a factor of 2 or so from soil to many fruits, vegetables, and plants as well as many parts of the human body (Section A2.3.2).

The concentration ratios for Sc and Y fall within the range for the lanthanides, and are not significantly different from those, but the variation is large (Section A2.5).

3.3 *Effect Concentrations for Soil Organisms*

To sum up the assessment in Appendix 3, when it comes to aggregated complex effects such as growth or death, there are in many cases little differences in toxicity between lanthanides. Low standard deviations in the percentage range have been noted for some monocellular organisms and male mice. Low standard deviations in the tens of per cent range have been demonstrated for female mice, plants, and soil invertebrates. It is thus a reasonable hypothesis that for effects on soil organisms that affect soil productivity and ecotoxicity, all non-radioactive lanthanides can be assumed to be equally effective on a molar basis. This is consistent with the findings of Xu and Wang (2001) that the influence of individual rare earths in mixtures on two discussed microbial processes can be additive. It does not exclude the possibility that different lanthanides have different effectiveness under other circumstances, as exemplified for luminescence of monocellular organisms. A beautiful example of systematic variation comes from the influence of lanthanides on red blood cell deformability (Alexy et al., 2011): the change in shear stress due to La, Sm, Eu, Dy, and Er varied from 0.1 to 0.7 and was very clearly related to the lanthanide ionic radius which only varied between 1.03 nm and 0.89 nm.

There are known anomalies for Ce, Eu, and Yb in the trend of soil concentrations versus atomic number (Section 2.1.2). Since Eu and Yb hold less than a few per cent of the sum concentration in soil, any aberration may not be significant for the health or environmental effects compared to effects of the sum of lanthanides. In contrast, Ce accounts for 40-60% of the total lanthanide concentration in soils, and differences in the health and environmental effects of Ce in relation to other lanthanides could lead to important differences in the total lanthanide effects. Potential such differences should be reviewed when threshold concentrations are discussed.

3.4 *Effects on Mammals*

The thresholds for effects of rare earth intakes on mammals (Section A3.2.4) can be translated to thresholds for soil concentrations using the concentration ratios (Appendix 2).

According to the experiences of feed supplement for cows, sheep, and goats (Redling, 2006), addition of 400 mg rare earth element per kg feed does not seem to entail any adverse effects. The found concentration ratios for pastures have a range of 0.002-0.2 (Section A2.4). If the geometric mean 0.02 is assumed to represent common conditions, the no-observed adverse effect level would be at least $400/0.02 = 20\ 000$ mg rare earth element per kg soil. Pigs and poultry would in nature be expected to have larger shares of feed with low concentration ratios such as grains and correspondingly higher soil thresholds.

Two studies with chronic exposures of rats and mice and one for rabbits are summarized in Appendix A3.2.4. None of them suggest any reduction in body weight or other adverse effects if they had been feeding in nature at a soil rare earth element concentration below 1000 mg per kg soil.

However, several studies suggest the lowest observed adverse effect level for neurotoxic effects in the range of only 1-10 mg rare earth element daily per kg body weight for chronic peroral administration to mice and rats. A level in the lower end of this range was found for neurological effects on the ensuing pups after shorter in utero

exposure of rats (Xiao et al., 2020). Using the above-mentioned common concentration ratio for pastures of 0.02, the lowest concentration of 1 mg/kg body weight may correspond to a soil concentration of $1/0.02 = 50$ mg La per kg soil. For a mixed diet, the threshold should be considerably higher.

3.5 Proposed Hypothetical Thresholds

3.5.1 Applicability

The proposed hypothetical soil thresholds are envisaged to be used in initial assessments of soil where the natural concentrations have been anthropogenically enhanced. They could be used together with detailed site assessments as described in Section 2.5.1. The use of agricultural land is the primary focus. Only effects on the environment have been considered, and the overall objective is to achieve a level of ecological functioning that sustains the primary activities associated with the chosen land use.

3.5.2 Assumptions for the Derivation

It is assumed that the effect is determined by the molar sum of all rare earth elements since effect concentrations are quite similar across all rare earth elements on a molar basis (Section A.3.3.2). There may be deviations from this pattern for Ce which require special scrutiny (Section 3.3). The potential influence of competition from Ca may also need attention (Section 2.1.2).

The ecological functioning is assumed to be sustained at a concentration below which 25% of the species concerned are protected. Such a concentration is assumed to be approximated by the 25th percentile of species sensitivity distributions obtained from a combination of concentrations giving 25th percentile effects. Some support for the assumption is given by Posthuma and De Zwart (2014) who showed that the ranking involved in species sensitivity distributions reflects expected relative ecological impacts.

When it comes to microorganisms, the species approach will not give useful results (Section 2.5.1(4)). Only when the overall functions of the microorganisms in the soil ecosystem are affected, the functioning of the soil ecosystem may be threatened. Indicators of 25% inhibition of such overall function have been used in threshold assessments.

Aging (Section 2.5.1(6) and Appendix A.2.1) is a real effect that is rarely dealt with in ecotoxicological studies. It is here handled by a correction for aging. This correction is not applied to data encompassing more than 6 months of soil equilibration and organism growth. For shorter studies, the effective concentration is multiplied by a factor that is 3.4 at 0 months duration and the correction factor then decreases linearly with time through 6 months.

3.5.3 Important Data Used

The most important information from the studies used for derivation of soil thresholds is summarized in Table 1. Generally, the studies are of too short duration to have accounted for the effects of aging of the supplied rare earth elements in soil. The exception is the 8 month study on invertebrates. There are 16 eligible entries for plants but only 2 for invertebrates and 4 for microorganisms.

The thresholds are expressed in mg rare earth element per kg soil. If they had been in terms of mol/kg, this would mainly have impacted the results for:

- 5 plants studied by Carpenter, Boutin, Allison, Parsons, and Ellis (2015) and Thomas, Carpenter, Boutin, and Allison (2014), where Y was also used. The mean IC_{25} of those plants across the elements would have been impacted by less than 10% and the derived threshold by about 2%
- the earthworm study of Wu, Feng, and Qian (2012), where the use of molar concentrations would have had a similar minor impact.

Therefore, the accounting for molar weights was omitted. There were no data for Sc where the correction by mol would have been larger.

In the later discussion, the results are compared to those of nanomaterials (Section 4.1), and no-effect findings (Section 4.2).

3.5.4 Proposed Hypothetical Thresholds

The data in Table 1 were fed into the United States Environmental Protection Agency toolbox for species sensitivity distributions (Center for Computational Toxicology and Exposure, EPA's, 2021). Data were fitted to a lognormal distribution using a maximum likelihood approach. The resultant 25th percentile of the distribution was 1125 mg rare earth element per kg soil (95% confidence interval 765-1674).

On a side note, the same data but uncorrected for aging gave the 25th percentile of 421 mg rare earth element per kg soil (95% confidence interval 279-676).

4. Discussion

Much research has been devoted to the effects of rare earth elements on organisms. For the development of thresholds, only a few studies have been selected, compatible to illustrate a level of ecological functioning that sustains the primary activities associated with the chosen land use. Some deselected studies could however give perspective on the proposed thresholds. These include investigations using nanomaterials, studies where no effects have been demonstrated, and deselected studies on invertebrates and mammals. In the following sections, results from such work are discussed as well as the validity of the used assumptions and future research needs.

4.1 Results From Nanomaterials

When nanomaterials came into use a few decades ago, there were fears that their small size would entail especially hazardous effects on organisms. Much work has been devoted to addressing such concerns.

Table 1. Biological effects of rare earth exposures re-layout

Organism	Elements studied	Effect	Exposure period	Corr. factor	Threshold mg/kg	Reference
Microorganisms						
Microorganisms	La, Ce, Pr	Dehydrogenase activity	Plant growth 9 w	2.56	691	El Ramady, 2008
Microorganisms	REE mixture	Microbial biomass	16 w	1.91	2174	Zhou, 2003
Microorganisms	La	Microbial carbon, nitrogen, CO ₂	16 w	1.91	2212	Chu, 2001
Microorganisms	La	Bacterial count	75 d	2.40	2880	Jiang, 2008
Invertebrates						
Soil fauna	La (Ce, Pr, Nd, Sm)	Mean of species richness, diversity & evenness index	8 months	1.00	4510	Huang, 2009
Earthworms	Y	Death	2 w	3.20	1120	Wu, 2012
Terrestrial plants						
<i>Asclepias syriaca</i> L.	Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Er	Biomass reduction	About 8 w	2.56	721	Carpenter, 2015; Thomas, 2014
<i>Brassica napus</i>	Mean of La, Nd, Ce	Suppressed leaf growth	Growth 70 d	2.56	768	Xiong, 1997
<i>Brassica napus</i>	REE mixture	Plant growth*	Emergence + 2 w	3.12	5086	Zhang, 2001
<i>Desmodium canadense</i>	Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Er	Biomass reduction	About 8 w	2.65	530	Carpenter, 2015; Thomas, 2014
<i>Glycine max</i>	Mean of La, Nd, Ce	Suppressed leaf growth	Growth 37 d	2.91	4651	Xiong, 1997
<i>Glycine max</i>	REE mixture	Plant growth*	Emergence + 2 w	3.12	2808	Zhang, 2001
<i>Oryza sativa</i>	Mixture	Biomass reduction	Assumed 4 months	1.80	1080	Wang, 2006
<i>Oryza sativa</i>	Mean of La, Nd, Ce	Suppressed leaf growth	Growth 33 d	2.96	8584	Xiong, 1997
<i>Oryza sativa</i>	REE mixture	Plant growth*	Emergence + 2 w	3.12	3245	Zhang, 2001
<i>Oryza sativa</i>	La (red soil)	Mean for ground biomass and yield	120 days	1.8	272	Zeng, 2006
<i>Oryza sativa</i>	La (paddy soil)	Mean for ground biomass and yield	120 days	1.8	612	Zeng, 2006
<i>Panicum virgatum</i> L.	Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Er	Biomass reduction	About 8 w	2.65	1258	Carpenter, 2015; Thomas, 2014
<i>Raphanus sativus</i> L.	Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Er	Biomass reduction	About 8 w	2.65	2737	Carpenter, 2015; Thomas, 2014
<i>Solanum lycopersicum</i>	Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Er	Biomass reduction	About 8 w	2.65	2499	Carpenter, 2015; Thomas, 2014
<i>Triticum aestivum</i>	Mean of La, Nd, Ce	Suppressed leaf growth	Growth 70 d	2.47	4119	Xiong, 1997
<i>Triticum aestivum</i>	Mixture	Biomass reduction	Assumed 4 months	1.80	3060	Wang, 2006

Note. The chemical form has been chloride except for the soil fauna for which oxides were used. In all cases the endpoint has been 25% inhibition of functions such as growth or enzyme activity. The concentration in soil with vegetation at which such inhibition occurs has been corrected for aging by the indicated multiplication factor. References are given as first author and year of publication. d = days, w = weeks. * mean of 3 soils.

