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REWIEV ARTICLE

# RARE EARTH ELEMENTS (REE) IN WILD MACROFUNGI: A REVIEW HIGHLIGHTING THE IMPORTANCE OF REQUISITE ANALYTICAL METHODOLOGY ON DATA QUALITY

*Jerzy Falandysz*[1], *Alwyn R. Fernandes*[2], *Anna Kilanowicz*[1], *Heesoo Eun*[3]

[1]Department of Toxicology, Faculty of Pharmacy, Medical University of Lodz, Poland
[2]School of Environmental Sciences, University of East Anglia, United Kingdom
[3]Research Center for Advanced Analysis, National Agriculture and Food Research Organization, Japan

## ABSTRACT

The accelerating global use of lanthanides in modern consumer goods has introduced a new source of environmental pollution and potential health hazards. Evaluating risk for human exposure to these rare earth elements (REE) is hampered by limited occurrence data in foods, partly because reliable, sensitive and accurate determination is challenging. An objective of this work was to critically review lanthanide occurrence in fruiting bodies (mushrooms) of edible wild terrestrial (epigeic) and subterranean (hypogeic) macrofungi and their soil substrates, while also assessing the reported data for analytical quality. Given the paucity of information, all available literature on lanthanides in wild mushrooms was considered. Key requirements for credible REE determination in fungal biomass include avoiding cross contamination from substrates, exclusion of spectral/non-spectral interferences through robust purification and selective, sensitive measurement procedures, inclusion of the full range of lanthanides and strict quality control. In general, both high and lower resolution ICP-MS techniques were evidentially able to provide more reliable outcomes if these requirements were followed. A second objective was to propose a rational approach to assess data reliability by combining the above methodological attributes with the characteristics of lanthanide occurrence in mushrooms: (i) adherence to Oddo-Harkins order, visualised as a descending sawtooth pattern – a result of unfractionated uptake and accumulation of lanthanides from soils and other substrates (ii) typical individual concentration ratios (e.g., La/Sm, Ce/Nd, Ce/Sm) that indicate reliable determination, (iii) bio-exclusion of lanthanides by wild fungi (bioconcentration factors < 1). Data from studies that met these requirements confirmed typically low concentrations (0.07 μg $kg^{-1}$ of Lu in *Suillus luteus* to 940 μg $kg^{-1}$ of Ce in *Cantharellus minor*) with patterns corresponding to Oddo-Harkins order across reported fungal types, maintaining the unfractionated REE substrate patterns. However, given the upward trend in REE usage, the continued monitoring of macrofungi is prudent.

**Keywords:** *fungi, forest soils, macrofungi, emerging metal pollutants, Oddo-Harkins order, rare earth elements distribution patterns, REE*

## INTRODUCTION

The rare earth elements (REE) include the fifteen lanthanides with atomic numbers 57-71 (Lanthanum, La 57; Cerium, Ce 58; Praseodymium, Pr 59; Neodymium, Nd 60; Promethium, Pm 61; Samarium, Sm 62; Europium, Eu 63; Gadolinium, Gd 64; Terbium, Tb 65; Dysprosium, Dy 66; Holmium, Ho 67; Erbium, Er 68; Thulium, Tm 69; Ytterbium, Yb 70; Lutetium, Lu 71), although some studies and organisations such as the IUPAC also include yttrium (Y 21) and scandium (Sc 39) because they exhibit similar chemical characteristics and often occur in the same mineral deposits [1-3]. In some sub-classifications, individual REE may be included in more than one group, e.g. lighter atomic weight elements (LREE) may include elements from La to Pr or Nd, with or without Sc; medium atomic weight REE (MREE) may include elements from Nd to Dy or Ho) and heavier REE (HREE) could include elements from Dy or Ho to Lu, with or without Y [4, 5]. They are considered as strategic metals and are essential components in a range of military equipment and consumer products such as sonar, radar, guidance systems, cellular telephones, computers and electric vehicles [6]. Unlike typical ores which contain significant deposits of some metals, REE are more widely distributed throughout the Earth's crust and soils (Figure 1) [4]. Individual environmental abundances of REE and their applications vary strongly depending on the

**Corresponding author:** Jerzy Falandysz, Department of Toxicology, Faculty of Pharmacy, Medical University of Lodz, 1 Muszyńskiego St, 90-151 Łódź, Poland; email: jerzy.falandysz@umed.lodz.pl


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element, e.g., Ce and Nd together with La, Pr and Sm which are LREE, are dominant in the Earth's crust, REE-bearing deposits and soils including forest soils. By mass, the LREE dominate the total REE volume used in applications [6-8]. Each REE has a practical but sometimes very minor specific application, including those elements that have a low occurrence in deposits and command a high price [6]. The currently known geological deposits of REE show a wide global distribution, e.g. major deposits are known at Mountain Pass in the US, Bayan Obo and other ion-adsorption deposits occur in Southern China, Myanmar and Mount Weld in Australia [9].

The rising demand for REE has encouraged more exploration for new deposits and has increased industrial activity involving extraction and processing. These activities that include primary and secondary (urban) mining, application and disposal of REE, Y and Sc products, have in recent time, raised concerns regarding the pollution of the natural environment and food webs by these "emerging contaminants" of concern [10-15]. Human activities such as oil refining that use zeolitic fluid catalytic converters, coal combustion or metal ore smelting and refining, result in emissions of particulate matter that contain a whole range of REE or an individual compound [16-21], which can potentially be emitted and deposited in the surrounding environment including forested land. Although the depositions from these thermal releases may be detectable in media that are in close vicinity to the source [21], they are not discernible when dispersed to forest soils on a wider or global scale (Figure 1) [22, 23]. Similarly, Gadolinium (Gd) is known locally or regionally as a contaminant of aquatic freshwater environments as well as drinking water and beverages but not of urban dust/soils or forest soils [1, 23-26]. This arises from its application in gadolinium-based contrast agents in medical magnetic resonance imaging, which helps to improve image clarity of internal structures, but are subsequently excreted through urine to waste waters.

Foods that are foraged from the wild either for economic reasons or as a leisure activity include numerous species of macrofungi. Some, such as chanterelles, *Cantharellus cibarius* (northern Hemisphere), boletes such as *Boletus aestivalis*, *B. bainiugan*, *B. edulis, B. pinophilus*, *Butyriboletus roseoflavus* (Europe/Asia), matsutake *Tricholoma matsutake* (Japan) are particularly prized foods while alba or white truffle *Tuber magnum* (Italy) are commercially very valuable. However most species of fungi, whether edible or not, can be impacted by anthropogenic or geogenic contamination such as As, Cd, Hg, Pb and other organic contaminants [27-29], the extent of which is a function of physiology, the biogeochemistry of the growing substrate and local pollution. Common examples of the resulting bioaccumulation are selenium which is beneficial or conversely, radioactive caesium which is toxic [30, 31].

Mushrooms, the edible fruiting bodies of many wild macromycetes (and in some cases, sclerotia) are popular foods or delicacies as in the case of species such as truffles, but over recent decades global demand has seen an increasing trend in the production of cultured species [32]. The global supply of edible mushrooms in 2021 was 44.2 million tons, of which China was a major producer, supplying 41.1 million tonnes [32], particularly from the Yunnan province which is the largest producer, consumer and exporter of wild mushrooms. In 2011, production reached 70,000 tonnes [33]. In contrast, the estimated annual quantity of wild mushrooms foraged from Polish forests amounted to 99.0 tonnes (mean value for 2006-2008). Of this total volume, 29.7 tonnes were purchased for industrial processing and export, 9.9 tonnes for roadside and market sales, leaving 59.4 tonnes for personal consumption [34]. Globally, a number of countries are home to discrete population groups that have a tradition of foraging wild mushrooms, either to supplement their food supplies or as hobbyists and gourmets who prize these foods, maintaining and fostering a tradition of identifying and collecting wild edible species [35, 36].

In recent decades, following the increasing commercialisation of REE, some studies have begun reporting the concentrations of these elements in the environment and in vegetation. This information is important to the consideration of REE as potential emerging contaminants which could pose risks for consumers, but good data quality is essential for an evidential and objective assessment. A few dozen review articles including books on various aspects of environmental occurrences of REE and potential risks associated with their production have been published since 2000, but none of these have included data on wild mushrooms and their habitats – forest topsoils and plant substrates [4, 5, 9, 11, 22, 36-46].

This is the first critical review of REE occurrence in wild macrofungi and their mycelial substrates which considers the quality and reliability of the applied determination methodologies. These attributes are crucial to the understanding of the trends in the occurrence of REE in fungi and in the environment because as seen in recent literature [47, 48] some reports of elevated levels may not be substantiated. The review used an open literature search using ISI Web of Science, Mendeley and Google Scholar (keywords: lanthanides, REE, rare earth elements, fungi and mushrooms) and additionally, targeted literature with documented analytical methodologies. It discusses studies published from 2001, the year when the first reports on all 14 REE (lanthanides) in wild mushrooms

using analytical methodologies for fungal biomass became available [2, 13, 23, 49-71]. Such data is scarce and a collation would be helpful for comparison of concentrations between species, assessing risk for the dietary intake of edible fungal parts and for examining any trends in occurrence. In recent years, some studies on Lanthanide contamination in fungi appeared to show elevated levels of some of these elements but critical reviews [47, 48, 64-67] suggested that stricter analytical control and pre-assessment of the data could lead to different outcomes. Thus, in addition to reviewing the quality of the analytics this review also assesses the reported data for natural distribution patterns of occurrence, concentrations and bioconcentration potential, and discusses the main requirements for providing reliable and credible data on REE in mushrooms.

## REE IN MUSHROOMS, FOREST SOILS AND PLANT SUBSTRATES

REE display a relatively narrow range of atomic weights and also of ionic and atomic radii, and a unique electronic configuration (all exist as stable +3 ions) and Ce can easily oscillate between +3 and +4 oxidation states (the only lanthanide stable in the +4 oxidation state at physiological conditions) [4, 15]. Consequently, as a group they are characterised by similar physical and chemical features, which also influence their similar fate in the geobiosphere [22]. Apart from this common stable ionic form, Sm, Eu, Tm and Yb can also occur in the +2 oxidation state but only $Eu^{2+}$ ions are sufficiently stable in natural aqueous solutions. In addition to Ce, Pr, Nd, Tb and Dy have also been reported to occur in the +4 oxidation state [4, 5, 25]. The natural occurrence of the lanthanides in biotic as well as abiotic environments including substrates for wild mushrooms (forest soils and various plant derived organic substrates) is characterised by a typical pattern when concentrations are plotted (Figure 1). This well-defined pattern results from the Oddo-Harkins (O-H) order of elemental abundances [77]. The O-H order states that elements, e.g. lanthanides, having an even atomic numbers as the atomic number increases are always an order of magnitude more abundant (higher Clarke concentrations) than the adjacent odd-numbered lanthanides, and display a larger number of isotopes [1]. The resulting order of lanthanide occurrence in most matrices appears as a descending sawtooth or zigzag pattern dominated by Ce, which endures despite the biodiversity of macrofungi or varying geochemical (forest soil or bedrock type) conditions (Figures 1-3, Tables 1-2). This pattern results from the undiscriminated mycelial uptake of individual lanthanides and is observed in both, wild and cultivated species, despite varying elemental

