

Gadolinium of anthropogenic origin in food crops

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The study is focused on the monitoring of rare earth elements (REE) in food crops with particular interest paid to the evaluation of gadolinium of anthropogenic origin. Macroscopic fungi were used as they are culinary processed and being also a good indicator of environmental pollution. In total, 46 dried mushroom samples originating from the Czech Republic and Slovakia were analysed. When using microwave decomposition of samples and the elemental analysis of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb using inductively coupled plasma mass spectrometry (ICP-MS), the respective analytical procedure was optimised and validated. The study also included the calculation of the gadolinium anomaly in the processed samples, as well as the calculation of the amount of anthropogenic gadolinium. In the case of the gadolinium monitored, the minimum value found was $1.41 \mu\text{g kg}^{-1}$; the maximum being $361 \mu\text{g kg}^{-1}$, and the average $33.7 \mu\text{g kg}^{-1}$. The contribution of gadolinium of the anthropogenic origin ranged from 0.77 to 270 g kg^{-1} .

Keywords: Rare earth elements; Mushrooms; Gadolinium anomaly; ICP-MS

Introduction

Food is an essential part of human life. With it, a person supplies the body with the necessary substances serving as a source of energy for the growth and development of each individual.

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In addition to essential substances, food can also contain harmful items. There are countless ways in which food can be polluted starting with possible improper handling during cultivation, transport, or storage [1]. The most discussed chemical pollutants are heavy metals originating mainly from anthropogenic activity. After their entry into the environment, these elements are deposited mainly in the soil, where they settle and can negatively affect the growth and development of plants and animals [2]. In recent years, there has also been a growing interest in the environmental monitoring of rare earth elements (REE), due to the increasing demand for their industrial use. One of them is gadolinium predominantly used as a contrast agent in magnetic resonance imaging [3].

Gadolinium, along with other REE, is naturally present in the soil directly depending on the composition of the bedrock. Anthropogenic Gd enters into the environment as a result of human activity. This form is more mobile than the naturally occurring Gd. It originates from various sources, with the largest amount coming from magnetic resonance imaging. Another source is a group of automotive catalysts, where the concentration of Gd decreases with the increasing distance from the roads and highways. Part of such Gd can then pass through the outflow from the road to sewers and can cause an increase of Gd in the sewage sludge [4]. Gadolinium is also used as an additive in fertilizers together with other REE to stimulate crop growth [5–7]. On the contrary, higher concentrations may inhibit growth and disrupt Ca and Mg metabolism [8]. REE are also applied as feed additives to livestock. It has been reported that small amounts of REE in animal feed can increase body weight gain in cattle, pigs, chickens, fish, and rabbits, as well as production of milk in dairy cows and eggs in laying hens [9].

Anthropogenic Gd enters the environment mainly through the aquatic system, largely due to the use of Gd-chelate complexes as magnetic resonance contrast agents which are water-soluble and highly stable [10]. Such a Gd complex is not metabolized in the human body and is excreted unchanged by the kidneys with subsequent urinary excretion. Excretion first shows an initial rapid elimination phase (half-life of approximately 2 hours) followed by a slower release with a half-life of approximately 6 days [11]. However, there is also a study reporting on the detection of contrast agents in patients 39 days after undergoing magnetic resonance [12]. After being excreted from the body, the complex enters the waste system. Due to its high stability, it is removed in wastewater treatment plant maximally from 10 %, the unremoved residue then passes into surface waters and, eventually, to drinking water. Due to the presence of these complexes in the aquatic environment, contrast agents can pass into the aquatic biota, thus reaching the human food chain. In more populated industrialised areas (especially those with developed health care), a positive Gd anomaly is detected in the aquatic system or even in drinking water [13].