In particular, nanosilver has been extensively studied and some general conclusions from that work may have a bearing on rare earth nanomaterials. Early on, an increasing number of studies had found that the release of ionic silver could not alone account for the toxic effects observed from nanosilver exposures. However, a special European assessment of nanosilver (European Chemicals Agency [ECHA], 2018) concluded that there was no

reason to classify the nano forms of silver more stringently than the easily soluble silver nitrate. Among other things, the conclusion was based on results for three different soil types showing that silver nitrate was equally or more toxic to soil microorganisms as compared to silver nanoparticles.

Different rare earth oxide nanoparticles can have strongly differing effects on living organisms. For instance, Ma et al. (2010) studied effects on plants of nanomaterials with Ce, La, Gd, and Yb and found a diversity of effect concentrations for root elongation and growth processes. Studies on cucumber (Ma et al., 2015) showed that La_2O_3 acted in the ionic form while CeO_2 displayed the behaviour of particles or particle-ion mixtures. Many studies of rare earth nanomaterial effects have concerned nanoforms of CeO_2 and these dominate the detailed discussion in the appendix (Section A3.4).

The results for nano-lanthanides are not inconsistent with the proposed hypothetical threshold for non-nano forms of rare earth elements of 1125 mg rare earth element per kg soil as corrected for aging. There is a discrepancy, however, for neurotoxic effects for chronic peroral administration to mice and rats which were observed in the range 1-10 mg rare earth element daily per kg body weight for non-nano forms of lanthanides (Section 3.1.5). A study for nanoform CeO_2 did not show any effects on rats (including neurotoxicity) after daily administration of 1000 mg/kg (Lee et al., 2020).

4.2 Results From No-Effect Studies on Microorganisms, Invertebrates, and Plants

Five results for arthropods are not inconsistent with the proposed threshold of 1125 mg rare earth element per kg soil:

- The three-year field plot experiments of Tang, Sun, Xia, Wen, and Zhang (2004, see Section A3.2.1) failed to show any significant reduction in the total number of bacteria, actinomycetes, or fungi below 700 mg/kg of mixed rare earth chlorides. In this case, no correction for aging is needed.
- Li, Jiang, Chen, Zou, and Zhang (2006) reported on a three-year study in a bean field where rare earth chloride was applied and sufficient soil aging should have been attained. Many invertebrate species were recorded. There was no effect on the number of species and the number of animals at rare earth element concentrations up through 3000 mg per kg soil.
- Huang (2009) found only increases in the number of invertebrates after the addition of 1000 mg/kg soil of La or Nd in a horticultural vineyard.
- Li, Hong, Yin, and Liu (2010) found a correlation between reduced numbers of some soil fauna (*Carabidae*, *Dermoptera*), but not others (*Formicidae*, *Coleoptera*, *Orthoptera*) at sum rare earth elements concentrations up to 27 000 mg per kg soil in a rare earth mining district.
- Effects on the fruit fly *Drosophila* were noted above 6 mg rare earth element per kg food (Huang, Li, Wang, & Hu, 2010). The concentration ratio from soil to orange juice and fruit, in general is about 0.000 5 (Section A2.4). If such food would be representative for *Drosophila*, a no-effect concentration would be 12000 mg element per kg soil.
- Three terrestrial plants (oat, oilseed rape (*Brassica napus*, dicotyledon), and soybean) were exposed for 21 days to a concentration of a commercial rare earth feed additive of 1,000 mg per kg soil dry weight (EFSA Panel, 2019). No adverse effects were seen on seedling emergence, the survival of emerged seedlings, and the shoot fresh weight. The corresponding lanthanide concentration is 269 mg per kg soil. Applying the template correction for aging of 3.1, the no-effect level would be 834 mg/kg. This may not be inconsistent with the proposed threshold of 1125 mg/kg.

4.3 Thresholds Suggested in Other Studies

Li, Verweij & van Gestel (2018) put their results for La exposure of 5 invertebrate species in the context of a species sensitivity distribution which also encompassed 7 plants and one bacterium. No correction was made for the aging of the elements in soil, and further the bacterium effect concerned bioluminescence. The 25th percentile of the distribution was 155 mg La per kg soil. In relation to the proposed hypothetical threshold of 1125 mg/kg soil in Section 3.5.4, the 25th percentile of Li, Verweij, and van Gestel (2018) differed in several respects, for instance:

- No correction for aging was made vs. a correction that would enhance the result of Li et al. (2018) by a factor of about 3.
- The basis for the species sensitivity distribution was IC_{10} vs. IC_{25} ; application of the latter would enhance the result of Li et al. (2018) by a factor of less than 2 for the invertebrates and about 2 for the plants of Thomas et al. (2014).

- For bacteria, one special effect (photoluminescence) was studied in one species while the current assessment has used the combined effects (total number, total nitrification, etc.) on all species that were judged to influence the functioning of the ecosystem.

Such differences might explain the numerical differences between the two estimates.

For the five invertebrates of Li et al. (2018), the 10% effect was in the range of 350-1120 mg La per kg soil. The 25% effect concentration would be nearly the same due to the steep dose-response curves. After correction for aging this would fall well into the range given in Table 1. The exception was the weight gain of the woodlouse *Porcellio scaber*, for which the 10% effect concentration was only 69 mg/kg. After aging correction by a factor of 3, the effective concentration of 207 mg/kg is lower than any entry in Table 1. It should be noted that the test conditions were quite artificial and far from those in natural vegetated soil.

Effects on mammals were summarized in Section 3.1.5. The suggested threshold for effects on mammals should be about 20 000 mg rare earth element per kg soil based on the use of rare earth elements for feed supplement, 128 000 mg/kg based on chronic exposures of rats and mice, and 12 000 mg/kg for exposure of rabbits. Much lower thresholds would be expected for neurotoxic effects in mice and rats, but these are not likely to affect the functioning of ecosystems. It should be noted that the concentration ratios used for the conversion from feed to soil concentration ratios are uncertain by about a factor of 10 up or down.

For the protection of humans, as a first approximation, the concentration ratio for cereals of about 0.0002 (Wang, 2020; Jiang, J. Yang, Zhang, & J. D. Yang, 2012) could be used; lower concentration ratios can be derived from a total diet study in Canada (Health Canada, 2007; La in 2001, 2002, 2005, 2006, 2007; Y and La in 1993, 1999), and a study of human feces in Europe (Ulusoy & Whitley, 2000). An acceptable daily intake of about 3 600 microgram rare earth elements per day was proposed by Zhu et al. (1996). That level was based on effects on the intelligence quotient, in line with the result from mammals that suggest that mammals are more sensitive to neurological effects than to others. The intake limit proposed by Zhu et al. (1996) would correspond to a soil concentration of 45 000 mg/kg, assuming a dry food intake of 0.4 kg/day. The limit should be lower for populations with a high intake of vegetables for which the mean concentration ratio might be about 7 times higher than for cereals. There should still be ample margin to the proposed soil threshold of 1125 mg/kg, in line with the assessment of Jiang et al. (2012) that the 90th percentile of intake would correspond to 3.5% of the acceptable intake.

For birds, only one eligible study on broiler chicken was found. While the result may not be at variance with the proposed threshold, more studies are necessary to corroborate this.

4.4 Potentially Different Threshold for Cerium

The cerium anomalies might conceivably also lead to important differences in the total lanthanide effects on health and the environment (Section 3.3). The paucity of data precludes any conclusions in this respect, but there is no support for comparatively higher toxicity of cerium:

- Indeed, the addition of up to 300 mg cerium oxide per kg feed of laying hen diets had positive effects on egg production, feed conversion ratio, and egg shelf life (Bölükbaşı et al., 2016), and the same addition to feed of rabbits did not affect their feed conversion factor (Adu, Akinmuyisitan, & Gbore, 2013).
- Application of 80 mg Ce per kg soil did not influence soil enzyme activities of maize and oilseed rape 66 days after sowing (El-Ramady, 2008).
- Improvements of plant growth or quality are known, for instance, Ce-induced growth enhancement of tomato plants by counteracting *Fusarium* wilt infection (Adisa et al., 2018).

4.5 Thresholds in Relation to Natural Soil Concentrations

Organisms are known to adapt to natural concentrations of elements in the environment. For instance, a significant correlation has been found between antibiotic resistance genes and soil metal concentrations (Knapp et al., 2011; Knapp et al., 2017). It has been recommended that future design of toxicology experiments should attempt to incorporate the dosage rate or the dietary influx rate to facilitate inter-comparison of the results of different studies (Wang, 2013). It is thus a natural hypothesis to assume that thresholds for health and environmental effects would be closely related to the natural exposures of the elements.

It has also been shown that thresholds for effects on soil organisms for many metals have been set at about 1-5 times the soil concentration for elements in period 4 of the periodic system (Bengtsson, 2019). For 3 elements in period 5, the thresholds were at about 10-20 times the natural concentration. For period 6, a threshold was only found for Hg, at about 50 times the natural concentration. Similar data were reported for much of period 4 and 5

elements concerning thresholds for human intake (upper limits of intake) divided by mean dietary intakes. Here more information was available for period 6 elements, confirming that their limits were more than 50 times the mean natural intake.

The proposed hypothetical threshold (Section 3.5.4) of 1125 mg rare earth element per kg soil corresponds to 8.46 times the mean global soil concentration of 133 mg/kg soil (Section 2.3). This would apply to the dominant rare earth elements in period 6, the lanthanides. For Sc in period 4 and Y in period 5, the threshold of 1125 mg/kg corresponds to 112 and 56 times the natural concentrations (taken from Table A1.1, Section A1.6). This is in line with the high ratios of upper limits of intake to dietary intakes at groups 4-6 of Bengtsson (2019).

4.6 Validity of the Used Assumptions

Effects of rare earths on plants depend highly on a great variety of factors (Redling, 2006), such as soil properties (pH, organic matter, cation exchange capacity, clay contents), rare earth contents in soil, contents of interfering elements such as Ca and P, application methods and their rates and timing as well as climatic and plant conditions (species, growth stage).

For data-rich elements, a threshold calculator has been developed taking partly into account corrections for pH, organic content, clay content, cation exchange capacity, background zinc concentration, aging, background concentration, secondary poisoning, and bioavailability (Oorts, 2020). Data enabling such a comprehensive evaluation are only available for a handful of elements (Cd, Co, Cu, Mo, Ni, Pb, Zn) belonging to group 9 of the periodic system or higher, excepting Mo in group 6. Inferences with respect to rare earth elements in group 3 will thus be farfetched.