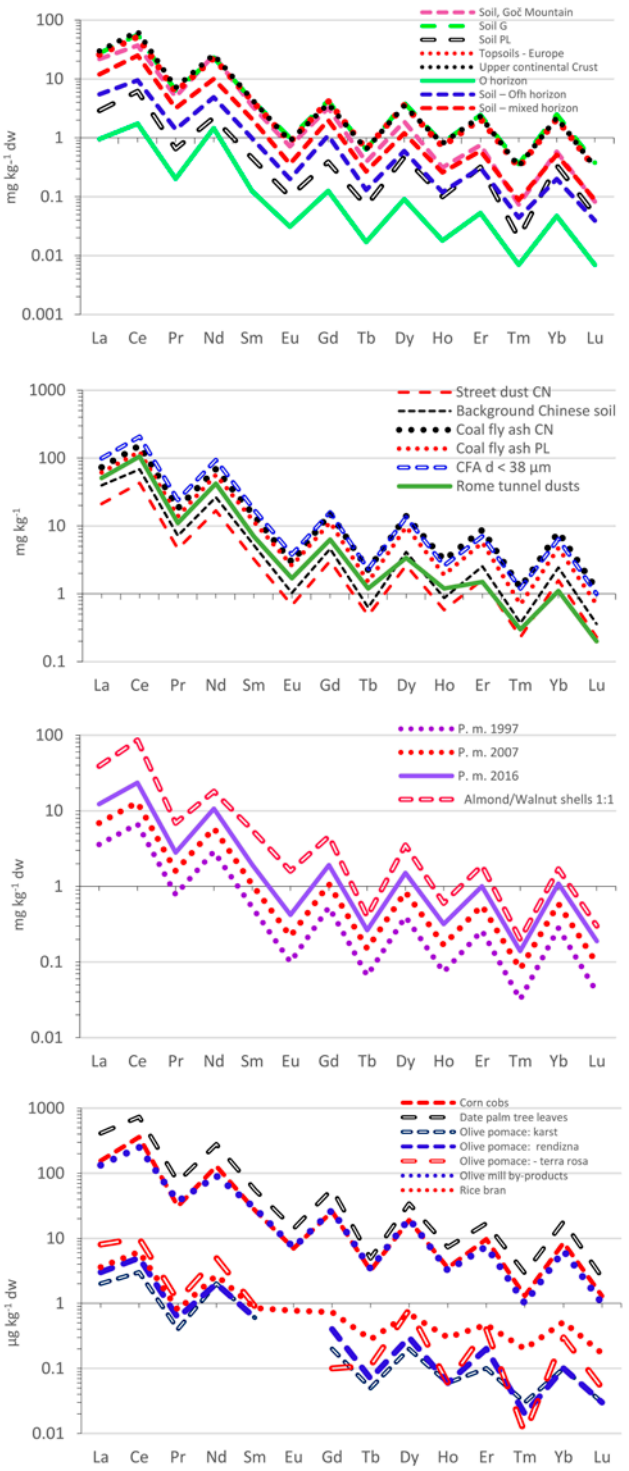


Figure 1. Distribution pattern of lanthanides concentrations in various environmental materials (forest topsoils – Serbia, Germany and Poland [8, 23, 61], topsoils in Europe) [7], upper continental crust [72], forest soil O horizon – Sweden [54], forest soil and mixed horizons – Poland [73], street dust and background soils and coal fly ash – China [86], coal fly ash – Poland and coal fly ash (< 38 µm fraction) – United Kingdom [19], tunnel dust in Roma – Italy [74], annual rings of *Pinus massoniana* – China [75], mixt of almond and walnut shells – Greece, corn combs and data palm tree leaves – Greece [78], olive pomace from olive trees grown on karst, rendzina and terra rosa soils – Adriatic Sea coastal region, olive mill by-product – Greece [78] and rice bran – Japan [76], adapted.

concentrations that arise from differences in species, the location of the sampling site, the soil or other media in which the mycelium develops, including prepared fungal compost [23, 78, 101]. Therefore, according to the O-H order, REE elements Er, Tm, Yb and Lu show the lowest concentration levels in natural environmental matrices including mushrooms, and may be several orders of magnitude lower than the most abundant REE. Practically, this can be observed in the currently reviewed data listed in Tables 1-2. The lowest concentrations are seen for the lanthanides with high atomic masses (the lowest reported concentrations is 0.07 µg $kg^{-1}$ dw of Lu in whole fruiting bodies of *S. luteus* while the highest value of 940 µg $kg^{-1}$ dw was reported for Ce in *C. minor*. An exception is the peridium – a thin external skin covering the flesh (gleba) of a truffle – with Ce concentrations ranging from 2100 to 4000 ± 5200 µg $kg^{-1}$ (Table 2). Additionally, if the occurrence of individual lanthanides are logarithmically plotted, the descending sawtooth pattern persists (Figure 3) despite the wide range of species and locations (including biogeochemical and pollution profile differences) from which these fruiting bodies were collected [49, 54, 62, 71, 101].

Some plants, e.g. ferns, *Pteropsida*, species like *Athyrium yokoscence*, *Dicranopteris dichotoma* or *Dryopteris erythrosora* will accumulate REE from soil [14, 79], and further participate in humus genesis in the highly organic layer of the forest soil horizon which is essential for mycelial development and the nutrition of many fungal species [80]. Thus, the composition of REE in ecosystems is strongly influenced by their genesis in soils, and their compositional pattern in biota is considered to directly reflect this origin [81, 82]. This typical sawtooth distribution is also seen in soil substrates (that are the habitat of many fungal species) from European forest topsoils collected in the last decade at mushroom collection sites and show the lack of site specific or regional specific discrimination between individual REE [8, 23, 61, 71, 101].

This collective behaviour that preserves the O-H order underlines the lack of fractionation by individual REE which is reported by a number of studies examining elemental contents of mushrooms (Figures 3-6, Tables 1-2). For example, several fungal species (*Caloboletus calopus*, *Cantharellus cibarius*, *Craterellus cornucopioides*, *Imleria badia*, *Laccaria amethystina*, *Lactifluus piperatus*, *Leccinum scabrum*, *Suillus grevillei* and *Sutorius brunneissimus*) collected in Belarus, China and Poland did not show any signs of the fractionation of the patterns of lanthanides or Y [23], nor *Pleurotus ostreatus* and *Cyclocybe cylindracea* cultivated on a range of substrates [78] or many other edible wild species collected in Poland and Croatia [49, 63]. However, in *Suillus luteus*, examined using the same methodology (and laboratory) as in article

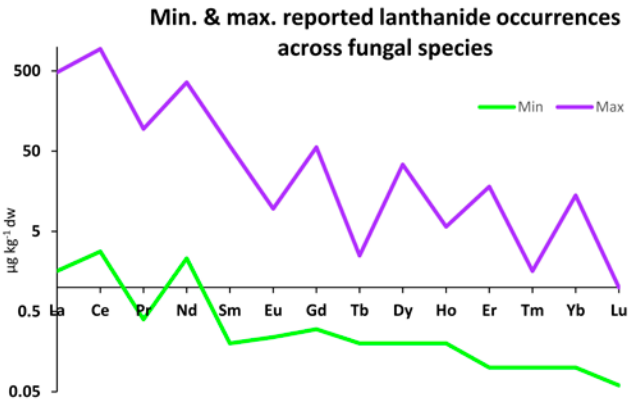


Figure 2. A plot of the range of lanthanide occurrences in mushrooms shows that the Oddo-Harkins order persists despite the different species, different biogeochemistry, varying pollution profiles and different data providers (Plot data taken from Table 1).

[23], a positive Y anomaly was detected [8], which was not detected in other *Suillus* species in independent studies [23]. Also several species of ectomycorrhizal and saprobic fungi in some other studies did not show the Y anomaly [59, 61, 63, 71, 101]. The Eu anomaly (negative and positive) has been noted in some studies, i.e. *Macrolepiota procera* and a range of saprotrophic and ectomycorrhizal species [49, 56, 59], but equally, this species did not show the Eu anomaly [61], nor did the mushrooms in some other studies. It has been reported that the Eu anomaly could be an artefact of spectrometric analysis [83, 84].

Notwithstanding their dispersion in terrestrial and marine environments and their trace or ultra-trace presence in foods of plant and animal origin, REE are not considered as essential in biology and or to human nutrition, as far as is presently known, e.g. Ce, the most abundant REE has no known biological role [85]. Nevertheless, methylotrophic bacteria from harsh environments, e.g. thermoacidophilic *Methylacidiphilum fumariolicum*, and *Methylorubrum extorquens* and *Methylobacterium radiotolerans* have been reported to utilise lanthanides (La, Ce, Pr, Nd) in methanol dehydrogenases in a similar manner to calcium [86-88].

## EFFECT OF SOIL, DUST AND SAND ON DRIED FUNGAL MATERIALS FROM HERBARIA

Although REE are commonly defined as “rare”, Ce, which is the most abundant of the lanthanides, is arguably as abundant as the bio-metal zinc (Zn), and is more abundant than tin (Sn) or lead (Pb) [85]. Soils and sands at locations in China are generally richer in REE than elsewhere in the world [43, 89]. Stijve et al. [53] were the first to document that soil dust (soil and