In geology, the term “anomaly” is used for deviations from normal values. As a result of the penetration of anthropogenic Gd into the environment, its concentration in water and soil increases compared to the natural level of

geological background and other REE. There are several ways to calculate the content of naturally occurring Gd. However, the most common procedure is data normalization according to the Post-Archean Australian Shale (PAAS) (1)

$$\text{Gd}_{\text{PAAS-geo}} = 0.33 \cdot \text{Sm}_{\text{PAAS}} + 0.67 \cdot \text{Tb}_{\text{PAAS}} \quad (1)$$

where $\text{Gd}_{\text{PAAS-geo}}$ is concentration of geogenic Gd normalised to PAAS, Sm_{PAAS} is concentration of Sm normalised to PAAS, and Tb_{PAAS} is concentration of Tb normalised to PAAS [14]. The gadolinium anomaly is then calculated using the relationship (2)

$$\text{Gd}_{\text{anom}} = \text{Gd}_{\text{PAAS-total}} / \text{Gd}_{\text{PAAS-geo}} \quad (2)$$

where (Gd_{geo} – concentration of geogenic Gd, Gd_{total} – total concentration of Gd, and Gd_{anom} – of Gd of anthropogenic origin). Bau and Dulski experienced this anomaly in 1996. Bau and Dulski experienced this anomaly in 1996. Since then, the gadolinium anomaly has been documented around the world and observed in many rivers, lakes, coastal waters, groundwater or even drinking water [15].

The determination of the individual REE can be complicated due to their similar physical and chemical properties, as well as by their usually very low concentrations in the environment. In the past, classical analytical methods such as gravimetry, spectrophotometry, or titrations, were used to determine REE in geological materials. However, these approaches were very time consuming, difficult to prepare and perform due to separation of other REE and necessity of preconcentration when being not sensitive enough [16]. Nowadays, with the availability of modern instrumentation, the measurement of trace concentrations has become a routine matter. Among instrumental methods currently available, inductively coupled plasma excitation optical emission spectrometry (ICP-OES), ICP-MS and X-ray fluorescence (XRF) are commonly used to determine REE in various types of materials. All these techniques are multi-elemental and capable to simultaneously detect multiple elements in a single analysis, offer high sensitivity, a wide linear dynamic range, and are easy to use [17]. Before analysis, ICP-OES needs to separate the individual REE because of the spectral interferences resulting from the closeness of the spectral lines of the individual REE. The respective LODs range from units to tens of $\mu\text{g L}^{-1}$. The most commonly used ICP-MS does not require separation and preconcentration of the elements. However, by including these steps, better detection limits can be achieved by several orders of magnitude [17,18].

Environmental pollution is naturally reflected in food quality. Mushrooms are an important bio-indicator as they are generally able to accumulate heavy metals more efficiently than vascular plants.

Edible mushrooms are used by humans as a low-caloric food or delicacy being typically a rich source of vitamins and minerals. Mushrooms are also used for their healing effects, having been shown to have a supportive effect on the function of the immune system. At the same time, mushrooms help to reduce the risk of cancer. In traditional Chinese medicine, they are used to treat colds and flu [19]. It is generally known that these living organisms are good metal absorbents. Different species of fungi have different abilities to accumulate heavy metals in fruiting bodies depending on the accumulation properties of the particular species and the concentration of elements of interest in the soil [20,21]. Fiket et al. (2017), have studied the content of REE in mushrooms. The level and distribution of REE in the soils, moss and fungi of the untouched temperate rainforest were monitored in order to characterize their environmental availability and mobility. It was found that the distribution of REE in fungi had been primarily influenced by the local pedological background. Higher levels of REE in fungi in the Prašnik area were attributed to the naturally occurring higher concentrations of REE in the soil. Positive Eu anomalies were detected and light REE prevailed over heavy REE in the soil. The intensity of REE accumulation was positively correlated with the organic content of the soil. The fungi showed differences in REE levels in different parts of the fruiting body. An increase in REE content was observed from the lower tubers to the pileus [22]. Siwulski et al. (2020) conducted a long-term study to monitor the REE content of mushrooms from 1974 to 2019. In total, over 21900 samples of fruiting bodies of four edible species of mushrooms were collected from 42 forest localities in Poland. A gradual increase in REE in the studied samples of fungi and related forest soil samples in the observed period and their strong correlation were observed. However, the measured concentrations during this period should not have affected the health of consumers [23].