Any suggestion for a single threshold for rare earth element effects must necessarily be a gross simplification without much possibility of a proportionality check. To achieve such a simplification, several assumptions were enumerated in Section 3.5.2. Some of the weaknesses of such assumptions are the following.

Life-time exposure is approximated. The representativity of less than life-long exposures was discussed in Section 2.5.1(6). While bones may serve as accumulators of rare-earth metals, the concentrations in other organs influencing growth, survival, and reproduction might be reaching semi-equilibrium within a few months, suggesting that exposures of such length may not grossly underestimate these effects. This should be considered a hypothesis until further research can give better information.

The effect is determined by the molar sum of all rare earth elements. Sections A3.2 and A3.3 give many examples for which the molar effect ratio is within a factor of 1.5 among lanthanides and Sc/Y. There are some examples of larger differences. For instance, the concentration in soil that caused 25% reduction in plant biomass (IC_{25}) for Y relative to the lanthanides had a range of 1.1-2.9.

The ecological functioning is assumed to be sustained at a concentration below which 25% of the species concerned are protected. The 25% mark is used for instance in Canada (Gaudet, Bright, Adare, & Potter, 2002) and Sweden (Swedish Environmental Protection Agency, 2016). The 5th percentile using the current data is 509 mg per kg soil, as compared to 1125 for the 25th percentile.

Correction for aging of metals in soil is in the range 1-3.4. This can be compared with the factor in the range 1.2-4 for the laboratory to the field (aging or aging + leaching) used in European REACH dossiers (Registration, Evaluation, Authorisation, and Restriction of Chemicals) (Oorts, 2020), which is of the same order of magnitude.

4.7 Research Needs

Similarities in effects among lanthanides. More studies are needed to elucidate the possible existence of common mechanisms or modes of action across the lanthanide series.

Role of competing elements. The links between thresholds for rare earth elements and concentrations of other elements, mainly Ca but also Mg and P warrant further studies.

Hazards from longer exposure times. The significance of exposure times approaching the life length and influencing growth, survival, and reproduction of long-lived plants, invertebrates, and mammals is poorly understood and deserves further study.

Secondary poisoning. Secondary poisoning of avian and mammalian wildlife needs further elucidation.

Microorganisms together with vegetation. Microorganisms behave quite differently in soil with vegetation (Section 2.5.3) compared with unplanted soil, and vegetation is the normal state for agricultural soils. Only a few studies were found with vegetation, so there is a need for further studies on microorganisms in vegetated soils, particularly at high concentrations of rare earth elements.

Year-long studies of invertebrates. Only one long-term study was found with effects on invertebrates, in addition to one short-term study, one where no effect was found, and one for unplanted soil. Research is needed on effects in planted soils over years on invertebrates, at rare earth element concentrations high enough to produce effects on the soil fauna.

Plants in equilibrated soils. The aging correction for the current eligible plant studies enhances the effect concentration about three-fold. Studies are needed with longer duration, and in soil where rare earth elements have been supplied in such time that they have become equilibrated in soil matrices.

5. Conclusions

Around the year 2000, mean anthropogenic contributions of lanthanides in European soil were at most a few per cent of the total soil content. Since then, they are likely to have strongly increased. Sewage sludge concentrations may be more than hundred-fold the unavoidable dietary contributions, with important inputs from the unintentional mobilization of lanthanides via fertilizers and detergents.

Rare earth concentrations in soils may vary more than a thousand-fold depending on location. The ten heaviest lanthanides may account for more than 30% of the total at low total concentrations, but less than 5% at the highest totals. Scandium and yttrium have relatively low concentrations.

Concentration ratios from soil to plants and animals may vary in the range of 0.000 002 to 0.2. Extreme variations may occur, such as a food sample with 20 000 times higher erbium concentration than the 90th percentile.

The proposed hypothetical soil thresholds are envisaged to be used in initial assessments of agricultural soil where the natural concentrations have been anthropogenically enhanced. Only effects on the environment have been considered, although a preliminary assessment for human neurological effect has been made. The overall objective is to achieve a level of ecological functioning that sustains agricultural activities. This functioning is assumed to be sustained at a concentration below which 25% of the species concerned are protected. The proposed hypothetical threshold for agricultural soils is 1125 mg total rare earth element per kg of soil. This threshold is about 8 times the natural soil concentration. The proposed threshold is based on a species sensitivity distribution of only 22 eligible studies but is not inconsistent with many no-effect studies and studies on nanoforms of rare earth elements. Some deviations justify continued scrutiny, such as the low thresholds for effects on *Porcellio scaber*. If the threshold proves tenable, it implies that general anthropogenic pollution by rare earth elements will not be a threat to agricultural sustainability for the coming generation.

The proposed hypothetical threshold builds on several assumptions:

- less than life-long exposures are useful,
- the effect is determined by the molar sum of all rare earth elements,
- aging of the elements in soils can be corrected in a simplistic way.

More research is needed to provide more eligible studies, particularly for invertebrates and mammals, and assess the validity of the assumptions.

Appendix 1

Soil Concentrations of the Selected Elements

The soil concentrations of different lanthanides depend on the geologic parent mineral and processes in the soil development, where many soil migration pathways have been isolated (M. T. Aide & C. Aide, 2012). Analytical methods may influence the apparent concentrations. Downward migration processes may generally but not always lead to reduced concentrations in the topsoil relative to those of the subsoil. The topsoil may also contain significant contributions from human activities. All these circumstances may lead to varying total soil concentrations of lanthanides and changing patterns of soil concentrations among the different lanthanides. These topics are elaborated below, and the discussion is concluded with a look at the soil concentrations of the non-lanthanide rare earth elements scandium and yttrium.

A1.1 Influence of Analytical Methods and Statistical Parameters

Sometimes the alleged relative concentrations depend on the analytical method used. For instance, *aqua regia* digestion may almost completely recover light lanthanides in Alfic Haplorthod soils but only to a small extent recover heavy lanthanides (M. T. Aide & C. Aide, 2012).

Another possible source of error may occur from the ashing of organic samples. The temperature in the sample may be inhomogeneous and the recovery of elements from ashing may be unpredictable. Factors involved include losses due to evaporation, insoluble residues, and material attachment to the used crucible (Mader, Száková, & Miholová, 1998; Harju et al., 2004).

One has also to watch out for the chosen statistical parameter. Concentration distributions may be quite wide and arithmetic, as well as geometric means may be used for their characterization. The difference might be substantial, as shown by several examples under Section A2.1.

A1.2 Anthropogenic Contributions Derived From Emissions

The anthropogenic contribution derived from emissions, mainly due to coal combustion, is discussed below and is in the following Section A1.3 compared with estimates from the topsoil/subsoil concentration ratio.

A1.2.1 Mean European Anthropogenic Soil Excess up to 3% Estimated From Emissions, Large Areas up to 30%

The mean lanthanide anthropogenic component for European topsoils has been estimated to be near 1.1% of the natural concentration except La 1.3%, Ce 1.8% and Eu 1.6% (Bengtsson, 2018). The dominant contribution comes from coal combustion. The calculation may not be grossly in error since the calculated excess was within about a factor of 3 from that estimated from topsoil/subsoil concentration ratios for other elements than lanthanides (A1.3.2). Some assumptions behind the lanthanide figures may imply underestimations:

- The assumed period for emissions was 1900-1999; 10-30% may additionally have accrued from emissions in the 19th century.
- Coal use statistics may be uncertain, particularly for countries in Eastern Europe, and other sources of statistics suggest a higher use by up to a factor of 2.
- Bengtsson (2018) pointed out that the assumed emissions are very approximate for Germany, where a large share of the coal use comes from lignite. Several trace elements may have much higher concentrations in lignite than the ones used in the calculations. Özbayoglu (2011) reported about 5 times higher concentrations of Ce and Nd than those assumed by Bengtsson (2018). Laudal, Benson, Palo, and Addleman (2018) report total lanthanide concentrations in the range 40-400 mg/kg, to be compared with the concentration 56 mg/kg used by Bengtsson 2018. Lower concentrations have however also been reported, (Životić et al., 2019; Adamidou et al., 2007).
- The assumed mean emission factor from coal of 80% may have been exceeded for some plants without emission limitation.

With these circumstances taken together, there is a possibility that lanthanide excess concentrations may be up to twice the estimate by Bengtsson 2018, or about 3% as a mean for European soils. Large areas may be exposed to 10 times the mean level (Bengtsson, 2019), that is, up to 30%. This is still not inconsistent with the estimate derived from topsoil/subsoil concentrations.

A1.2.2 High Concentrations of Lanthanides in Sewage Sludge

Indications for significant contamination with lanthanides also come from their concentrations in sewage sludge. The ratio of the mean national sludge concentration of some elements and the unavoidable dietary component of the sludge due to human intakes was 60-100 for 10 lanthanides (Ce, La, Er, Sm, Nd, Ho, Gd, Dy, Pr, Tm) for the

least contaminated set of sludge which emanated from Sweden 2016 (Bengtsson 2018). Typically, sludge from the major cities of Chongqing and Xiamen in south-east China had about 5 times (range 3-13) higher lanthanide concentrations than the mentioned Swedish ones (Suanon et al., 2017). A major source of such enrichment was likely to be phosphate coming from detergents and fertilizers, but erosion and weathering processes of rocks were thought to be the main responsible for the lanthanide contents according to Folgueras, Alonso, Folgueras, and Lage (2018). The phosphate contribution is a reminder that unintentional mobilization of lanthanides can be of the same order of magnitude as the intended global production (Emsbo, McLaughlin, Breit, du Bray, & Koenig, 2015).

A1.3 Topsoil Versus Subsoil Reveals Minute Anthropogenic Contribution

The concentration of many metals in superficial soil layers decreases with time due to downwards transport (Bengtsson, 2015). Important parameters controlling the transport rate are pH, the concentration of sand versus clay and silt, and concentration of organic matter, for instance in the form of total organic carbon, TOC (Bengtsson, 2015; Sadeghi & Andersson, 2015). These parameters were measured for both topsoil and subsoil at about 800 European sites (Salminen et al., 2005). The concentration ratio topsoil/subsoil for lanthanides shows some correlation with the corresponding pH, sand fraction, and TOC ratios. The interpretation of those correlations needs to account for several circumstances:

- The topsoil may have had recent additions from the deposition of lanthanides.
- Recently deposited lanthanides may be more loosely bound and transported down through the topsoil at greater rates than the original lanthanides deposited in residual soil from geological processes
- Lanthanide transport through the subsoil may be controlled by complex processes. In general, the rate may be higher than the topsoil rate, but special conditions such as intervening clay layers may lead to slower transport of metals. In uncontaminated control soils, the metal concentration ratio topsoil/subsoil may in some cases exceed 1 (Bengtsson, 2015).