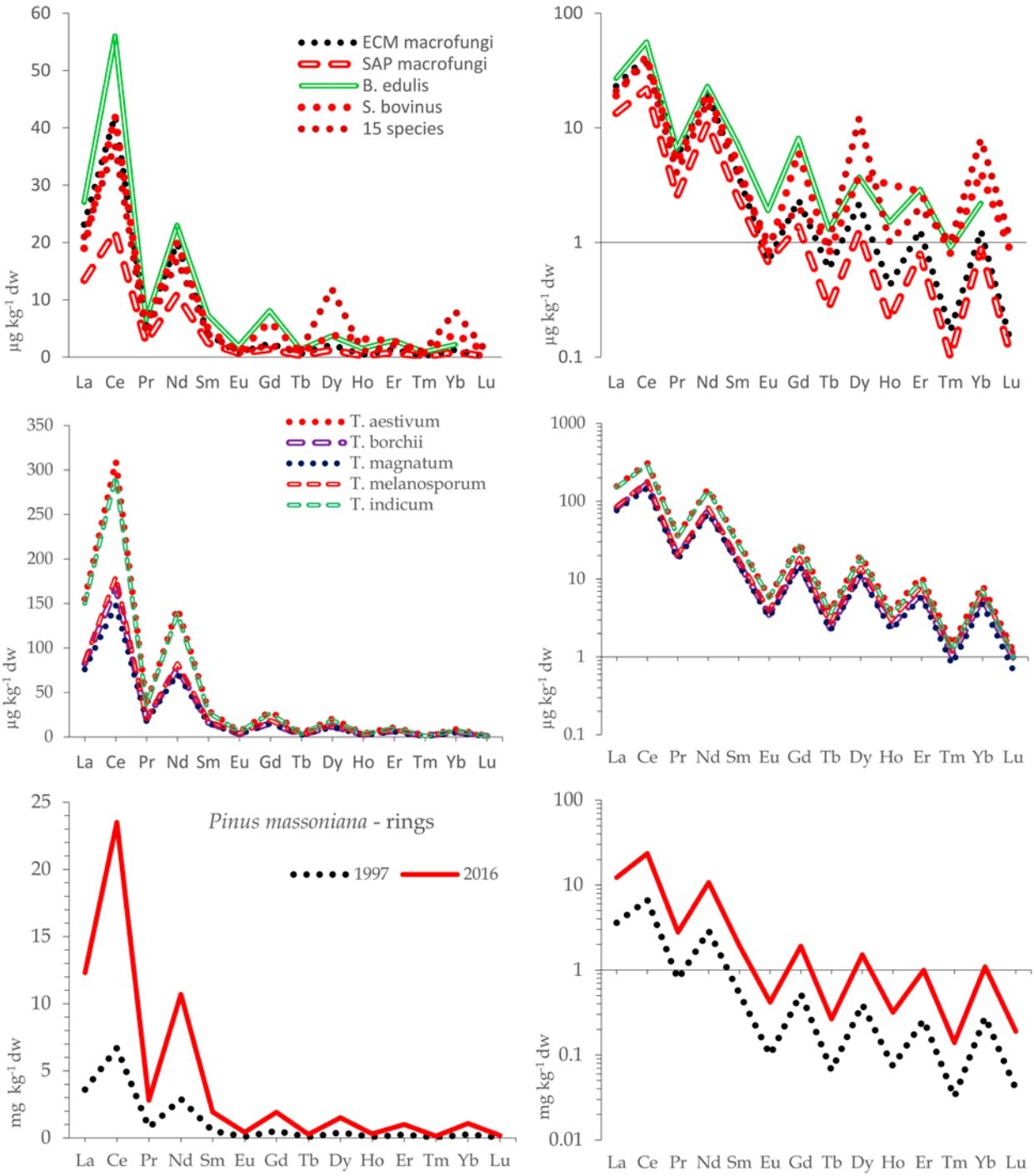


Figure 3. Distribution of REE – natural sawtooth concentrations pattern in ectomycorrhizal and saprobic mushrooms and the species *Boletus edulis* – King Bolete and *Suillus bovinus* – Cow bolete (upper plots), black (*Tuber melanosporum*, *T. aestivum* and *T. indicum*) and white truffles (*T. magnatum* and *T. borchii*) (middle plots) – as determined by direct aspiration of an acid oxidized digest into a sector field mass spectrometer and in annual tree rings of *Pinus massoniana* (bottom plots) – by quadrupole mass analyzer, after [49, 56, 62, 75].

sand particles) adhered to fruiting bodies can cause a spurious increase in actual REE concentrations. In their first study, Stijve et al. determined La, Ce, Nd, Gd, Sm, Er and Dy (also Ag, Al, Ca, Co, Fe, Ga, Mo, P, Pb, Th, V and Y) in fruiting bodies of *Albatrellus pes-caprae* (current name, *Scutiger pes-caprae* (Pers.) Bondartsev & Singer) collected in Switzerland, Germany and the USA. They also reported on the sum of Ce, La and Nd (also Al, Ca, Fe and Th) in various wild and cultivated mushrooms: "*Agaricus bisporus*, *A. arvensis*, *Agaricus bitorquis*, *Agaricus gaestrani*, *Agaricus silvicola*, *Boletopsis grisea*, *Boletopsis*

Table 1. Concentration (µg $kg^{-1}$ dw) of lanthanides, yttrium and scandium in terrestrial fungi biomass (means and uncertainty) and selected analytical method parameters – adapted from the references cited – all data rounded for two significant figures if different from zero

| Species / element | King Bolete | | | Slippery Jack | | Cow Bolete | Larch Bolete | Hedgehog Fungus | Yellow or Golden Chanterelle | | Small Chanterelle | Bitter Beech Bolete | Various mushrooms |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *B. edulis* | | | *S. luteus* | | *S. bovinus* | *S. grevillei* | *H. repandum* | *C. cibarius* | | *C. minor* | *C. calopus* | *15 species* |
| | C* *n* = 1 (3) | W *n* = 1 (1) | W *n* = 14 (261) | C *n* = 1 (3) | W *n* = 1 (3) | C *n* = 1 (3) | C *n* = 1 (4) | W *n* = (4-5) | W *n* = 3 (146) | W *n* = 22 (2235) | W *n* = 1 (153) | C *n* = 1 (11) | *n* = 19 |
| La | 27 ± 14 | 14 | 51 | 5.3 ± 2.5 | 6.4 | 19 ± 23 | 15 | 1.6-2.2 | 55 (22-91) | 27 | 480 | 41 | 21 (3-93) |
| Ce | 56 ± 25 | 24 | 95 | 9.3 ± 4.7 | 11 | 42 ± 56 | 28 | 2.8-3.6 | 120 (51-210) | 35 | 940 | 105 | 37 (6-140) |
| Pr | 6.5 ± 3.9 | 2.8 | 9.7 | 1.7 ± 0.6 | 1.2 | 5.0 ± 6.1 | 0.5 | 0.4-0.5 | 16 (12-22) | 2.3 | 95 | 9.4 | 4 (1-17) |
| Nd | 23 ± 12 | 10 | 32 | 6.7 ± 2.3 | 4.7 | 20 ± 22 | 15 | 2.3-3.5 | 46 (20-79) | 9.2 | 360 | 38 | 17 (2-63) |
| Sm | 7.3 ± 4.2 | 2.3 | 5.5 | 2.0 ± 1.0 | 1.1 | 5.0 ± 5.2 | 2.8 | 0.2-0.3 | 8.3 (3.9-14) | 3.1 | 58 | 8.0 | 4 (1-11) |
| Eu | 1.9 ± 0.6 | 0.52 | 1.1 | 0.67 ± 0.0 | 0.24 | 0.80 | 0.5 | ≤ 0.1 | 1.4 (0.7-2.2) | 0.5 | 9.6 | 2.1 | 1 (< MQL-2) |
| Gd | 8.1 ± 3.5 | 2.7 | 5.1 | 1.4 ± 0.8 | 1.2 | 6.2 ± 6.5 | 2.4 | 0.3 | 5.6 (3.2-11) | 2.2 | 56 | 8.2 | 2 (< MQL-2) |
| Tb | 1.3 ± 0.6 | 0.38 | 0.9 | WD | 0.17 | 0.80 | 0.3 | < 0.1 | 0.9 (0.5-1.3) | 0.5 | 2.5 | 1.2 | 1 (< MQL-2) |
| Dy | 3.7 ± 2.5 | 2.3 | 5.0 | 1.1 ± 0.5 | 1.0 | 3.8 ± 3.7 | 1.8 | 0.2-0.3 | 4.6 (2.6-7.0) | 2.0 | 34 | 6.9 | 12 (8-20) |
| Ho | 1.5 ± 1.2 | 0.44 | 1.0 | 0.70 | 0.19 | 3.2 | 0.3 | < 0.1 | 0.8 (0.5-1.1) | 0.5 | 5.7 | 1.3 | 1 (< MQL-3) |
| Er | 2.9 ± 1.5 | 1.2 | 3.4 | 0.65 ± 0.07 | 0.58 | 2.8 ± 2.8 | 0.8 | 0.1-0.2 | 2.0 (1.3-2.8) | 2.5 | 18 | 3.4 | 2 (< MQL-6) |
| Tm | 0.90 | WD | 0.6 | 0.70 | WD | 0.80 | WD | < 0.1 | WD | 0.5 | 1.6 | WD | 1 (< MQL-1) |
| Yb | 2.2 ± 1.2 | 0.90 | 3.2 | 0.70 | 0.42 | 4.1 ± 3.5 | 0.7 | 0.1-0.2 | 1.4 (1.0-1.8) | 0.5 | 11 | 2.7 | 8 (6-14) |
| Lu | WD | 0.12 | 0.5 | 0.70 | 0.066 | 0.80 | 0.1 | < 0.1 | 0.2 (0.1-0.3) | 0.5 | < 1.0 | 0.3 | 1 (< MQL-1) |
| ∑REE | 140 | 62 | 310 | 32 | 36 | 110 | 43 | WD | 260 (110-440) | 77 | 2070 | 190 | 120 (31-450) |
| Y | WD | 18 | 42 | WD | 8.7 | WD | 4.1 | 1.3-1.6 | 23 (14-30) | 22 | 200 | 44 | 16 (2-82) |
| Sc | WD | WD | 35 | WD | WD | WD | WD | 10-20 | WD | < 1.0 | 66 | WD | 34 (4-99) |
| Sample (mg) | WD | 50 | 200 | WD | 150 | WD | 1000 | 750 | 1000 | 1000 | 1000 | 1000 | 50 |
| Digestion | $HNO_3$ | $HNO_3$/HCl | $HNO_3$/HF | $HNO_3$ | $HNO_3$ | $HNO_3$ | $HNO_3$/HCl | $HNO_3$ | $HNO_3$/HCl | $HNO_3$/HCl | $HNO_3$/HCl | $HNO_3$/HCl | $HNO_3$/HF |
| Acid volume | 5 mL | 3 + 1 mL | 3 + 1 mL | 5 mL | 5 mL | 5 mL | 15 + 2.5 mL | 10 mL | 15 + 2.5 mL | 15 + 2.5 mL | 15 + 2.5 mL | 15 + 2.5 mL | 7 + 0.1 mL |
| S & P | No | Yes | No | No | Yes | No | Yes | No | Yes | Yes | Yes | Yes | No |
| Measurement | ICP-SFMS | ICP-QMS | ICP-MS | ICP-SFMS | ICP-QMS | ICP-SFMS | ICP-QMS | ICP-MS | ICP-QMS | ICP-QMS | ICP-QMS | ICP-QMS | ICP-SFMS |
| Instrument | PlasmaTrace, VG Elemental | NexION 300 ICP-MS | ELAN DRC-e | PlasmaTrace, VG Elemental | NexION 300 ICP-MS | PlasmaTrace, VG Elemental | NexION 300 ICP-MS | ELAN-6000 | NexION 300 ICP-MS | NexION 300 ICP-MS | NexION 300 ICP-MS | NexION 300 ICP-MS | Element 2, Thermo Scientific |
| Reference | [49] | [2] | [100] | [49] | [8] | [49] | [23] | [54] | [23] | [68] | [68] | [23] | [63] |

Notes: *C (caps)/W (whole) and number of pools/samples (and total number of fruiting bodies); WD (without data); S & P (separation and pre-concentration).

Table 2. Concentration (μg $kg^{-1}$ dw) of lanthanides, yttrium and scandium in subterranean (truffles) and terrestrial fungi biomass (means and uncertainty) and selected analytical method parameters – adapted from the references cited – all data rounded for two significant figures if different from zero