From the discussion in Appendix 1, Sections A1.2 and A1.3, it appears that soil properties are the main factors behind relatively high topsoil concentrations, rather than unusually high depositions.

A1.3.1 Equal Transport Conditions for Topsoil and Subsoil May Be Used to Infer Recent Depositions

The lanthanide concentration ratios topsoil/subsoil of Salminen et al. (2005) were analyzed for topsoil/subsoil ratios near one with respect to sand fraction, pH, and total organic carbon (TOC), on the assumption that the same soil parameters in topsoil and subsoil would imply equal conditions for downward transport. The dependencies on sand fraction, pH, and TOC were assessed in 3 tiers. To avoid undue influence of extreme outliers among the hundreds of samples, the 5 highest (range 3.9-18) and 5 lowest (range 0.08-0.31) lanthanide topsoil/subsoil ratios were deselected from the assessment.

- The dependence on pH was assessed first since the topsoil/subsoil pH ratio had a narrow range of 0.60-1.45. With the pH ratio averaged over 0.1 units intervals the lanthanide topsoil/subsoil ratio was,
Lanthanide ratio = $-1.9790 \times \text{pH}^2 + 4.1106 \times \text{pH} - 1.1389$, with a coefficient of determination $R^2 = 0.78$.

In the pH ratio interval of 0.8-1.2, the mean lanthanide ratio had no significant variation with a range of 0.90-1.05 and a mean of 0.96.

- For the selected pH ratio range 0.8-1.2, the mean ratio of lanthanide concentrations in topsoil and subsoil averaged over sand fraction topsoil/subsoil ratio intervals of 0.2 depended on the sand fraction ratio according to,

$$\text{Lanthanide ratio} = 0.957 \times (\text{Sand fraction ratio})^{-0.446}, \text{ with a coefficient of determination } R^2 = 0.95.$$

For a sand fraction ratio of 1, the lanthanide topsoil/subsoil concentration ratio was 0.957.

- The lanthanide topsoil/subsoil concentration ratio was corrected to correspond to a sand fraction ratio of 1. The corrected ratio averaged over a factor of 2 intervals depended on the TOC topsoil/subsoil concentration ratio as,

$$\text{Lanthanide ratio} = 0.9563 \times (\text{TOC ratio})^{-0.042}, \text{ with a coefficient of determination } R^2 = 0.92.$$

For a TOC ratio of 1, the lanthanide topsoil/subsoil concentration ratio was 0.956.

After the third tier, the lanthanide topsoil/subsoil concentration ratio corresponding to equal levels of pH, sand fraction, and TOC in the topsoil and subsoil was estimated to be 0.96.

The corresponding ratio for a Chinese agricultural test site was 0.92-0.96 (Liu, Wang, & Zhang, 1997). A relatively low ratio would be expected since the agricultural topsoil would have a rather high TOC concentration compared to the subsoil.

A1.3.2 Non-Lanthanides Topsoil/Subsoil Ratio May Give Clues to Expected Ratios of Lanthanides

Mean anthropogenic components of natural elements in European topsoils have been estimated by Bengtsson (2018). Generally, the dominant contributions come from coal combustion. The calculation may not be grossly in error; the calculated excess was within about a factor of 3 from that estimated from topsoil/subsoil concentration ratios for elements with large anthropogenic components. Non-lanthanide elements were identified from the data set of Salminen et al. (2005) with soil concentration data determined with inductively coupled plasma analysis and with relatively low detection limits. Of these, 5 elements in the periodic system groups 3-5 (Sc, V, Hf, Ta, and U) had a predicted anthropogenic fraction in the topsoil of less than 2.3% with a mean of 1.7%. For these elements, soil samples with topsoil/subsoil ratios in the range 0.9-1.1 for pH and sand fraction, and 0.8-1.3 for TOC were selected, resulting in 17 soil samples with similar topsoil and subsoil parameters. The mean topsoil/subsoil concentration ratio was 0.946 (95% confidence interval 0.925-0.969) while that for the lanthanides was 0.930 (0.915-0.945) with an estimated mean anthropogenic fraction of 1.2%.

A1.3.3 Residence Time Relatively Long for Anthropogenic Contributions

Over the decades preceding the measurements of Salminen et al. (2005), the world production of rare earths had increased exponentially with a doubling time of about 15 years (USGS, 2021). In the same period, emitted fractions were reduced at a similar rate (Bengtsson, 2018). Anthropogenic contributions to soil concentrations related to consumption might therefore be decades old. The larger contributions from fossil fuel combustion would have peaked around 1975 (Bengtsson, 2018) and typically be a few decades old at the time of the measurements of Salminen et al. (2005). Most of these contributions would have stayed in the 25 cm topsoil if penetration followed the conditions for other cationic metals (Bengtsson, 2015). Larger losses might be associated with a combination of low pH, high sand fraction, and high TOC concentration (Section A1.3.1).

A1.4 Total Concentrations of Lanthanides

Results on the mean soil concentrations of Europe (Salminen et al., 2005) have been important sources for understanding lanthanide soil concentrations. As discussed in the preceding section, the anthropogenic component has been estimated to be at the percentage level (Bengtsson, 2018) and thus insignificant to assess health and environmental effects.

The mean national sum lanthanide concentrations divided by the mean concentration of the upper continental crust (Salminen et al., 2005) have a variation from about 0.4 for Ireland to 1.6 for Croatia, with Denmark as an outlier at 0.2.

China with rather high soil concentrations (Hu et al., 2006) had an average of about 0.8 of that of Croatia. In China, lateritic red earth soils stand out with about three times higher rare earth concentrations than the typical ones (Liang et al., 2005).

Analysis of the European topsoil data showed that the mean total lanthanide concentration increased strongly with the sand fraction, from 34 mg/kg at a sand fraction around 0.05 to about 150 mg/kg at sand fractions above 0.6. There was also a TOC dependence, from 53 mg/kg at TOC < 0.5% to about 130 mg/kg with large variations at TOC > 5%. No strong dependence on pH was found.

For elucidating health and environmental risks, a world soil average sum lanthanide concentration of 133 mg/kg was used (Table A1.1). This can be compared with an average sum concentration of 126 mg element per kg dry soil for Europe (Salminen et al., 2005) and a sum concentration of 177 mg element per kg dry soil for China (Liang et al., 2005).

A1.5 Relative Concentrations Among Lanthanides

Generally, the lighter lanthanides La, Ce, Pr, and Nd have higher soil concentrations than the heavier ones. Depending on the geologic origin, however, the concentration distribution among lanthanides can be very variable. This has been illustrated for the mineral francolite which almost alone bears the rare earth elements of phosphate-rich rocks (Emsbo, McLaughlin, Breit, du Bray, & Koenig, 2015). The shale-normalized concentrations can vary from being very nearly independent of lanthanide element (Pleistocene-recent, upper Ordovician Richmondian) to having a very pronounced peak at Sm-Eu-Gd (upper Mississippian Serpukhovian) to having a large dip for Ce (middle Mississippian Viséan). For the francolite, the highest total lanthanide concentrations are associated with the Sm-Eu-Gd peaking distribution implying comparatively low contributions

from light lanthanides, while the lowest total concentrations exhibit relatively flat shale normalized concentrations.

For other minerals, other distributions occur. Xenotime minerals may have extremely high fractions of heavy lanthanides, while bastnäsite may be extreme the other way towards light lanthanides (Dostal, 2017). The mineral distributions are reflected in soil concentrations.

Heavier lanthanides tend to be less prevalent in soils when the total concentration of lanthanides is high. For carbonatites and alkaline igneous rocks, this has been demonstrated for La versus Yb (Dostal, 2017). The circumstance can be illustrated by the relation of some heavy lanthanides (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) to the sum of all lanthanides (Figure A1.1). With the large variation among different minerals, it is not surprising that the ratios of heavy to total lanthanide soil concentrations are highly variable. In areas with high sum concentrations of lanthanides, such as in areas where rare earth elements are being mined, comparatively small contributions can be expected from heavy lanthanides.

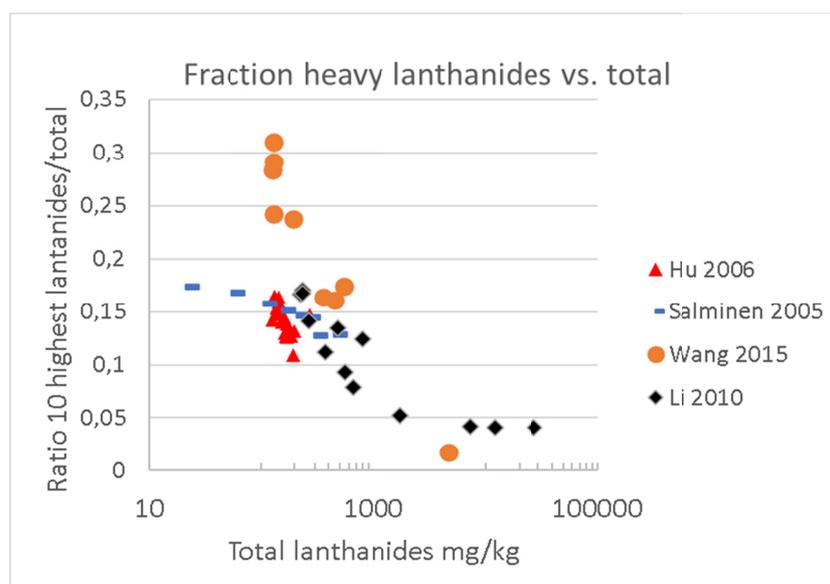


Figure A1.1. Ratio of topsoil concentrations of heavy and total lanthanides versus the total lanthanide concentration, for soils in Europe and China

Note. For Europe, data were obtained using inductively coupled plasma mass spectrometry (Salminen et al., 2005), for China using various techniques (Hu et al., 2006). The European data pertained to many soils and were assessed for 50 mg/kg intervals of total lanthanide concentrations. Data of Hu et al. (2006) also concerned many different soils. The results of Wang and Liang (2015) concerned soils in many directions within several kilometers from the Baodou mine site. The results of Li, Hong, Yin, and Liu (2010) concerned the same site but about 10 km in the downwind direction and with a different composition where the heavy lanthanides included Y but not the heaviest elements Ho, Er, Tm, Yb, and Lu; the latter comprised 29% of the 10 heaviest elements in European soils (Salminen et al., 2005).