| Species/ element | Summer truffle* | | | Whitish truffle* | White truffle (n=13) | | Black truffle* | Asian black truffle* | | | Saprobic fungi | Mycorrhizal fungi | Field parasol* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *T. aestivum* | | | *T. borchii* | *T. magnatum* | | *T. melanosporum* | *T. indicum* | | | | | |
| | Peridium | Gleba (flesh) | Peridium | Peridium | Peridium | Blend | Peridium | Peridium | Peridium | Gleba (flesh) | WD | WD | C** |
| | *n* = 25 | WD | *n* = 26 | *n* = 4 | *n* =13 | *n* = 9 | *n* = 8 | *n* = 8 | *n* = 1 | *n* = 1 | *n* = 25 | *n* = 25 | *n* = 19 |
| La | 520 ± 400 // WD | 79 | 160 ± 170 | 82 ± 69 | 76 ± 46 | 10 0 ± 130 | 86 ± 59 | 150 ± 140 | 910 | 34 | 13 | 23 | 66 ± 60 |
| Ce | 4000 ± 5200 // 4300 ± 5700 | 140 // 350 ± 210 | 310 ± 380 | 170 ± 14 | 150 ± 87 | 190 ± 150 | 180 ± 120 | 290 ± 320 | 2100 | 73 | 22 | 42 | 190 ± 200 |
| Pr | 660 ± 620 // WD | WD | 37 ± 42 | 20 ± 17 | 18 ± 11 | 24 ± 150 | 20 ± 14 | 35 ± 34 | 250 | 10 | 2.5 | 5.6 | 14 ± 14 |
| Nd | 1700 ± 2100 // WD | 42 ± 40 | 150 ± 170 | 77 ± 62 | 71 ± 43 | 97 ± 160 | 82 ± 52 | 140 ± 130 | 1000 | 38 | 11 | 20 | 67 ± 58 |
| Sm | 390 ± 400 // WD | WD | 30 ± 34 | 16 ± 12 | 15 ± 10 | 21 ± 160 | 18 ± 12 | 27 ± 25 | 240 | 10 | 2.5 | 4.1 | 21 ± 20 |
| Eu | WD // 6.4 ± 77 [INAA] | WD // 6 [INAA] | 5.8 ± 6.1 | 3.5 ± 2.3 | 3.2 ± 2.0 | 5.4 ± 180 | 3.9 ± 2.6 | 5.8 ± 4.3 | 68 | 3 | 0.68 | 0.68 | 3 ± 3 |
| Gd | 350 ± 430 // WD | WD | 29 ± 32 | 16±11 | 15 ± 9.7 | 21 ± 140 | 19 ± 11 | 27 ± 23 | 230 | 10 | 1.4 | 2.3 | 11 ± 11 |
| Tb | 62 ± 54 // 68 ± 58 | WD | 3.9 ± 4.2 | 2.3 ± 1.7 | 2.2 ± 1.4 | 3.1 ± 210 | 2.7 ± 1.9 | 3.6 ± 3.0 | 46 | 2 | 0.27 | 0.59 | 1.5 ± 1.3 |
| Dy | 260 ± 31 // WD | WD | 21 ± 22 | 12 ± 8.0 | 11 ± 6.7 | 18 ± 180 | 14 ± 9.7 | 19 ± 16 | 200 | 8 | 1.2 | 2.2 | 6.6 ± 6.2 |
| Ho | 68 ± 59 // WD | WD | 3.9 ± 4.0 | 2.5 ± 1.7 | 2.2 ± 1.4 | 3.3 ± 260 | 3.0 ± 2.2 | 3.5 ± 2.8 | 48 | 2 | 0.21 | 0.42 | 1.2 ± 1.1 |
| Er | 150 ± 180 // WD | WD | 11 ± 11 | 6.6 ±**4.4** | 6.0 ± 3.4 | 9.5 ± 200 | 8.1 ± 5.5 | 9.5 ± 7.7 | 120 | 5 | 0.79 | 1.3 | 2.8 ± 2.5 |
| Tm | 25 ± 20 // WD | WD | 1.4 ± 1.4 | 1.0 ± 0.8 | 0.80 ± 0.47 | 1.3 ± 260 | 1.2 ± 1.1 | 1.2 ± 1.0 | 24 | 1 | < MQL | 0.17 | 1.1 ± 0.7 |
| Yb | 210 ± 190 // WD | WD | 8.4 ± 8.5 | 5.7 ± 3.8 | 4.8 ± 2.7 | 7.9 ± 210 | 6.7 ± 4.5 | 7.2 ± 5.8 | 97 | 4 | 0.87 | 1.3 | 2.4 ± 2.1 |
| Lu | 28 ± 21 // WD | WD | 1.2 ± 1.2 | 0.99 ± 0.75 | 0.68 ± 0.40 | 1.2 ± 250 | 1.1 ± 1.0 | 1.0 ± 0.8 | 23 | 1 | 0.10 | 0.13 | 0.4 ± 0.3 |
| ∑REE | 8423 // WD | WD | 770 | 416 | 376 | 503 | 446 | 720 | 5356 | 201 | 56 | 104 | 388 |
| Y | 1500 ± 1600// WD | 190 ± 61 | 110 ± 110 | 70 ± 46 | 65 ± 43 | WD | 99 ± 54 | 110 ± 86 | 1307 | 46 | WD | WD | 30 ± 27 |
| Sc | WD // 390 ± 480 [INAA] | 22 ± 16 [INAA] | 57 ± 67 | 29 ± 31 | 33 ± 20 | WD | 24 ± 25 | 47 ± 37 | 1022 | 17 | WD | WD | 113 ± 73 |
| Sample (mg) | 250 | 250 | 100 | 100 | 100 | 50 | 100 | 100 | 100 | 100 | 250-350 | 250-350 | 500 |
| Digestion | $HNO_3$/HF/$H_3BO_3$ | $HNO_3$/HF/$H_3BO_3$ | $HNO_3$/$H_2O_2$ | $HNO_3$/$H_2O_2$ | $HNO_3$/$H_2O_2$ | $HNO_3$/$H_2O_2$ | $HNO_3$/$H_2O_2$ | $HNO_3$/$H_2O_2$ | $HNO_3$/$H_2O_2$ | $HNO_3$/$H_2O_2$ | $HNO_3$ | $HNO_3$ | $HNO_3$/$H_2O_2$ |
| Acid volume | 6+2 mL /+12 mL | 6 + 2 mL /+ 12 mL | 4 + 1 mL | 4 + 1 mL | 4 + 1 mL | 1 + 4 mL | 4 + 1 mL | 4 + 1 mL | 4 + 1 mL | 4 + 1 mL | WD | WD | 7 + 1 mL |
| S & P | No | No | No | No | No | No | No | No | No | No | No | No | |
| Measurement | ICP-MS // INAA | ICP-MS // INAA | ICP-Q-MS | ICP-Q-MS | ICP-Q-MS | ICP-MS | ICP-Q-MS | ICP-Q-MS | ICP-Q-MS | ICP-Q-MS | ICP-SFMS | ICP-SFMS | ICP-MS |
| Instrument | PerkinElmer Elan DRC II | PerkinElmer Elan DRC II | Agilent 7700x | Agilent 7700x | Agilent 7700x | Agilent 7500cx | Agilent 7700x | Agilent 7700x | Agilent 7700x | Agilent 7700x | Element 2, Thermo Scientific | Element 2, Thermo Scientific | iCAP Q, Thermo Scientific X series 2 |
| Reference | [60] | [60] | [62] | [62] | [62] | [101] | [62] | [62] | [62] | [62] | [56] | [56] | [61] |

Notes: *Summer truffle or Burgundy truffle; Whitish truffle or bianchetto truffle; Black truffle, or Périgord truffle or French black truffle; Asian black truffle or Chinese black truffle; Field parasol or Parasol mushroom; **C (caps)/W (whole) and number of pools/samples (and total number of fruiting bodies); WD (without data); S & P (separation and pre-concentration).

*leucomelaena*, *Bovista plumbea*, *Clathrus crispus*, *Endoptychum agaricoides*, *Endoptychum depressum*, *Entoloma caccabus*, *Entoloma lividoalbum*, *Geastrum triplex*, *Gyrophragmium dundalli*, *Inocybe haemacta*, *Laterna pusilla*, *Lepista nuda*, *Limacella guttata*, *Longula texensis*, *Mycena pura*, *Panaeolus retirugis*, *Phaeolepiota aurea*, *Phallus impudicus* - gelatinous layer, *Podaxis pistillaris*, *Protubera maracuja*, *Psilocybe subcubensis*, *Psilocybe cubensis*, *Psilocybe semilanceolata*, *Russula amoena*, *Russula velenovskyi*, *Sepultaria sumneriana*, *Suillus placidus*, *Tricholoma imbricatum*" purchased from markets in the Lake Geneva region and also obtained from the USA, the Netherlands, Germany, France, Switzerland, Thailand and Brazil [50]. The study investigated all REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in the previously mentioned species – *A. gaestrani*, *E. caccabus*, *G. triplex*, *I. haemacta*, *P. pistillaris* and *T. imbricatum*. The concentration levels for the sum of La, Ce, Nd, Gd, Sm, Er and Dy in *A. pes-caprae* ranged from 74 to 2420 μg $kg^{-1}$ dw (rounded values; some REE were not determined quantitatively because they were below the individual method limit of quantification (MQL) of 50 μg $kg^{-1}$ [50]. It is evident that the MQL of 50 μg $kg^{-1}$ dw for individual REE elements in biological materials such as mushrooms or in staple foods is much too high to allow for reliable measurement given the generally low concentrations. Where measured, the sum of Ce, La and Nd was around 50 μg $kg^{-1}$ dw in the samples of *A. bisporus* and *P. subcubensis*, around 100 μg $kg^{-1}$ dw in *E. agaricoides, P. maracuja* and *R. velenovskyi*, and from 160 μg $kg^{-1}$ dw in *A. silvicola,* up to 62,000 μg $kg^{-1}$ dw in *P. pistillaris*. The sum of 14 REE in six selected species of mushrooms was reported to range from 3800 to 74,600 μg $kg^{-1}$ dw [50, 51].

These concentrations appear to be uncharacteristically high and in a follow-up to the above study, Stijve et al. [53] explained that contamination of fungal material with soil particles had been a major source of error (and erroneously high values) in the determination of the lanthanides (and also for Al, Ca, Fe and other elements) in the earlier study. Both studies used a mass analyzer with a quadrupole mass filter for the measurement. The method used a sample aliquot of 0.75 g which was decomposed with 10 mL of $HNO_3$. Indium ($^{115}In$) was used as an internal standard in all samples, blanks, and standards [50, 53, 90].

Soil incorporated at 0.1 % in the dried fungal biomass was reported to contribute 70 mg $kg^{-1}$ of Al, 40 mg $kg^{-1}$ of Ca and 60 mg $kg^{-1}$ of Fe [53]. Karkocha and Młodecki (1965) [91] determined from their study that the amount of sand in commercial consignments of dried mushrooms (*A. bisporus*, *Boletus edulis*, *Cantharellus cibarius* and *Gyromitra esculenta*), ranged from 0.55 to 1.8%. Contamination of fungal materials with particles of sand or debris from the soil substrate will substantially influence the reported results, not only of REE but also of Al, Ca, Co, Cr, Fe, Li, Ni, Sr, Th, Ti or V, but not of Hg, Cd or Se elements [53, 92]. In other words, unusual concentrations of REE, Al, Ca, Co, Cr, Fe, Li, Ni, Sr, Th, Ti or V in mushrooms could arise from secondary contamination of a sample, if there is no other valid reason. Thus, data from dried fungal samples from herbaria, which are very difficult to clean, may not be entirely reliable [56]. Assuming that the methodology used is reliable and well validated, secondary contamination from soil dust will result in elevated concentrations of REE in fungal materials but will not affect the natural distribution reflected by the typical sawtooth pattern when concentrations are plotted.

## OVERVIEW OF ANALYTICAL METHODS OF REE DETERMINATION IN WILD MUSHROOMS

In general, the methods that are discussed here on trace REE determination in fungal matrices are restricted to results from laboratory-based studies and in particular, from studies that have not been the subject of subsequent comments regarding inconsistencies in presented data [64-67]. As evidenced (sections 1 and 2, Figures 1-3), the uptake of REE in wild mushrooms reflects the growing substrate. Some indications in a few publications on possible fractionation of some REE by fungi appear controversial and are not supported by other reports with well-validated data, suggesting that the analytics may contribute to the anomalies [69]. Concentration data obtained for many species of fungi from diverse environments does not support fractionation, for example, no anomalies regarding individual REE and Y composition against the European Shale Composite were observed [23]. However, a lower concentration of Dy, Ho, Er, Yb and Lu in the topsoil seemed to favour their slightly better bioconcentration than of the La, Ce, Pr, Nd, Pm, Sm, Eu, Gd and Tb in the fruiting bodies [23], but the relevance of this needs to be investigated. A study on biological behaviour of REE through omics approaches using a unicellular fungus *Saccharomyces cerevisiae* showed a higher toxicological risk of a group from Dy to Lu than from La to Tb (Ce not studied) [15]. It is known that Tb, Dy, Ho, Er, Tm, Yb and Lu, as heavier lanthanides (with increasing atomic number), have smaller atomic and ionic radii than the lighter La, Ce, Pr, Nd, Pm, Sm, Eu and Gd (lanthanides contraction effect), while none of the REE are considered nutritional for fungi, at least in typical Ca-rich soil environments. Many forest fungi are mutualistic feeders and their mycelial networks readily uptake inorganic compounds

from the soil solution while also actively searching for nutrients originating from rock and mineral bio-weathering, by excreting chelating agents [93]. The literature data reviewed in this work, showed that LREE (from La to Sm) comprise 87% (74 to 96%) of Σ13-14 REE (Tables 1-2).