Besides the just mentioned shifts with total lanthanide concentrations, the distribution of the soil concentrations among rare earth elements tends to be similar for the 25 European countries reviewed by Ramos et al. (2016).

A1.6 Soil Concentrations of Sc and Y

Soil concentrations of Sc and Y have been reviewed by Ross, Wood, Copplestone, Warriner, and Crook (2007) and Salminen et al. (2005). Their data is compared in Table A1.1 with the sum concentrations of lanthanides and with the concentrations in the Upper Continental Crust UCC.

Table A1.1. Sc and Y concentrations in topsoil and upper continental crust UCC compared with the sum concentration of the lanthanides

Region	Mean concentration Sc (mg/kg)	Mean concentration Y (mg/kg)	Mean concentration sum lanthanides (mg/kg)
Soil Europe ^a	9.1	22.7	126
Soil China	15 (5-28) ^b	22 (11-39) ^b	177 ^c
Soil World	10 (7-15) ^b	20 (14-25) ^b	133 (112-154) ^d
Upper continental crust ^e	14	21	148

Note. The ranges in parentheses are only indicative. The rounded mean values indicated for World are used in the current assessment. ^a Salminen et al. (2005); ^b Ross et al. (2007); ^c Liang et al. (2005); ^d Ross et al. (2007; their quoted data from Bowen, 1979; Laul et al., 1979; Kabata-Pendias, 2000; Govindaraju, 1994); ^e Rudnick and Gao (2003).

There is some trend for Europe to exhibit low concentrations and China to exhibit high ones. Topsoil concentrations tend to be lower than upper continental crust concentrations, as expected from the migration patterns in topsoil (M. T. Aide & C. Aide, 2012). Sc concentrations tend to be about one-tenth of the sum lanthanide concentrations, Y concentrations about one-fifth.

Appendix 2

Transfer From Soil to Biota

Soil to biota transfer data is available for many parts of the transport from soil to food. Conceivably, they might be related to thresholds for effects on biota. The discussion below starts with an elaboration of some uncertainties and defines the terms used. It continues with the differences among the elements and then discusses the extent of transfer from soil to biota. Finally, the transfer of Sc and Y is examined.

A2.1 Uncertainties in the Soil to Biota Transfer and Biota Effect Thresholds

Aging. The aging phenomenon is well known. If sufficient time of several months has not been allowed for equilibration of the rare earth elements in soil, aging processes have not been completed, involving fixation of the elements in matrices from which they are less available to biologic matter. The median lowering of sensitivity for a large number of studies (Smolders et al., 2009) was 3.4, and differences up to one-hundredfold were noted. Many factors affect the aging and account for a large variability, as illustrated by a major study for molybdenum (van Gestel et al., 2012). Correction factors are available for data-rich metals (Oorts, 2020), but the only general correction given is for the element lead with a factor of 2. For rare earth elements, little information has been found. As a first hypothesis, it has here been assumed that aging is complete after 6 full months and justifies an increase by a factor of 3.4 in the effect concentration established after 0 months, and the correction decreases linearly with time in-between. The breakpoint time of 6 months is quite arbitrary but for instance for lead, no major change in sensitivity occurred after 6 months (Zhang & Van Gestel, 2019). The assumed curve is given in Figure A2.1 which also illustrates the only found information for rare earth elements, from Jiang, Weng, Huang, Jiang, and Wang (2008). Considering the large variation up to a factor of 100 (Smolders et al., 2009), the measured points are not inconsistent with the assumed curve.

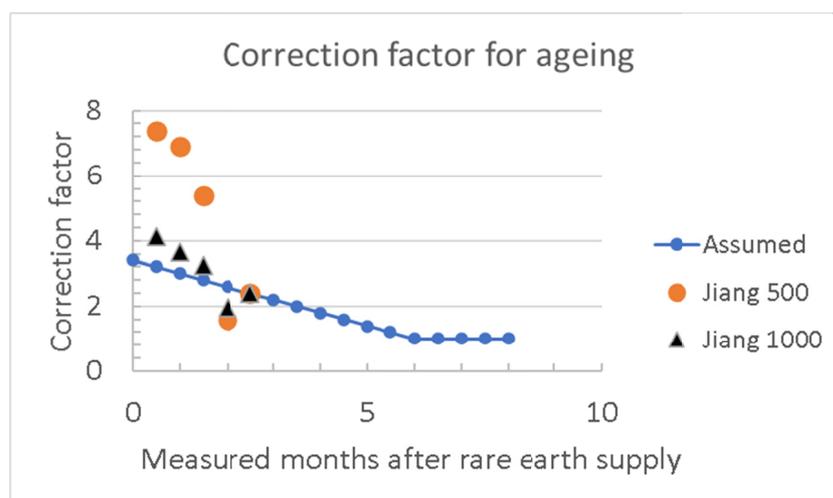


Figure A2.1. Assumed correction factor for ageing

Note. It should be noted that literature data encompass up to about a hundredfold change in sensitivity. The lowering of sensitivity by a factor of 3.4 after 6 months aging represents the median of a large number of studies (Smolders et al., 2009). The break in the relation is set relatively arbitrarily at 6 months. The two sets of points marked Jiang represent the total soil bacterial count in pots with grass after exposure to 500 mg/kg and 1000 mg/kg lanthanum (Jiang et al., 2008). They denote the change in sensitivity normalized to the assumed relation at 2.5 months which was the longest time studied by Jiang et al. (2008).

Leaching loss. Some studies have investigated the loss of metal from the upper soil layer of 15-20 cm concomitant with aging (Oorts, Ghesquiere, & Smolders, 2007; van Gestel et al., 2012). These have concerned freshly prepared soils which may have been less stable than well-established soils. Experience from long-term field studies for many cations suggest typical leaching of about 10% after 6 months from 15 cm tilled soils, and about 30% in extreme cases (Bengtsson, 2015). This leaching is judged too small to warrant consideration, in relation to uncertainties of a factor of 2 or more, and no correction is made in the current assessment.

Variability. The concentration ratio of biota/soil can be very fluctuating. For different soils in Japan, Tagami, Uchida, and Zheng (2019) report concentration ratios per million,

- For La in the range 7-500 for rice and 100-18 000 for leafy vegetables, and
- For Ce in the range 2-400 for rice and 100-10 000 for leafy vegetables.

The variability is also noticeable among more than 1100 food samples from China measured by Jiang et al. (2012); here the maximum concentration divided by the median was 3600 for La and 600 for Ce, and in the extreme cases of Dy and Er it reached above 50 000 and 200 000, respectively.

Statistical parameter choice. Data on concentration distributions in soil and biota are sometimes including arithmetic means (AM) and other times using geometric means (GM). For a lognormal distribution, $AM = 1.65 \times GM^2$ and the arithmetic mean may sometimes be ten times as high as the geometric one, so the difference may be exceptionally important.

The extremely high lanthanide concentration in some foodstuffs may be reflected in the geometric standard deviation for an assumed lognormal distribution. This standard deviation departing from the four lightest lanthanides was in some examples quite high, being:

- 2.52 for the concentrations in about 1200 food samples from China given by Jiang et al. (2012), derived from the 97.5th percentile concentration which on average was 140 times the median ($AM = 10.5 \times GM$). The maximum values were about 3400 times higher than the median corresponding to a geometric standard deviation of about 2.25.
- 0.95 for the vegetable segment of Jiang et al. (2012) (about 470 samples from China, $AM = 1.5 \times GM$).
- 1.69-2.19 for wheat grains (Liang et al., 2005) (42 samples from China and 18 samples from other countries, $AM = (4.7 - 7.9) \times GM$).

- 1.23 for cereals (Zhuang et al., 2017) based on an interquartile range of 1.94-2.11 times the median concentration ($AM = 2.5 \times GM$).

Fractionation. Concentrations in biota should as a first approximation follow the concentration of lanthanides in soil. However, the concentration in biota divided by soil concentration is often subject to large statistical variations that preclude the definition of any trends with lanthanide atomic number. Uptake in plants may be fractionated in very variable ways to plant parts like root, stems, leaves, and seeds, i.a depending on the species concerned (Liang et al., 2008; Grosjean et al., 2019).

Lack of threshold data. For rare earth elements, no thresholds have been found relating to mammals in a soil environment. However, many data from the effects of lanthanides intake are available. These might be translated to threshold soil levels if the transfer relations soil-mammal-diet can be determined.

A2.2 Terminology

The following terminology is used, adapted from International Atomic Energy Agency [IAEA] (2010).

- Concentration ratio (dimensionless): For soil to biota transfer, the ratio of the element concentration in the biota (mg/kg dry mass) to that in the soil.

A2.3 Relative Concentrations Among Lanthanides

Three conditions are discussed below concerning the relative transfers from soil to biota among lanthanides:

- Aberrations for Ce, Eu, and Yb in relation to the immediate lanthanide neighbor elements.
- Biota showing little variation in transfer among lanthanides.
- Biota for which there are clear trends in transfer among lanthanides.

A2.3.1 Aberrations for Ce, Eu, and Yb

Based on the mentioned atomic properties (Section 2.1.1) it could be expected that there might be differences in organic matter concentrations relative to soil concentrations for light versus heavy lanthanides, and Ce, Eu, and Yb. Any aberrations might be masked by analytical uncertainties for heavier lanthanides due to their low concentration, which is generally less than one-tenth of the Ce concentration. Thus, aberrations might above all be found for Ce (Wyttenbach, Furrer, Schleppe, & Tobler, 1998). Factors influencing the Ce and Eu anomalies have been discussed by Kovaříková, Tomášková, and Soudek (2019).

Some clear anomalies can be demonstrated, where the aberrant concentration divided by the soil concentration is higher than that for the neighboring elements. In many cases, the aberrant plant/soil ratio is up to a factor of 5 higher for Eu. In a few cases, there is also enhancement or depletion for Yb and in a few cases depletion for Ce, as detailed below. The enhancement factor is:

- 4 times for Eu in cereals from a mining area and 2 for a control area (derived from Zhuang et al., 2017); no anomaly could be found for Yb; for the control area Ce was depleted in relation to La and Pr but La was strongly enhanced in cereals in relation to the mean soil concentration.
- 4-4.5 times for Eu in wheat grain derived from data of the soil dressing study of Liang et al. (2005), applying to the control soil and a soil subject to rare earth dressing, but not to the soil with three times higher dressing; the latter result seems to be an outlier or possibly a misprint. In the highly dressed soil, there was also an outlier for the grain/soil concentration ratio for Ce. For the control and slightly dressed soils, there was no anomaly for Ce. For the three soil cases, there was a depletion in the Yb grain/soil concentration ratio to 0.2-0.4 of the Tm and Lu ratios.
- 5 times for cereals and 2-3 times for other plants for Eu (Uchida, Tagami, & Hirai, 2007); no data were given for Yb; there was a small tendency for a depletion of Ce by less than a factor of 2.
- 1.9 times for Eu and 3.0 times for Yb for human excreta derived from Ulusoy and Whitley (2000), normalized to English rural soils (Ross et al., 2007); there was no anomaly for Ce.
- 2.2 times for Eu but no effect for Yb for whole fish collected in an unimpacted reservoir in Washington state, USA (Mayfield & Fairbrother, 2015); there was a small depletion for Ce.