The moisture normalized concentrations of REE in mushrooms are far lower than in the surrounding soil or substrate when compared on a dry weight basis or in other words, REE and Y are bio-excluded, i.e. the bioconcentration factor (BCF), is less than one. In the present context, BCF is the quotient of an element's concentration in the mushroom and in the substrate (on a dry weight basis) [8, 23, 61]. BCF data are considered as environmental characteristics that are helpful in assessing the reliability of analytical results for the full range of REE determination in biological matrices. Additionally, plotting of the data in log scale enables rapid visualisation of wide concentration ranges, from several hundred ppm down to about 0.1 ppb (Figs 1-6), and also allows the credibility of the data to be verified along with the identification of REE anomalies, e.g. by normalisation against a shale, chondrite, etc. [2, 8, 23].

Various spectrometry techniques with varying outcomes have been used in studies of REE in wild mushrooms and their growing substrates and bioconcentration potential. The so called "non-destructive" (of the sample matrix) techniques used in determinations were X-ray fluorescence analysis (XFR) and neutron activation analysis (instrumental – INAA and prompt gamma-ray – PGAA, PGNAA). Other techniques require acid digestion (decomposition – oxidization) to dissolve the solid biological matrix prior to analysis to obtain solubilised REE (dissolved minerals in the sample of < 0.2%) suitable for determination by inductively coupled plasma (ICP) mass spectrometry (MS). The literature describes a range of techniques and applications (with and without sample pre-treatment) used for REE determination in organic and inorganic matrices other than mushroom and includes laser ablation-ICP coupled with mass spectrometry (LA-ICP-MS) [2, 40, 82]. Similarly, isotope dilution-thermal ionization mass spectrometry (ID-TIMS) is also a recent technique for sensitive REE analysis, but it is not used for determining mono-isotopic REE (Pr, Tb, Ho, and Tm).

*XRF*

XRF (secondary emission) spectrometry is generally applied to the determination of the elemental composition of materials and is "applicable to the concentration range of REEs from 100% down to absolute 0.01%" [5]. As mentioned, XRF is non-destructive of the sample matrix, but the disadvantages of using this technique in REE analysis are the possibility of high error and inadequate MQLs which range from 1 to 10 mg $kg^{-1}$ [94]. When XRF was applied to the determination of Ce and Nd, elevated and atypical concentrations were reported in mushrooms [55, 57], e.g. Nd ranged at 2800 ± 650 to 7100 ± 490 μg $kg^{-1}$ dw in mature fruiting bodies of nine species of wild mushrooms [55]. In the later study by Campos et al. [57], Ce ranged from 6000 to 14,000 μg $kg^{-1}$ dw, and Nd, ranged from 1000 to 9000 μg $kg^{-1}$ dw in another set of eighteen (ectomycorrhizal, saprotrophic and epiphytic) species of mushrooms. However, as reported by Borovička et al. [56], the result of using XRF for this application was not satisfactory.

*INAA and PGAA*

Řanda and Kučera [52] used long-term INAA and provided concentration data on La and Sc (Ce, Sm and Eu were not detected above MQL) in a series of wild mushrooms collected in Bohemia. Lanthanum concentrations were in the range from 12 ± 3 μg $kg^{-1}$ dw in *Lycoperdon perlatum* to 320 ± 22 μg $kg^{-1}$ dw in *Agaricus xanthodermus* (total range < 7 to 840 μg $kg^{-1}$ dw for 115 samples). Scandium in these mushrooms was detected in the range from 2.5 ± 0.3 in *L. perlatum* to 76 ± 2 in *C. cibarius* (total range from 2 to 240 μg $kg^{-1}$ dw). Yttrium was determined in 3 samples but was only detected in *A. xanthodermus* at 0.0051 μg $kg^{-1}$ dw. More recently, Rossbach et al. (2019) [60] determined Eu by INAA, and Gd and Sm by prompt-gamma neutron activation analysis (PGAA) in a set of truffles (*T. aestivum*). These activation techniques have several drawbacks, the major ones being access to a nuclear reactor, high cost, length of time required for analysis and safety issues when working with radioactivity. The rapid developments in the use and application of ICP-MS for elemental analysis saw a decline in the use of INAA in REE determination [95].

*ICP-MS*

Inductively coupled plasma mass spectrometry (ICP-MS) with appropriate mass resolution (double focusing sector field mass spectrometry, which uses a static electric or magnetic sector, or a combination of the two as a mass analyzer) is a proven, established technique enabling the determination of REE in parallel with other metallic elements occurring in trace and ultratrace concentrations in biological materials [5, 90, 96, 97]. REE and Y determination can be strongly affected by polyatomic molecular interferences and careful corrections need to be applied "based on matrix-matched determinations of the yields of molecular ions" [98].

Reliable determination using this technique requires acid treatment of the solid biological matrix to provide

a digest which is internally standardised in order to control interferences. Typically, the sample digestion and purification process used for ICP-MS analysis involves oxidation of the dried fungal material using concentrated nitric acid (65%) either on its own or in combination with hydrogen peroxide ($H_2O_2$, 30%) or ultrapure or pro-analysis grade hydrofluoric acid (HF, 40% to 48%) in a pressurised polytetrafluoroethylene vessel with the aid of microwave energy. At low or ultralow REE concentrations, the digested solution obtained from this process can be further treated to exclude other metals "to remove the effects of potential isobaric interferences from molecular ions of non-REE and Y analytes", e.g. double charged ions (Ca, Ba, Sr) and particularly of Ba in Ba-rich matrices [2, 82, 98], and preconcentrated – if a direct spectrometric analysis for all REE and Y is not feasible [2, 8, 23, 99]. In order to control the recovery of REE after the matrix separation step, a Tm spike can be used [2] (Tm typically occurs at ultra-low concentration in biological samples) but this results in the loss of the original Tm concentration (see Fig. 5 A). REE were often determined in mushrooms with other metallic elements (in multi-element methods) and other internal standards were used to monitor for changes in MS operating conditions and sample-specific matrix effects, e.g. $^{115}$In [49, 63], $^{6}$Li, $^{45}$Sc, $^{115}$In and $^{159}$Tb [61] or $^{102}$Ru, $^{185}$Re and $^{209}$Bi [2, 8]. These extracts may be directly aspirated into the instrument plasma for ICP-MS measurement.

Other ICP-MS techniques with varying mass resolutions that have been successfully used for the analysis of some or all REE in cap mushrooms and truffles (genus *Tuber*), include double focusing sector field mass spectrometry (ICP-SFMS with higher mass resolution) [49, 56, 63] and quadrupole mass spectrometry (ICP-QMS; mass resolution can vary depending on the age and type of instrument) [2, 8, 23, 53, 54, 59, 62, 68, 100]. ICP-MS methodologies used in the studies of REE in wild edible mushrooms and associated outcomes are discussed below in more detail. Other studies that commonly use ICP-OES (ICP coupled with optical emission spectroscopy) for the determination of multiple elements including REE in forest mushrooms have been discussed, but the occurrence patterns and elemental ratios obtained for REE do not follow the normal distribution as predicted by the O-H order [after 48, 64-67, 69].

One of the early studies of 14 REE in mushrooms used SFMS [49] (Figure 3, Table 1). The determinations were carried out by direct elementary measurements of acid oxidized solutions without any pre-treatment. The high mass resolution achieved by SFMS analysis helps to achieve "high sensitivity for ultratrace levels of elements, the simultaneous measurement capabilities of multiple isotopes for precise isotope ratio measurements and the high-resolution capabilities to resolve spectral interferences" [102].

Apart from elimination/reduction of spectral interferences, the higher resolution of up to 10,000 res. [116, 102] provides low instrumental detection and quantification limits which results in more sensitive measurement ("the limits of detection are one to two orders of magnitude lower") compared to QMS without preconcentration [5, 96, 102]. SFMS was also used in later studies on trace and ultra-trace multi-elemental analysis including REE in the fruiting bodies of terrestrial (epigeic) and subterranean (hypogeic) fungi, i.e. truffles (Figures 3 and 4; Tables 1 and 2) [56, 62, 63].

The early studies of REE in mushrooms using SFMS showed low levels, i.e. Σ13/14 REE occurred at a concentration of 32 μg kg$^{-1}$ dw in *S. luteus* (caps), 82 μg kg$^{-1}$ dw in *Tricholoma equestre* (previous name *T. flavovirens*; caps), 114 μg kg$^{-1}$ dw in *Suillus bovinus* (caps), 140 μg kg$^{-1}$ dw in *B. edulis* (caps), 160 μg kg$^{-1}$ dw in *L. amethistina* (whole fruiting bodies) and 363 μg kg$^{-1}$ dw *Armillariella mellea* (caps) [49]. Borovička et al. [56] determined Σ14 REE at median concentrations of 103 μg kg$^{-1}$ dw of ectomycorrhizal, and 57 μg kg$^{-1}$ dw of saprobic, mushrooms, which agreed well with results from the earlier study of Σ13/14 REE which ranged from 32 μg kg$^{-1}$ dw to 363 μg kg$^{-1}$ dw [49]. The SFMS determination of heavy REE such as Tb, Dy, Ho, Er, Tm, Yb and Lu which can occur in mushrooms at concentrations below 1 μg kg$^{-1}$ dw (< 0.1 μg kg$^{-1}$ fresh weight) can be challenging (Table 1).

*ICP-QMS*

Low resolution mass spectrometers (e.g., ICP-QMS with collision and reaction cells, CRCs) are commonly used in the spectroscopic determination of REE in mushrooms. As far as currently reported, a triple quadrupole ICP-MS (ICP-QQQ) has not been used to study REE in fungi. The mass resolution of the ICP-QMS systems that have been used in mushrooms research is limited in comparison to SFMS and is related to the number of serial quadrupoles used (usually two quadrupoles – the main analyser and a dynamic collision cell in tandem, ICP-MS/MS) to reach the required resolution. Although considered as a lower resolution MS, QMS can be a powerful and reliable tool for the determination of REE in biological materials provided that the additional stages of analyte separation from interfering background and pre-concentration are carried out before instrumental analysis.

Thus, direct aspiration of acid oxidized (thermally digested) solid sample digests (without further treatment) into the plasma of the ICP-QMS in low-resolution mode is not suitable for determination of

REE in mushrooms. On the other hand, analytical procedures in which acid digests were further purified to exclude interfering macroelements and pre-concentrated before ICP-QMS measurement provided reliable data on REE in mushrooms and their soil substrates [2, 8, 23]. Separation from the interfering background in low resolution mode is also required for the precise determination of ultra-low concentrations of REE in inorganic materials, e.g. iron-rich monominerals, e.g. Fe-olivine and meteorites, using high resolution ICP-MS, was achieved after effective iron removal (by around 99%) following chemical purification by polyurethane foam [99]. There are a number of other independent studies utilizing various ICP-QMS instruments for the determination of REE. These have used direct aspiration of acid digested fungal matrices into the argon plasma with appropriate AC/AQ protocols [51, 53, 59, 61, 62, 68, 100], and some results from these studies are plotted and presented in Figure 4.