No aberration could be seen for Eu or Yb in the wheat sample study of Liang et al. (2005). That study, however, concerned only 60 samples, 18 of which were from outside China, so there were confounding factors that might have masked any anomalies. No Ce anomaly could be found. For Ce, any effect might have been masked by the high concentrations of La.

Most of the mentioned apparent anomalies should be viewed as hypothetical since the soil used for normalization is not the exact soil from which the organic matter was derived. It is well known that the Ce (Kraemer, Tepe, Pourret, & Bau, 2017) and Eu (McLeod & Krekeler, 2017) anomalies can appear as both positive and negative concentration changes in rock material. Local soils may therefore be aberrant relative to national averages; the only of the enumerated cases where the local soils were used for reference were the dressing cases of Liang et al. (2005). In addition, concentrations tend to be lognormally distributed both for soils and organic matter with typical geometric standard deviations of 1-2. The geometric means of soil and organic matter concentrations are often reported while the arithmetic mean may be several times higher with a possibility for large impact of single samples with extremely high concentrations, a fact that suggests caution in the interpretation, particularly at small sample sizes. An extreme case in point is the maximum concentration of Er in food samples (Jiang et al., 2012) which is at 20 000 times the 90th percentile concentration (see *Variability* under Section A2.1).

Since Eu and Yb hold less than a few per cent of the sum concentration in soil, any aberration may not be significant for the health or environmental effects compared to those of the sum of lanthanides. In contrast, Ce accounts for 40-60% of the total lanthanide concentration in soils, and differences in the health and environmental effects of Ce in relation to other lanthanides might lead to important differences in the total lanthanide effects. However, Ce concentrations could be enhanced, depleted or non-anomalous (Section A1.5) so any major influence on ecological effects is unlikely.

A2.3.2 Biota Showing Little Variation in Transfer Among Lanthanides

There was no significant trend with lanthanide atomic number for the assessed quantity divided by the soil concentration for,

- Parsley roots (Kučera, Mizera, Řanda, & Vávrová, 2007)
- Alfalfa, oats, and a range of fruits and nuts that are grown on sandy soil (Napier, Fellows, & Minc, 2014); the elements assessed were La, Ce, Sm, Eu, and Sc
- Food or horticultural waste ashes (El-Ramady, 2008), based on soil concentration for Japan from El-Ramady (2008), max/min = 5.8 and 1.5, respectively.
- Hair and urine of people living in agricultural soil near smelting and mining areas in Hezhang County, China (Meryem, Ji, Gao, Ding, & Li, 2016).
- The concentrations in human rib bone (S. Zaichick, V. Zaichick, Karandashevc, & Nosenkoc, 2011), (max/min = 2.3).

A2.3.3 Biota for Which There Are Clear Trends in Transfer Among Lanthanides

There were clear trends with lanthanide atomic number for the assessed quantity divided by the soil concentration in some cases:

- The geometric mean concentration ratios for wheat seeds (Liang et al., 2005) decreased systematically with the atomic number from 0.005 for La to 0.0005 for Lu with a mean for the lighter lanthanides around 0.001. A similar pattern exists for the factors for wheat, maize, and legume reported by Zhuang et al. (2017). In a follow-up study from Japan (Tagami et al., 2019), the concentration ratio from soil to leafy vegetables showed relatively small variations (max/min = 6.7) but that for brown rice increased systematically by a factor of 20 from La to Lu. The concentration ratios varied between samples by about a factor of 100, so the means were uncertain but increased by the atomic number to about the tenth power.
- Yuan et al. (2018) studied the naturally growing herbaceous plant *Phytolacca americana* L. All tissues were characterized by a light rare earth element enrichment and a heavy element depletion. This trend however applied to the absorption process (from soil to root) and the reverse was true for translocation process (from stem to leaf).

For aquatic food chains, there were large variations:

- For some turtles (Censi et al., 2013) the concentration ratio blood/sea water was relatively independent of the lanthanide element whereas for others, the concentration ratio was almost four times higher for light lanthanides than for the heavy element Lu, and for the scute, the concentration ratio was up to 40 times higher for the intermediate lanthanides Eu and Gd than for Lu.
- Lanthanides of lower atomic mass were consistently more concentrated in sea urchins, freshwater benthos, crabs, soft tissues of mussels, as well as in freshwater mosses; however, while preferential light

lanthanide concentrations occurred in natural benthos samples of bivalves, medium lanthanide concentration in bivalves was preferred in an acid mine drainage exposure experiment (Blinova et al., 2020).

A2.3.4 Summing up Trends in Biota Concentration Ratios

Because of lack of evidence and the soil concentration dominance of light lanthanides over heavy, the best description of overall transfer in relation to effects might be that:

- There is no trend with the atomic number at all for the transfer of lanthanides from soil to human intake.
- Except that aberrations for Ce might be important according to the section below.

A2.4 The Extent of the Transfer From Soil to Biota

The concentration ratios of La and Ce from biota to soil span the range 0.000 002-0.018 for rice and leafy vegetables, according to measurements across Japan (Tagami et al., 2019). Some examples of transfer data have been given in Section 3.1. Others are:

- The concentration ratios for radioactive materials (IAEA, 2009) from soil to cereals span almost three orders of magnitude, from 0.000 03 for rice (La and Pm) to 0.014 for wheat grain (Pm).
- There is a tendency for concentration ratios for tropical conditions to be higher than subtropical ones (Velasco & Yuri Ayub, 2009).
- Redling (2006) quotes data by Shan et al. (2003) on transfer of La, Ce, Pr and Nd to wheat shoots (mean concentration ratio 0.004) and roots (0.19). Data by Eriksson (2001) for wheat grain correspond to an arithmetic mean concentration ratio for light lanthanides of 0.000 01, which is less than one-tenth of the results of other studies.
- For a limited number of lanthanides, the concentration ratio was for parsley root 0.02, for lucerne and for wheat chaff 0.002, for wine grapes 0.001, for kale 0.0008 and for wheat and apricot 0.0005 (Kučera et al., 2007).
- Under natural conditions, the mean concentration ratio across lanthanides was for leafy vegetables 0.002 (Tagami et al., 2019), and for fresh vegetables 0.0016 (Jiang et al., 2012).
- Under natural conditions, for pasture plants, the mean concentration ratio across rare earths was for ryegrass 0.02-0.2 dependent on soil type (Liang et al., 2005; for recently added rare earth elements, the concentration ratio for ryegrass was up to 4 times higher, dependent on soil type), and for alfalfa 0.002-0.01 (Napier et al., 2014).
- The concentration ratio for radioactive cerium to fresh fruit was 0.0004 (IAEA, 2009), and for many lanthanides to orange pulp 0.00025 (Cheng et al., 2015) or 0.0009 (Turra, 2010).
- The concentration ratio for cereals for human consumption in a control group (Wang, Zhou, Xiong, Liu, & You, 2020) was 0.000 2 with no clear trend versus atomic number (range 0.000 03-0.000 6) when compared to average Chinese soils (obtained from El-Ramady, 2008).
- Data on the relation between rare earth elements in soil and fish are highly conflicting, with the arithmetic mean of the sum concentration of lanthanides in the dry fish muscle being in the range of 0.002-3 mg/kg based on sediments to biota or water to fish bioaccumulation factors (IAEA, 2009), and measured concentrations in fish (Mayfield & Fairbrother, 2015; Donald & Sardella, 2010).

The conclusions concerning soil to biota transfer are given under Results Section 3.1.

A2.5 Concentration Ratios for Scandium and Yttrium

Some concentration ratios for Sc and Y are given below in Table A2.1.

Table A2.1. Examples of concentration ratios for rare earth elements

Transfer chain and unit	Reference		Concentration ratio		
	Receptor	Soil	Scandium	Yttrium	Lanthanides
To human food items China	Jiang, 2012	Liang, 2005	0.00123	0.00077	0.00116
To plants Canada	McMillan, 2017	Liang, 2005		0.00046	0.00080
To hare, ptarmigan, caribou muscle Canada	McMillan, 2017	Liang, 2005		0.000008	0.000015
To roots of rye and wheat	Shtangeeva, 2004	Shtangeeva, 2004	0.017		0.019
To leaves of rye and wheat	Shtangeeva, 2004	Shtangeeva, 2004	0.0024		0.0031
To food scrap ashes	El-Ramady, 2008	Salminen, 2005	0.34	0.40	0.40
To animal waste ashes	El-Ramady, 2008	Salminen, 2005	0.54	0.46	0.64
To horticultural waste ashes	El-Ramady, 2008	Salminen, 2005	0.85	0.78	0.74
To alfalfa and oats	Napier, 2014	Napier, 2014	0.0025		0.002
To fruits and nuts	Napier, 2014	Napier, 2014	0.0026		0.004

Note. The references give first author and year.

The concentration ratios are not significantly different between Sc, Y, and lanthanides but the variation is large. Assuming the same ratios for Sc and Y as for the mean of the lanthanides would be consistent with all the table entries within about a factor of 2.

Appendix 3

Examples of Effects of Rare Earth Elements

A3.1 Variations in Sensitivity Among Rare Earth Elements

A3.1.1 Monocellular Organisms

The findings by Su, Tai, Li, and Ke (2005) suggest that there may be small variations in sensitivity for the rare earth elements. The concentration that resulted in 50% reduction in growth of the exposed alga (*Chlorella autotrophica*) varied only in the range 29.00 ± 0.50 $\mu\text{mol/liter}$ for 12 lanthanides. A later follow-up by the same group (Tai, Zhao, Su, Li, & Stagnitti, 2010) with 13 lanthanides confirmed for a different alga (*Skeletonema costatum*) the small variation, 29.04 ± 0.61 $\mu\text{mol/liter}$. In that case, the response to the total concentration was the same if lanthanides were mixed. The corresponding concentrations for Sc were 21 $\mu\text{mol/liter}$ and for Y 43 $\mu\text{mol/liter}$. It appears that the response depends only on the total concentration of the lanthanides, not on the individual lanthanides involved.

For other monocellular organisms, a somewhat larger sensitivity range has been reported. Kurvet et al. (2017) studied the concentrations of La, Ce, Pr, Nd and Gd nitrates that affected one-half of the organisms in monocellular strains of a bacterium (luminescence) and a protozoan (viability). The more complex effect viability was associated with less variability (highest concentration 1.5 times the lowest, relative standard deviation 20%) than the less complex effect luminescence (6 times, 81%). The luminescence effect concentration decreased clearly with atomic number.

Rucki et al. (2021) studied the acute oral toxicity of the well-established mouse fibroblast 3T3 cells using the Neutral Red Uptake cytotoxic assay. The concentrations that led to a 50% reduction in cell growth IC_{50} were calculated and a 50% lethal dose LD_{50} was estimated. Salts of 14 lanthanides and yttrium that were chloride hexa- or heptahydrates except for the thulium anhydrous chloride were used. The calculated IC_{50} had a range of $\pm 12\%$ from the mean with Y 2% above the mean. The estimated LD_{50} in mol per kg body weight had a standard deviation of 17% among the elements. Yttrium had the lowest LD_{50} , 18% below the mean.

From pot studies of ammonium oxidation and mineralization of nitrogen by microorganisms, Xu and Wang (2001) concluded that the influence of individual rare earth elements in the mixtures on the two processes could be additive.

A3.1.2 Terrestrial Plants

The uptake of rare earth elements to different parts of plants depends on many factors as discussed in depth by Kovaříková et al. (2019). Transfer tends to decrease with increasing atomic mass and decreasing ionic radius. Often, however, the effect concentrations differ by less than a factor of 2, as also the following examples show.

Xiong and Zhang (1997) performed pot experiments where the growth periods were 33-70 days for wheat, soybean, rice, and rape. The ratio of the concentrations of Ce and Nd resulting in a 25% reduction in leaf or root weight to those for La had no systematic trend and a range of 0.6-1.4.

Corn and mungbean root and shoot mass reductions were affected in similar ways by La and Ce (Diathloff, Smith, & Asher, 2008).

Effects on wheat seedlings were generally similar for La and a mixture of rare earth elements at the same concentration, but some effects differed, for instance in the induction of antioxidant enzymes (d'Aquino, de Pinto, Nardi, Morgana, & Tommasi, 2009).

A3.1.3 Invertebrates

The small compost-living nematode *Caenorhabditis elegans* was studied by Xu et al. (2017). For tri-chloride rare earths, the median lethal concentrations were 100 mg/liter for Nd, 157 for Pr, and 106 for Sc. The corresponding numbers were 0.40, 0.63, and 0.70 mmol of rare earth element per liter. There was thus rather small variation in sensitivity to the three rare earth metals. There were some differences in behavioural and neural toxicity between the three chlorides with Sc generally being less toxic than Nd and Pr.

Huang et al. (2020) studied the effects of exposures to La, Ce and Gd on the annelid ringed worm *Enchytraeus crypticus*. The overall uptake rates and ultimate LC₅₀ values (LC_{50,e}) were within about 10% of the mean value over the three elements while elimination rate constants were within about 25%.

Rucki et al. (2021) studied the sediment living ringworm *Tubifex tubifex*. The 50% effect concentration of 14 lanthanides and yttrium for inhibition of movement had a range of $\pm 12\%$ on a molar basis for salts that were chloride hexa- or heptahydrates except for the thulium anhydrous chloride. Yttrium fitted well into the toxicity pattern of the lanthanides.

A3.1.4 Mammals

Effects of rare earth nitrates intraperitoneally administered in female mice were early on studied for all 14 non-radioactive lanthanides (Bruce, Hietbrink, & DuBois, 1963). The dose that was lethal to 50% of the mice was in the range 0.73-1.53 of the geometric mean with a relative standard deviation of 23%. A compilation of data for chlorides in male mice encompassing 8 lanthanides (Ramos et al., 2016) showed a corresponding range around the geometric mean of 0.91-1.10 with a relative standard deviation of 6%.

Rucki et al. (2021) used the 3T3 Neutral Red Uptake (NRU) Phototoxicity assay on mouse fibroblast cells to estimate rodent oral intake LD₅₀ concentrations for 14 lanthanides and yttrium. The estimated LD₅₀ concentration in mg per kg body weight had a range of 0.90-1.18 in relation to its mean. Y fitted well into the toxicity pattern of the lanthanides, also per mol of rare earth element.

A3.2 Examples of Effects

A3.2.1 Microorganisms

Tang et al. (2004) report three-year field plot experiments to study the ecological effects of low dosage mixed rare earth elements accumulation on major soil microbial groups in a yellow cinnamon soil. The crop rotation encompassed rice, rape-seed, soybean, wheat, rice, and horse bean. There was no significant reduction in the total number of bacteria, actinomycetes, or fungi below 700 mg/kg of mixed rare earth chlorides, but the composition of the species changed.

Dehydrogenase activity is considered as a suitable indicator of microbial activity in soil (Wolińska & Stępniewska, 2012). The influence of lanthanide applications on dehydrogenase activity was studied in pot experiments by El-Ramady (2008) for fields sown with maize and oilseed rape. Harvest was 66 days after application of lanthanides and sowing. No decrease in dehydrogenase activity could be seen except in maize soil after application of 270 mg/kg of mixed rare earth elements; the mean decrease for maize and rape was 75%. No significant decrease could be seen in soil microbial counts (heterotrophic bacteria + actinomycetes + fungi) after the application of 270 mg/kg of mixed rare earth elements.

After 16 weeks of exposure in rice soil, the microbial biomass decreased by 10% after exposure to about 600 mg/kg of rare earth elements and by 25% after 1140 mg/kg (Zhou, Chen, Cao, Pu, & Peng, 2003).

Chu, Li, Xie, Zhu, and Cao (2001) applied La in a rice potted plant test. The geometric mean of soil microorganism nitrogen, carbon, and carbon dioxide emission were reduced by 25% at 1160 mg La per kg soil after 16 weeks.

A3.2.2 Invertebrates

Huang et al. (2009) studied soil fauna in a plum orchard. Arthropods dominated. There was a clear and strong effect on the number of individuals at apparently relatively low concentrations of lanthanides. However, the description of soil concentrations is brief and not verified, and concentrations are given as mg/kg and mg/L, casting doubts on the real concentrations, so the results are deselected.

From the same university, Huang (2009) looked at the addition of 1000 mg/kg soil of La or Nd in a horticultural vineyard. The number of species was 10-40% higher and the number of individuals 60-80% higher at the lanthanide plots compared with the control. This would suggest that the no-effect concentration would be well above 1000 mg/kg.

Li et al. (2018) exposed 5 species of invertebrates for 3-4 weeks in La spiked soil without vegetation that was equilibrated for at least 2 weeks. Juvenile earthworms were exposed additionally for 4 weeks. Inhibition concentrations that affected the organism reproduction to 25% were respectively 420, 920, 1160, 1190, and 160 mg La per kg dry soil. The authors note that aging had not been complete and that the arthropods had been exposed for a relatively short fraction of their lifetime. For survival, the concentrations were several times higher.

Six community parameters of 19 invertebrate species were studied by Li et al. (2006) (diversity index, evenness, species richness, dominant index, dominant centralization and species number). No parameter was significantly changed from yearlong exposures in a bean field up to 3000 mg mixed rare earth element per kg soil. The study had poor statistical power. A non-significant trend towards a smaller number of individuals at higher rare earth concentrations was found, with a 25% decrease at 4600 mg rare earth element per kg soil.

A3.2.3 Terrestrial Plants

The concentrations of 6 lanthanide chlorides (Pr, Nd, Sm, Tb, Dy, Er) in soil that caused a 25% reduction in plant biomass (IC_{25}) were assessed for 2 species by Carpenter et al. (2015). The same group (Thomas et al., 2014) added assessments for 2 further lanthanides (La, Ce) and another rare earth element (Y). Results were also obtained for some of the elements for 3 additional plant species, and for Ce two different values of pH were used. The results were highly variable but exhibited no clear trend with atomic number. The smallest variation among the elements was obtained for the species *Asclepias syriaca* L (minimum IC_{25} = 0.32 of the mean, maximum = 1.29). For the other species, the minimum was 0.10-0.21 of the mean, and the maximum 1.68-2.00. The extremes were obtained at different combinations of species and elements, but Dy entailed the least sensitivity for 4 of the 5 species. Large variation was also obtained for the exposures to Ce at different pH, where the IC_{25} at low pH varied from 0.26 to 1.48 of that at high pH across the plant species.

The mean IC_{25} concentrations across the 9 rare earth chlorides (Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Er) were 212, 156, 370, 805, and 735 mg/kg, respectively for the 5 species. During the approximate 2-month period of the study, aging could hardly be expected to have been fully developed, suggesting an underestimation of the long-term effect concentrations.

Onion bulbs (*Allium cepa* L.) were exposed in 6 months aged soil containing La and Ce up to 200 mg/kg soil (Kotelnikova, Fastovetsa, Rogovaa, Volkova, & Stolbova, 2019). No significant effects on root length were found but for both La and Ce, the mitotic index was significantly reduced at 200 mg/kg but not at 100 mg/kg. The conditions were quite artificial, with exposures only 5 days in test tubes with only 5 g of soil and often low statistical power.

Turra et al. (2015) exposed Rangpur lime (*Citrus Limonia* Osbeck) to lanthanum chloride heptahydrate and measured plant mass and length after 3 weeks. Extrapolation suggests that the 25% plant mass reduction level was about 350 mg La/kg soil. No significant effect on plant height was observed. The substrate was extremely rich in organic matter and not here considered representative of common soils.

Xiong and Zhang (1997) performed pot experiments where the growth periods were 33-70 days. The ratio of the concentrations of Ce and Nd resulting in a 25% reduction in leaf or root weight to those for La had no systematic trend and a range of 0.6-1.4. The mean concentrations resulting in a 25% reduction in leaf weight were 1670 mg/kg for wheat, 1600 mg/kg for soybean, and 2900 mg/kg for rice. For rape, there was an increase in leaf weight at 250 mg/kg and a strong decrease at 500 mg/kg, so the 25% reduction concentration should be around 300 mg/kg.

Zeng, Zhu, Cheng, Xie, and Chu (2006) studied the effects of La on rice. The concentration that reduced the mass of tillers and the height by 25% was 480 ± 40 mg La per kg soil.

Hu, Song, Lan, Lin, and Ren (2009) studied the development of mulberry leaves after La exposures 22-48 days. For many endpoints, there was no significant adverse effect at the maximum concentration of 600 mg La/kg soil. However, a 25% reduction in height and diameter of young sprout was noted after about 250 mg La/kg soil.