A recent study on REE in edible and inedible mushrooms and their topsoil and plant (tree) substrates also used aspiration of sample digests directly into the ICP-MS – PlasmaQuant MS Q with integrated Collision Reaction Cell (iCRC) [103]. The soil mushrooms that were investigated were: *Agaricus arvensis*, *Calvatia gigantea*, *Chlorophyllum rhacodes* (inedible), *Lyophyllum fumosum*, *Paxillus involutus* and *T. equestre*, and the wood growing mushrooms were: *Auricularia auricula-judae*, *Cerioporus squamosus*, *Flammulina velutipes*, *Fomitopsis betulina*, *Ganoderma applanatum*, *Ganoderma resinaceum*, *Laetiporus sulphureus*, *Pholiota aurivella*, *Pleurotus ostreatus* and *Sparassis crispa*. The study, reported that "detection limits" were "at the level of 1 to 10 µg $kg^{-1}$ dw for all elements determined (3 times standard deviation of blank analysis (n=10))" [103]. The reported mushroom concentrations of Ce, Nd, Pr, Er and Tm (no data was reported for La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu) did not follow the natural distribution pattern of REE (the sawtooth or zigzag pattern predicted by the O-H order). Additionally, the absolute concentrations of particularly, Er and Tm but also of Ce, Nd and

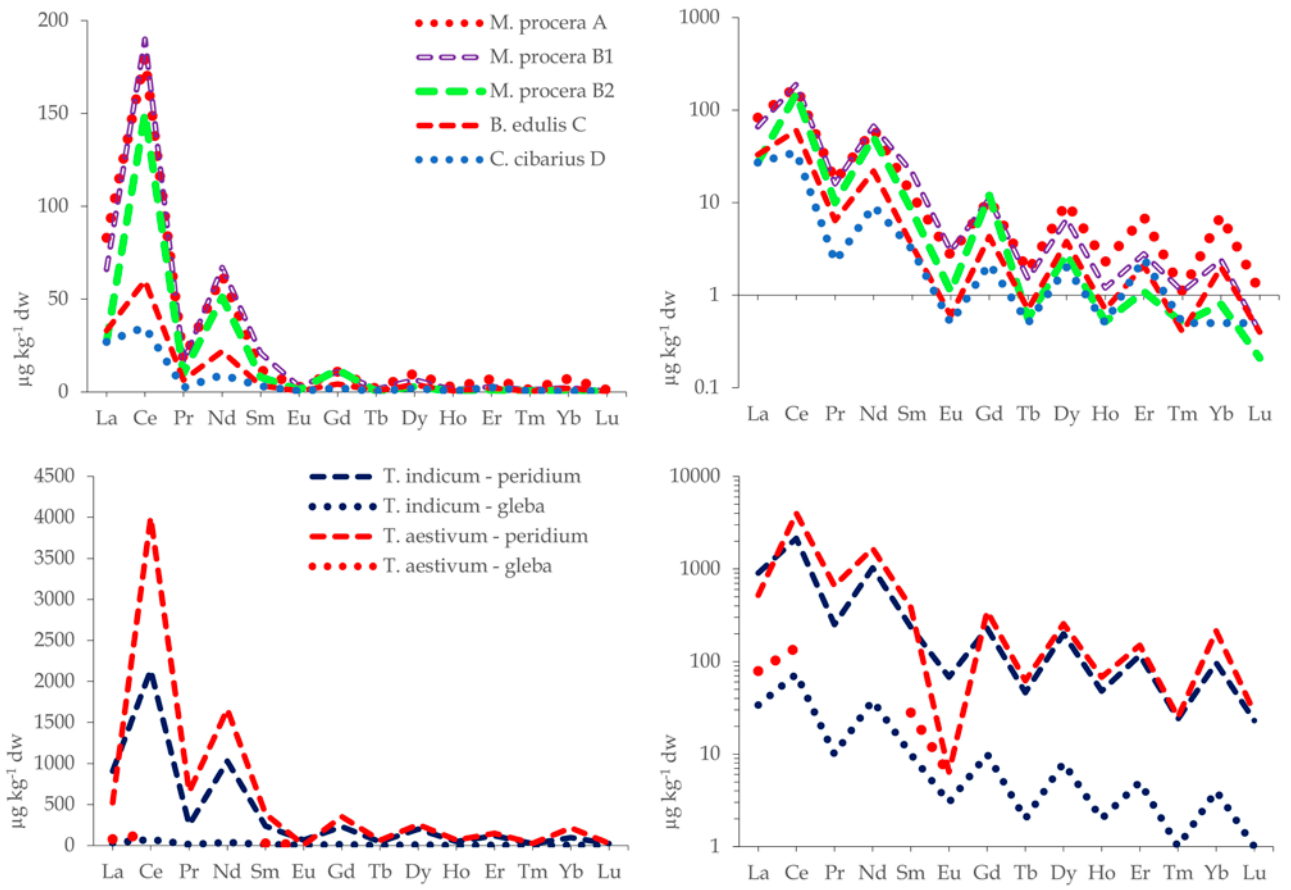


Figure 4. Normal and logarithmic scale distribution patterns of REE in several species of mushrooms (caps of *Macrolepiota procera*, *B. edulis* and a whole *C. cibarius*) as determined by aspiration of sample digests directly into the argon plasma of a quadrupole mass analyzer (upper plots) and in the peridium and gleba of the truffles, *T. indicum* (by sector field mass spectrometer) and *T. aestivum* (by quadrupole mass analyzer; Eu by neutron activation) (bottom plots), after [59, 60-62, 67, 100].

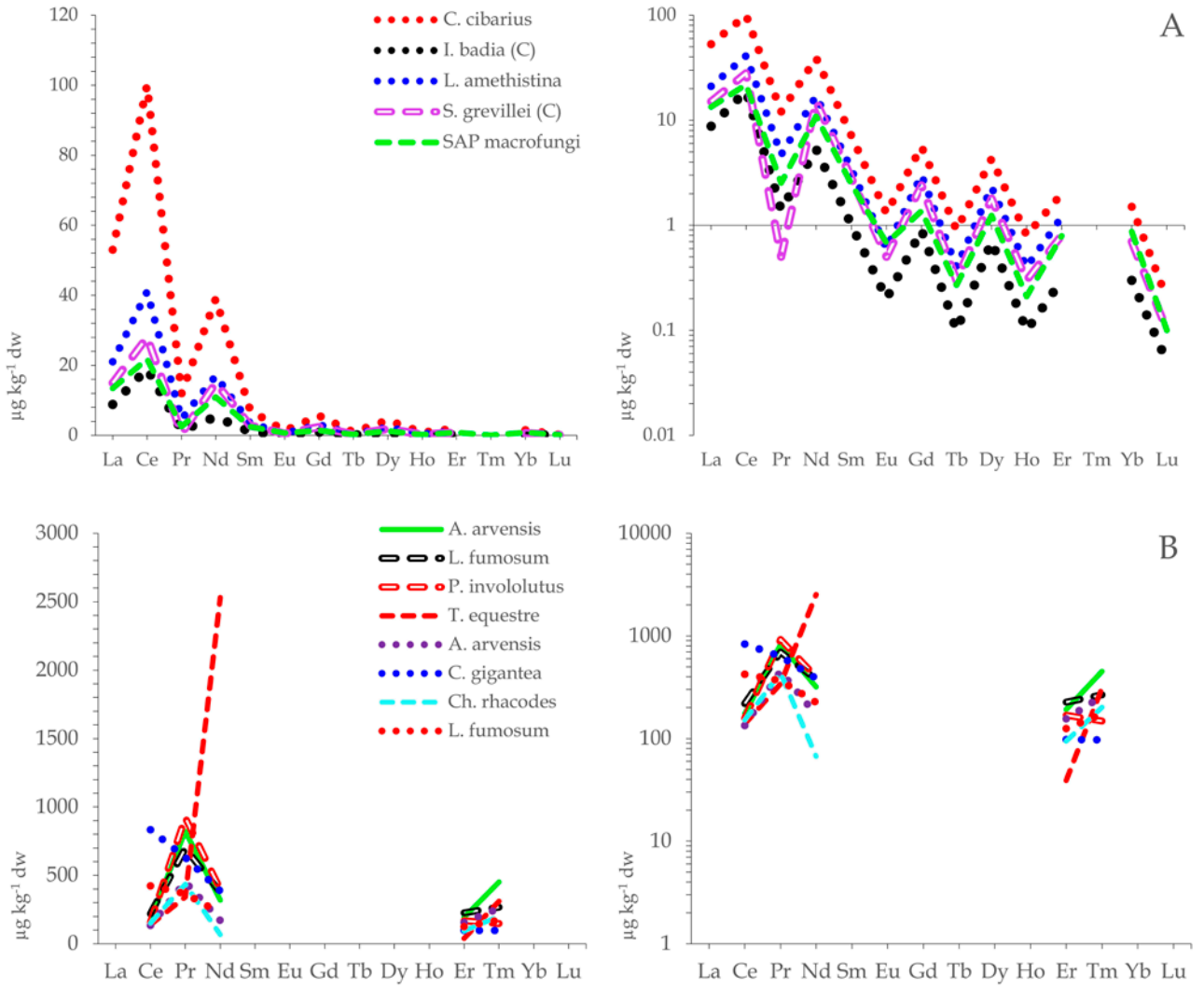


Figure 5. Normal and logarithmic scale distribution patterns of REE – natural concentrations (µg kg$^{-1}$ dw) in mushrooms of *C. cibarius*, *Imleria badia*, *Laccaria amethistina* and *Suillus grevillei*, determined by quadrupole mass analyzer after separation and pre-concentration on ion exchange resin [23], in a collection of saprotrophic species by sector field mass spectrometer [56] (upper plots A), and in some species of mushrooms (lower plots B), adapted – cited from [64].

Pr appeared to be highly elevated relative to other reported data (data for Ce, Nd, Pr, Er and Tm are plotted in the lower half of Figure 5) [65].

*ICP-OES*

ICP-OES has some basic drawbacks (potential spectral interference and relatively poorer sensitivity) which results in insufficient instrumental and method detection and quantification limits when used for the determination of metallic elements in biological matrices [104]. This can be seen at macro-, micro- and ultra-trace concentration levels, particularly when sample introduction is by direct aspiration of a mineralized sample solution into the plasma [104]. It also applies to the determination of REE which typically occur in wild mushrooms at concentrations of up to a few tens of µg per kg dw as in the case of Ce and down to sub-µg per kg dw in the case of the Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu (Tables 1 and 2). Apart from the spectral interference of ions from the biological sample matrix [5], the resulting REE emission spectra can also be very complex [105]. Ce, Pr, Nd which have relatively higher occurrence in mushrooms, have the most complex emission spectra while the heaviest REE (Y, La, Eu, Gd, Yb, Lu) have relatively simple spectra and also the lowest (best) detection limits [5]. However, the heavy REE occur at ultra-low concentrations which are beyond the range of ICP-OES for direct measurement. Nevertheless, there have been several reported studies of REE (a few or all 14 elements) in wild mushrooms, that have used direct aspiration of nitric acid digests into the plasma by ICP-OES [58] as discussed elsewhere [48, 64-69].

As is evident from this section on analysis techniques, a number of measurement techniques have been used for the analysis of REE in fungal matrices. The accuracy and sensitivity of the measurement process will continue to improve with more information and experience and particularly with the introduction

Table 3. Summary of analytical techniques that have been used to determine REE in mushrooms

| REE analysis technique (Abbr.) | Advantages | Disadvantages | Possible application (REE) |
|---|---|---|---|
| X-ray fluorescence (XRF) | Non-destructive of sample | Poor sensitivity, possible errors from inadequate selectivity | Screening mineral content or highly contaminated soil |
| Instrumental neutron activation analysis (INAA) prompt-gamma neutron activation analysis (PGAA) | Non-destructive of sample | Requires access to nuclear reactor, expensive, safety issues, long duration of analysis | Screening environmental matrices or for analysis at high concentrations |
| Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) | Relatively inexpensive and laboratory bench-top sized instrument | Inadequate sensitivity and selectivity, particularly when used without additional digest purification | Could be used for initial screening, but confirmation is advised. Direct sample aspiration is not advised for fungal material analysis |
| Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) | Relatively inexpensive and laboratory bench-top sized instrument | Sensitivity may not be enough for low concentrations, stringent sample purification required to avoid interferences | Can be used for biota/fungi if levels are not too low |
| Inductively Coupled Plasma – Sector Field Mass Spectrometry (ICP-SFMS) | Good sensitivity and selectivity | Expensive, requires adequate space and cooling | Variety of REE analyses possible, including measurement of low concentrations in fungi |
| Inductively Coupled Plasma – Quadrupole Mass Spectrometry (ICP-QMS) | Adequate sensitivity and selectivity (depending on quadrupole type) | Depending on the achievable selectivity, may require stringent clean-up for biota analysis | Variety of REE analyses possible, measurement of low concentrations may require good digest purification and preconcentration |

of newer instrumentation. The techniques used thus far have been summarised in Table 3 above.

## RELIABILITY OF ANALYTICAL DATA ON REE IN WILD MUSHROOMS

The recent interest in the potential for increasing environmental pollution by REE has led to a number of studies on the occurrence of these elements in environmental and food matrices. As mentioned, REE in foodstuffs are relatively difficult to analyse compared to other elements, particularly because of the low concentrations and also because of the contribution of the matrix to interference during determination. The analytical methodology used for determination should give careful consideration to sample pre-treatment (a key factor that affects the determination of REE in biological materials), processing/purification techniques and the use of appropriate instrumentation, in order to avoid unreliable data. Other considerations that are specific to mushrooms are the potential for cross-contamination from substrate particles that can adhere strongly to the sample. The use of certified reference materials (CRMs) and independent validation by participation in interlaboratory studies (or performance testing) will also help to avoid unreliable data. Where occurrence data is reported, in addition to samples processing and instrumentation, detailed metrological parameters such as linearity, measuring range, instrumental limit of detection (LOD) and quantification (LOQ), method limit of detection (MDL) and quantification (MQL), repeatability or intermediate precision, and results of control materials/certified reference materials, should also be included.

Some authors reported multi-element data measured by ICP-OES, including the concentrations of 13 REE (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in mushrooms that were referred to as "above-ground species" and "wood-growing species". The reported summed concentrations (Σ13 REE, Eu was not determined) in the "above-ground species" were: 1070 μg $kg^{-1}$ dry weight (dw) in *C. cibarius* (yellow chanterelle), 870 μg $kg^{-1}$ dw in *L. amethistina*, 730 μg $kg^{-1}$ dw in *Leccinum scabrum*, 980 μg $kg^{-1}$ dw in *Lepista gilva*, 860 μg $kg^{-1}$ dw in *L. fumosum*, 600 μg $kg^{-1}$ dw in *M. procera*, 860 μg $kg^{-1}$ dw *P. involutus*, 750 μg $kg^{-1}$ dw in *S. bovinus*, 5030 μg $kg^{-1}$ dw in

*S. luteus* and 2180 μg $kg^{-1}$ dw in *T. equestre*. Σ13 REE in the "wood-growing species" were: 1440 μg $kg^{-1}$ dw in *Armillaria mellea*, 1930 μg $kg^{-1}$ dw in *A. auricula-judae*, 960 μg $kg^{-1}$ dw in *F. velutipes*, 4190 μg $kg^{-1}$ dw in *G. applanatum*, 940 μg $kg^{-1}$ dw in *Grifola frondosa*, 1660 μg $kg^{-1}$ dw in *L. sulphureus*, 590 μg $kg^{-1}$ dw in *Piptoporus betulinus*, 700 μg $kg^{-1}$ dw in *P. ostreatus*, 2430 μg $kg^{-1}$ dw in *Pleurotus* spp. and 1610 μg $kg^{-1}$ dw in *Polyporus squamosus* [58]. These Σ13 REE values, which ranged from 590 μg $kg^{-1}$ dw to 5030 μg $kg^{-1}$ dw, were more than an order of magnitude above normal occurrence values in comparison to previously reported data (Tables 1 and 2) from studies using SFMS [49, 56] and additionally, individual REE data differed from those seen in normal distribution patterns. The authors reported that the mushrooms were collected in 2014 from a site located "up to 40 m from a heavily trafficked road" in a mixed forest of acacia, acer, pine and oak. The composites used for analysis were made using three to eleven samples per species, which were cleaned "from the rest of underlying substrate to prevent contamination with REE…" using distilled water [58]. Thus, primary contamination of the mushrooms samples (including the "wood-grown species") with soil debris or sand may have been avoided. The stated aim of the study: "was to compare the ability of 20 wild mushroom species growing near a busy trunk road to accumulate particular elements of PGE (platinum elements) and REE (including Y) groups, and that this is so far the broadest study on the occurrence of these elements in mushrooms" [58].

A valid hypothesis to explain the higher reported REE levels could consider whether "a busy trunk road" was potentially a source of the highly elevated fungal concentrations of Er and also of Σ13 REE. However, the study did not consider this hypothesis [58]. Ce, La, Nd and Gd are used in oil refineries, and some REE are used in electric automobiles but these vehicles were rare or absent in Poland in the year that the samples were collected. An earlier study [106], reported that the enrichment of REE in surface soil samples in public parks of São Paulo city could not be clearly attributed to automobile traffic, instead the high background concentrations were associated with the natural composition of the soils.

The occurrence and distribution of REE in soils is mainly determined by the mineral composition of parent rocks, with primary and secondary sources being minerals of acid, siliceous and sedimentary rocks [4]. REE have very similar chemical and physical properties and behave collectively as a group in the biotic environment, including in their uptake and distribution characteristics in vegetation and animals, food web relations and metabolism [1, 4, 37, 81].

A graphical representation of the REE distribution patterns in mushrooms plotted in normal or logarithmic scale (both, normalized or not, to any reference sample such as shale, chondrite or soil) is useful for a visual identification of any possible natural anomaly and can also reveal if the data is biased (not credible). The REE distribution pattern drawn for a randomly selected species of mushrooms from the study by [58] is presented in Figure 6. This distribution pattern is very different from that seen for mushrooms and other environmental materials from other studies (as referenced above) and does not follow the expected pattern arising from the O-H order (Figures 3 and 4). Instead, it shows an unprecedented anomaly of erbium (Er) concentrations but also of other REE (Figures 5 and 6).

Another approach to evaluating elevated REE concentrations would be through examination of the bioconcentration factors for REE in wild mushrooms. These data are scarce but recently Zocher et al. [8] provided data on REE in the *S. luteus* fungus and in forest top-soils. BCF values of 0.0001 for Ce and 0.0002 for Er were calculated from the concentration data on *S. luteus* and the underlying soil substrate. These very low values suggest almost total bio-exclusion of Ce and Er (and most likely of the other REE as well because they show similar behaviour) by *S. luteus*. If these BCF values are applied to the mean concentrations of Ce and Er (600 μg $kg^{-1}$ dw, and 3500 μg $kg^{-1}$ dw respectively) in *S. luteus* as reported by [58], it is possible to estimate the concentrations in the soils in which these mushrooms were collected. So, the above mean concentrations of Ce and Er divided by their respective BCF values [8] would yield dried soil concentrations of 6.0 g $kg^{-1}$ and 17.5 g $kg^{-1}$, respectively. These concentrations are unlikely in roadside topsoil or other soils as they are far higher than REE concentrations in the most abundant ore deposits, e.g. ~66 mg $kg^{-1}$ [107]. Similarly, the maximum ΣREE value of 5030 μg $kg^{-1}$ dw in *G. applanatum* reported by [58], would require extremely high and therefore unlikely concentrations in the tree wood substrate in which this fungus grows.

An example of a genuine and explained anomaly of REE occurrence is that of Gadolinium (Gd) which can pollute surface waters (possibly also sediments), through its application in magnetic resonance imaging [24] as described in section 1. After use, Gd is excreted from the body via urine, survives waste water treatment, and contaminates riverine waters downstream of the source. This was reported as a high positive anomaly of Gd with slightly negative Er (compared to typical occurrence) in a study of riverine waters downstream from a municipal sewage treatment plant [24]. In another recent example, *Boletus edulis* sampled from an abandoned military area overgrown with forest showed higher REE levels and a more perturbed occurrence pattern than mushrooms