Wang et al. (2005) cultured rice and wheat in greenhouse conditions. Exposure to mixed rare earth elements reduced the biomass of maturity rice by 25% at a concentration of 600 mg per kg soil and of maturity wheat at 1 700 mg/kg. The pot experiment was repeated for two years. The description is brief and does not give the rare earth compound or the length of exposure.

Zhang et al. (2001) studied the growth rate of rice, rape, and soybean for red soil, yellow tide soil, and yellow-brown soil exposed to rare earth chloride mixtures. The geometric means across soils of the concentration that reduced the growth rate by 25% were 400 mg rare earth element per kg soil, 400 mg/kg, and 510 mg/kg, respectively. The geometric mean across soils of effect concentrations for emergence was higher: 25% reduction at 1100, 670, and 510 mg/kg respectively. It should be noted that the exposure situation with soil in Petri dishes was rather artificial.

Zhang et al. (2015) studied an *Eucalyptus grandis* × *Eucalyptus urophylla* hybrid in a pot experiment. No effects were found at La concentrations up to 500 mg/kg soil.

A3.2.4 Mammals

Hutcheson, Gray, Venugopal, and Luckey (1975) studied the nutritional safety of La, Sm, Eu, Tb, Dy, Tm, Yb, Sc, and Cr oxides and barium sulfate in two species. The mouse study was conducted for three generations, including reproduction. The mice were not affected by quantities of metals in the feed which were 1 000 times the anticipated levels. To achieve such a concentration in nature, the soil concentration would have had to be 1 000 times the normal one, or about 130 000 mg/kg soil. It is conceivable that analytical and other methods have improved since this early study.

According to Fang et al. (2018), no loss of body weight and food intake occurred for 90 days daily exposure of rats by gavage to 10 mg La per kg body weight. The daily feed intake is 0.078 kg feed per kg body weight, so 10 mg intake would correspond to a concentration in a normal diet of $10/0.078 = 128$ mg per kg feed. The typical soil concentration to give this intake would be about 128 000 mg/kg soil if the mice had a standard diet (LabSupply, 2021), and the mouse diet had a similar metal composition as a human diet, which is suggested by the similarity of the composition of other metals to the human dietary composition of Bengtsson (2018). Fang et al. (2018) found a significant effect on body weight and feed intake at 6 times higher concentration, or 60 mg La per kg body weight. However, Cao et al. (2020) found no effect after a shorter 28-day exposure to 129 mg/kg body weight by gavage but a clear effect at the ten-fold concentration. This shorter exposure should be less representative of continuous exposures than the 90-day exposures of Fang et al. (2018).

Adu, Akinmuyisitan, and Gbore (2013) exposed rabbits for 8 weeks to CeO₂. There was no effect on weight gain after feeding the rabbits a diet containing 240 mg Ce per kg feed. If rabbits in nature only consumed pasture with a concentration ratio of 0.02, the no-effect level would be 12 000 mg per kg soil.

A3.2.5 Birds

There was no significant influence on growth performance, relative organ weight, and excreta microflora for broiler chickens supplemented for 28 days with 1 500 mg per kg feed of rare earth elements-enriched yeast (Cai, Park, Seong, Yoo, & Kim, 2015). The concentration of the elements La plus Ce was 113 mg per kg feed. With a concentration ratio of 0.02 (Section 3.4), the threshold would be 5 650 mg per kg of soil. Note that this was a short exposure compared to broiler life. In nature, many large birds would have a life expectancy above 10 years.

A3.3 Effects of Sc and Y

A3.3.1 Examples of Effects

- Wu, Feng, and Qian (2012) exposed earthworms to natural soil contaminated with yttrium nitrate. The concentration leading to 25% mortality was 350 mg Y element per kg soil.
- Luo et al. (2018) exposed soil in pots to YCl₃ for a study of soil microbial community structures after 120 days incubation. The soil organic matter content was not significantly changed at 114 mg Y per kg soil, but a significant decrease was found after 228 mg/kg. There was no vegetation in the pots and the significance of the findings for plant growth is unclear.
- Kastori, Maksimović, Zeremski-Škorić, and Putnik-Delić (2010) quote an early study by Young 1935 which found that 500 mg Y/kg soil had a stimulating effect on the growth of the grass timothy.

- Wu, Zhang, Yang, Liu, and Mo (2006) studied the effects on rat brains of long-term intake of Y in drinking water. A water concentration of 0.534 mg Y per liter water might improve the function of learning and memory while 53.4 mg/L had little effect and 5340 mg/L could strongly restrain both the function of learning-memory functions and growth-development in rats. Similarly, Zhang, Yang, Liu, Zhang, and Xue (2006) found a boost to the immune response (IgG and IgM) at 0.534 mg/L, no response at 53.4 mg/L and strongly impaired immune functions and strong weight loss of spleen and thymus at 5340 mg/L. The clear effect dose at an assumed water intake of 0.05 L/d (Toxicology Excellence for Risk Assessment, 2021) gives 267 mg/d for 0.4 kg body weight or about 700 mg/d per kg. With a food factor of 0.078 kg food intake per day per kg body weight, the food concentration would have to be 9 000 mg element per kg food. A concentration ratio soil-food of 0.02 (Section 3.4) would imply a clear effect from 450 000 mg element per kg soil. No effect was observed at one-hundredth of this corresponding to 4 500 mg/kg.

Also, the ECHA registration dossier for yttrium (ECHA, 2021) contains information suggesting a no observed effect level of 1 000 mg per kg body weight per day, based on oral exposures of Wistar rats of both sexes. This is the same as the level that can be derived from the data of Shin, Kim, and Rim (2019). It can be compared to the effective dose of 700 mg/kg/day of Wu et al. (2006). Neurotoxic effects in rats have been found at about one-thousandth of these concentrations for Y (Feng et al., 2007) and La (Xiao et al., 2020).

A3.3.2 Sc and Y Effects in the Context of Lanthanides

Concentration ratios from soil to plants have been dealt with in Section A2.4. For Y, the concentration ratio was 0.6 and 1.05 of the mean for lanthanides for plants (MacMillan, Chételat, Heath, Mickpegak, & Amyot, 2017) and horticultural waste ashes (El-Ramady, 2008), respectively. For Sc, the corresponding ratio for horticultural waste ashes was 1.15. Considering the uncertainties, the same concentration ratio soil-plants should be applied for Sc and Y as for lanthanides, and data suggest this is accurate to better than a factor of 2.

The discussion below puts Sc and Y in relation to mean lanthanide effect concentrations. The results suggest that within about a factor of 2, organisms have the same sensitivity per mol to Sc and Y as they have to lanthanides.

- In Section A3.1.1, studies on two algae were mentioned where the concentration that resulted in 50% reduction in growth for 12 or 13 lanthanides had small variation around 29 $\mu\text{mol/liter}$. The corresponding concentrations for Sc were 21 $\mu\text{mol/liter}$ and for Y 43 $\mu\text{mol/liter}$.
- Ramos et al. (2016) compiled data on LD_{50} for male mice after intraperitoneal administration of rare earth chlorides. For Sc element the LD_{50} was 130 mg/kg body weight whereas it was the range 300-350 mg/kg for other lanthanides. In terms of mmol per kg, the numbers are 2.9 vs. 2.0-2.3. It should be noted that all the lanthanides data were obtained by one research team while the Sc data were acquired by another team.
- The effect concentration of chlorides of Sc, Pr, and Nd in wells (48 h) was studied by Xu et al. (2017) for the nematode *Caenorhabditis elegans*. In relation to Pr, the effect concentrations for Sc in terms of mol per unit volume were in the range 0.39-1.3 (mean 0.73) for median lethal concentration after 48 h and 96 h, as well as for 25% reductions of body length, track length and mean speed. The corresponding ratio Nd/Pr had the range 0.25-1.26 (0.89).
- Y was included among the elements tested on plants by Thomas et al. (2014) (compare Section A3.2.3). The concentration in soil that caused 25% reduction in plant biomass (IC_{25}) for Y was not significantly different from that for 8 lanthanides tested on 3 species by Thomas et al. (2014) and Carpenter et al. (2015). The results were highly variable but the mean IC_{25} ratio for Y relative to the lanthanides had a range of 1.1-2.9 in terms of mol per kg soil.
- On a molar basis, the 50% lethal effect concentration for *Daphnia* (EC_{50}) for Y was 0.99 of that for Sc (Okamoto 2014).

A3.4 Effects of Nano-Lanthanides

Studies of rare earth nanomaterial effects are dominated by research on cerium oxide nanoparticles. No adverse effect on plant yields have been reported for cilantro (500 mg CeO_2 per kg soil; Morales et al., 2013); cucumber (1000; Zhao et al., 2013), corn (1000; Zhao et al., 2015), radish (500; Corral-Diaz et al., 2014); wheat (500; Rico et al., 2014; and 400; Du et al., 2015); barley (500; Rico et al., 2015, and 1000; Pošćić, Mattiello, Fellet, Miceli, & Marchiol, 2016); tomato (130; Wang, Ma, Zhang, Pei, & Chen, 2012); soybean (1000; Priester et al., 2012—no effect on total plant but a low weight on pods that singly stands out), the brush *Clarkia unguiculata* (290 dosed each of 8 weeks; Conway, A. L. Beaulieu, N. L. Beaulieu, Mazer, & Keller, 2015) and common bean (500; Majumdar et al., 2015).

Generally, these have had a duration of less than 3 months although one was a life cycle study of 7 months (Du et al., 2015). The studies suggest that CeO₂ nanoparticles had no adverse effects on plant yields below Ce element concentrations in the soil of 800 mg per kg soil, or about 2400 mg/kg when corrected for aging. The nutritional content may however be changed. For instance, Rico et al. 2013 showed changes in many nutritional parameters for rice at 500 mg of CeO₂ nanoparticles per kg soil.

Broader effects of CeO₂ nanoparticles were noted in two studies. Zhang et al. (2017) observed a 25% weight loss in romaine lettuce (*Lactuca sativa* L.) at 744 mg element per kg soil (2300 mg/kg when corrected for aging). Priester et al. (2012) found a decrease in soybean plant stem length at 81 mg Ce per kg soil that almost disappeared at 814 mg/kg.

In a study on rats, CeO₂ nanoparticles up to 1000 mg daily per kg body weight were administered by gavage to parental rats for 4 weeks (Lee et al., 2020). No marked toxicities (including neurotoxicity) were observed in any observation parameters in parents or pups.

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Abbreviations

IC_{XX}: XX% of the maximal inhibitory concentration, representing the point in which a compound of interest produces complete inhibition of a biological or biochemical function.

LD₅₀: Median lethal dose, the dose required to kill half the members of a tested population after a specified test duration.

TOC: Total organic carbon.

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