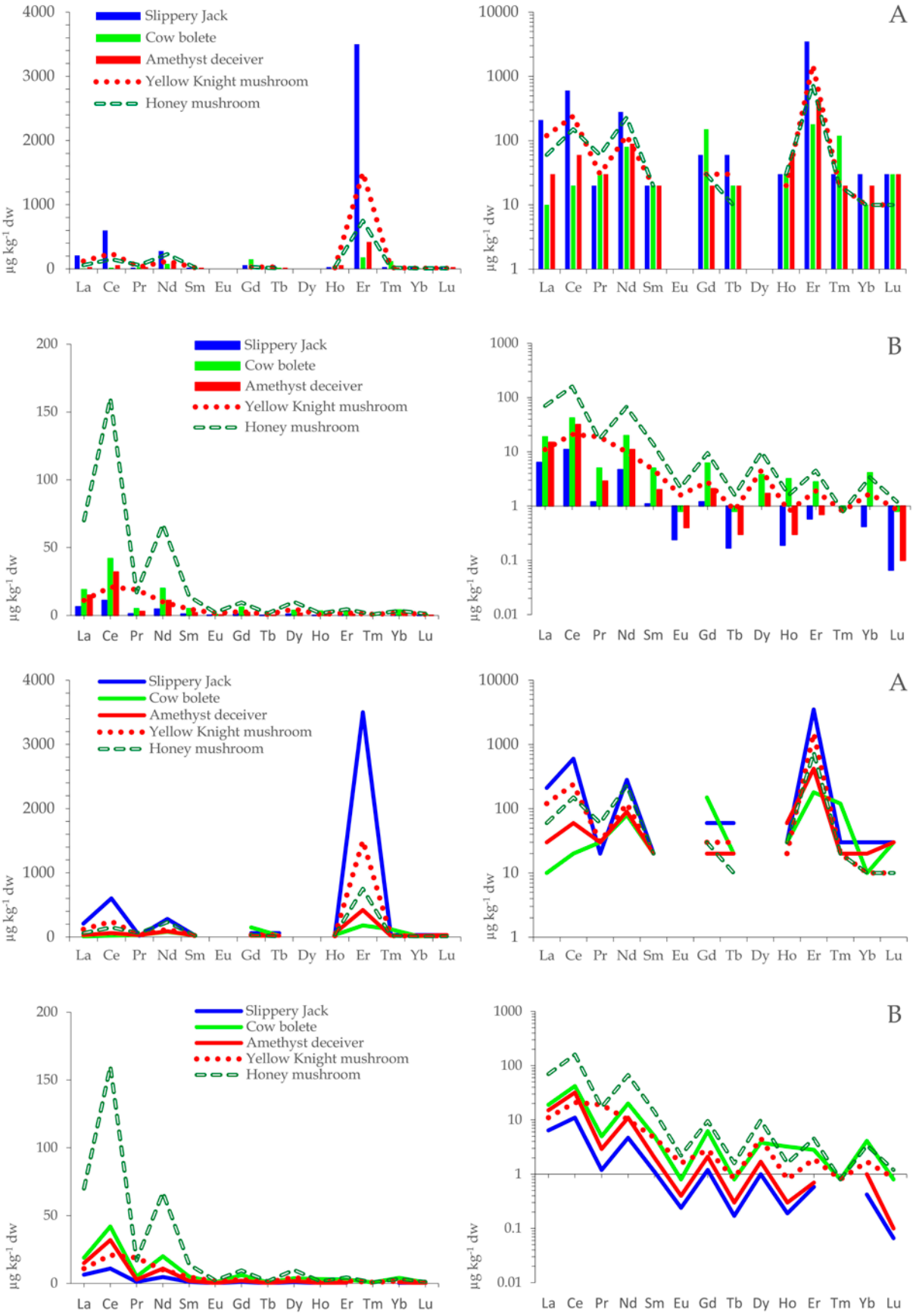


Figure 6. Normal and logarithmic scale distribution patterns of REE – natural concentrations (µg kg$^{-1}$ dw) in the mushrooms *Suillus luteus* – Slippery Jack, *Suillus bovinus* – Cow bolete, *Laccaria amethistina* – Amethyst deceiver, *T. equestre* – Yellow Knight mushroom and *Armillariella mellea* – Honey mushroom – plots labelled A (after [58]) and in the same species by other authors – plots labelled B (after [8, 23, 49], respectively).

from other forested sites, probably as a result of earlier military activities, but this was not studied [100]. So, there is no wider evidence so far that "anthropogenic activities" disrupt the balances and relationships of lanthanides in natural forest soil and their uptake by macromycetes.

Thus, the disposition of lanthanides in most natural matrices including soils, mushroom, other biota, etc. follows a pre-defined pattern – one that was predicted by the Oddo-Harkins rule and which is reflected in the pre-historic bedrock. This does not preclude the possibility of anomalies in some of these patterns that can arise from diverse anthropogenic sources but the appearance of these should be investigated and rationalised if the sources are identified or reasonably hypothesised when the supporting information is not available.

## DISCUSSION

*Analytical chemistry considerations*

The determination of REE in biological matrices and particularly mushrooms has developed with the concurrent exploitation and application of these elements in high-technology applications. Many of the studies on REE in fungal materials were initiated by the potential of REE to become more prominent environmental and food contaminants in line with their increasing production and applications. It is evident from Tables 1 and 2 that reliable REE occurrence data on mushrooms is scarce. Part of the reason for this is related to the higher threshold of analytical accessibility, particularly in achieving the relatively low method detection limits that are essential for reliable determination in biological matrices. It is clear from the earlier sections that the key requirements for providing reliable and credible data on REE in mushrooms are:

- Avoiding cross-contamination from the substrate - which requires stringent cleaning of the freshly picked mushrooms to remove substrate particles. Lack of care at this stage would result in erroneously higher concentrations originating from the residual substrate.
- Using effective sample digestion and digest purification methodology – which should allow thorough removal of the sample matrix that could lead to spectral and non-spectral interferences and provide preconcentration of the digest to allow adequate MQLs to be achieved during measurement (e.g. at least 0.1 μg $kg^{-1}$ dw or better). The inclusion of matrix matching, and standard addition techniques could also be considered to correct for matrix effects and improve reliability.
- Using instrumental techniques that are sensitive enough to achieve the required MQLs while being simultaneously capable of sufficient resolution to exclude interferences (e.g. the use of ICP-SFMS at high resolution (≥ 10,000) or the newer triple-quadrupole mass spectrometers – the enhanced ion filtering achieved by the additional quadrupole can effectively exclude both plasma-based ions and prevent unwanted reactions with residual matrix ions.
- Incorporating effective QA/QC tools – such as the use of procedural blanks, internal standards (e.g. $^{115}In$, $^{45}Sc$, $^{115}In$, $^{159}Tb$ etc.), recovery spike(s) and the use of reference materials such as BCR-668 (mussel tissue; REE, Th and U), NCS ZC73018 (citrus leaves; multielement), NCS ZC73022 (scallop; multielement) or REE-1 (an ore; REE, Zr and Nb). These measures would allow validation of the reported data.

At the end of the 20th century some laboratories participated in an interlaboratory study on REE determination which aimed to certify reference materials such as tuna muscle, mussel tissue, aquatic plants and estuarine sediment samples [108]. Since then, other CRMs have been developed which can be helpful to maintain AQ/AC standard in REE determination [2, 8].

The use of lower resolution ICP-MS instrumentation is feasible for the analysis of REE providing the purification procedure used prior to measurement are effective in removing non-spectral interferences (due to matrix effects and instrument drift) – through discussed internal standardisation, standard additions or isotope dilution, and in removing spectral interferences [98]. Direct measurement of biological sample digests is ill-advised with these systems, particularly for some fungal digests which are rich in mono- and divalent metallic ions (e.g. median concentrations of K and Rb in *B. edulis* and *C. cibarius* can range from 20,000-38,000 and 39,000-60,000 mg $kg^{-1}$ dw, respectively with rubidium occurring at 190 and 590-1600 mg $kg^{-1}$ dw respectively [109, 110]. Although SFMS and the newer triple-quadrupole mass spectrometers (TQMS; with two quadrupole mass analysers in series and with a non-mass-resolving quadrupole – collision cell in between) allow exclusion of isobaric and polyatomic spectral interferences that arise from these high concentration co-extractives, and overcome spectral interferences caused by REE themselves (REE oxides and hydroxides interfere with other REE) and chloride species, reliable measurement with lower resolution instruments would require additional purification and concentration stages to minimise or remove these interferences [97, 105]. However, despite the better sensitivity afforded by SFMS/TQMS, care should be taken when analysing low concentration fungal materials as some spectral interferences (e.g., from the formation of oxides,

hydroxides and doubly charged ions) may still persist. Resolving some of these at higher resolution can incur the cost of a consequential loss in sensitivity and additionally, requires frequent recalibration of the mass axis.

*Peer review as a control on reliability of data*

Good peer-review of REE data is critical in order to evaluate whether the reported concentrations in mushrooms and other biological materials are credible or have been compromised during the determination process. Review of fresh data is considerably aided by the adherence of REE occurrence in most biotic and abiotic matrices to the very characteristic pattern predicted by the O-H order as visualised in Figures 2-5 in earlier sections. This distinctive pattern derives from the predicted elemental occurrence and the fact that individual REE show a collective behavioural similarity in biotic and abiotic environments arising from their similar physical and chemical characteristics. The occurrence pattern is thus maintained from the parent bedrock and mineral sources through environmental processes like soil formation [81], reflected in topsoil concentrations and through the process of uptake by plants and mushrooms [8, 23]. The normal (natural) or logarithmic plot of these occurrences provides a simple but effective evaluation of data, particularly when concentrations for all or most of the REE are reported. The persistence of this pattern (Figures 1, 3 and 4) across the data reported listed in Tables 1 and 2, notwithstanding the differences in species, location, biogeochemical substrate influences and pollution profiles, demonstrates the validity of this assessment for the full set of lanthanides. When data is partial, i.e. only some of the REE are reported, then evaluation of the individual concentration ratios (e.g. La/Sm, Ce/Nd, Ce/Sm and La/Tm) also provides a good indication of the reliability of the determination [47, 65]. Anomalous concentrations are possible as seen in the case of Gd in waste waters and beverages [24, 25] and the increasing use of individual REE in specific applications could result in data that does not follow the predicted patterns, but these anomalies should be identified and explained, at least through hypothesis. As reviewed by Migaszewski and Gałuszka, an example of such an anomaly is seen in the data on La, Ce and Sm in < 1.1 μm particulate matter during studies on local pollution of ambient air [1].

The potential of REE to become more prominent food contaminants and pose a health risk is inherent in the rapidly increasing production and utilisation of these chemicals. It is therefore important that occurrences in environmental and food matrices are monitored for any increasing trends, but this requires a very reliable baseline for evaluation. It is clear from published data [8, 23, 56, 76, 111, 112, 113] and from Tables 1 and 2, that such a resource is currently very sparsely populated, and more credible data is essential. Most reported concentrations of individual REE in wild mushrooms and other terrestrial vegetation are low, typically ranging from sub-ppm to low or sub-ppb levels (Tables 1 and 2 [114]), although seaweed species may show higher values [115]. These lower concentration levels are expected not only because of the relatively lower amounts of REE that are naturally available, but crucially, also because plants and particularly mushrooms are known to bio-exclude REE [23, 61, 76]. Highly elevated REE concentrations in mushrooms are therefore unlikely even if the data demonstrate the predicted sawtooth pattern, because in this case, cross-contamination by the substrate is a possibility [53]. Higher individual concentrations are seen for the light REE such as La, Ce, Pr and Nd, and also Sc and Y, which geologically are more naturally abundant.

The credibility of data is essential, particularly in reports on elevated individual REE concentrations in wild mushrooms which may suggest a rapid rise in environmental pollution. This is of course a plausible scenario given the increase in production and use (and also disposal of REE containing products), but data that suggests such elevations above the background should be backed by good quality protocols and critical peer review. It is also very clear that considerably more data on REE occurrence in wild (and cultivated) mushrooms is required to indicate any trend to higher levels in this important food and indeed, the environment.

## CONCLUSIONS

REE have no currently known biological or nutritional role but they have the potential to become contaminants of emerging concern because of their rapidly increasing applications in consumer goods and other products. An evaluation of this status, particularly any upward trend in environmental and food levels requires reliable occurrence data. Mushrooms, a popular food, absorb and accumulate these elements from their growing substrates and could provide an early indication of any such trend.

In the absence of any external sources, REE occur in a characteristic pattern in wild mushrooms which reflects the composition of their substrates without any fractionation of individual elements. Any anomalies to this pattern that cannot be attributed (even hypothetically) to proximate sources are like to arise from inadequacies in analytical methodologies or analytical instrumentation. This is due to the very low concentration level (< 1 μg $kg^{-1}$ dry weight) of certain REE (Eu, Tb, Ho, Er, Tm, Yb, Lu) in fungi

and the additional challenge of overcoming matrix and instrumental interferences.

Reliable data can be obtained by avoiding cross-contamination, using effective digest purification methodology and sensitive measurement techniques that are capable of excluding spectral and other interferences. Confidence in the data can be enhanced through the use of rigorous QA/QC protocols and review of the REE occurrence patterns for any unexplained deviations from the natural distribution. Data from studies that met these requirements confirmed typically low concentrations of REE in mushrooms (0.07 μg $kg^{-1}$ of Lu in *Suillus luteus* to 940 μg $kg^{-1}$ of Ce in *Cantharellus minor*), confirming the bio-exclusion of REE and preserving the elemental Oddo-Harkins patterns of their growing substrates. However, the database is currently very small so further monitoring is essential in order to confirm the current findings and additionally, the widespread and increasing global use of REE does not preclude an increase in occurrence in the future.

**Disclosure conflict of interest**

*The authors declare that have no relevant affiliations or financial involvement with any organization or entity with a financial interest in or financial conflict with the subject matter or materials discussed in the manuscript.*

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