The aim of this work was (i) to monitor the REE in crops intended for food purposes and (ii) to evaluate Gd of anthropogenic origin as Gd anomaly.

Materials and methods

Reagents and standards

Ultrapure water used throughout the analysis was prepared by using an Ultra Clear GP TWF UV UFTM (0.07 $\mu\text{S}/\text{cm}$ conductivity, Evoqua Water Technologies, Germany). Ultrapure nitric acid (65%) (Lach-Ner Neratovice, the Czech Republic) used for leaching laboratory dishes, decomposing fungal samples and stabilizing calibration standards was obtained by distillation in sub-boiling distillation apparatus BSB-939-IR (Berghof GmbH, Königsee, Germany). A multi-element calibration standard M008 containing $100 \pm 0.002 \text{ mg L}^{-1}$ Ce, Nd, La, Pr and $20 \pm 0.002 \text{ mg L}^{-1}$ Dy, Er, Eu, Gd, Ho, Lu, Sm, Tb, Tm, Y and Yb was used for the preparation of the calibration standards (Analytika s.r.o.

Prague, the Czech Republic). As an internal standard, In was used at a final concentration of $1 \mu\text{g L}^{-1}$. The concentrations of individual standards are summarized in Table 1.

Table 1 Concentrations of the calibration standards for ICP-MS analysis (in $\mu\text{g L}^{-1}$)

Standards	S1	S2	S3	S4	S5	S6	S7
A*	0.01	0.05	0.1	0.5	1	5	10
B*	0.002	0.01	0.02	0.1	0.2	1	2

A*: Y, Yb, Ce, La, Nd, Pr; **B***: Dy, Er, Eu, Gd, Ho, Lu, Sm, Tb, Tm

Samples

A total of 46 dried mushroom samples used in this study were processed, where 45 samples came from the Czech Republic and 1 from Slovakia. A number of 45 samples came from the individual collections and 1 sample was purchased in a common store. All the samples were dried in a laboratory oven at $50 \text{ }^\circ\text{C}$ for 24 hours and then homogenized manually using a mortar and a pestle. A portion of 0.35 g of each sample was decomposed in Speedwave XPERT microwave oven (Berghof GmbH, Germany). Complete decomposition was achieved in a mixture of 6 ml 32.5% HNO_3 + 1 ml 30% H_2O_2 when using decomposition program named “Plants” at a temperature of $220 \text{ }^\circ\text{C}$; detailed decomposition conditions are given in Table 2. The mineralised sample was filled up with ultrapure water to the final volume of 50 ml. For the ICP-MS analysis indium (In) was used as an internal standard. The volume of 4.9 ml sample was mixed with 0.1 ml of In solution at a concentration of $50 \mu\text{g L}^{-1}$ to achieve the final concentration of $1 \mu\text{g L}^{-1}$ In.

Table 2 Experimental conditions for mushroom samples decomposed in Speedwave XPERT microwave oven

Step	T [$^\circ\text{C}$]	p [bar]	Increase [min]	Holding [min]	P [%]
1	170	50	5	15	80
2	220	75	3	20	80
3	50	75	0	30	0
4	50	40	0	0	0
5	50	40	0	0	0

T – Temperature, p – Pressure, P – Performance

Instrumentation

Elemental analysis of REE was performed by ICP-MS in the mode of inductively coupled plasma orthogonal ion acceleration time of flight mass spectrometer with (oaTOF-ICP-MS) OptiMass 9500 (GBC Scientific Equipment Pty., Australia). The operating conditions for ICP-MS were as follows: plasma power, 1200 W; multiplier gain, 2770 V; plasma, auxiliary and carrier gas flow rates were 12, 0.55 and 0.91 L min⁻¹; 3 replicates, and 5s acquisition time. Because some of REE occur naturally in multiple isotopes, one isotope was always selected for the analysis of polyisotopic elements, based on its highest abundance and, at the same time, that one which does not suffer from isobaric and polyatomic overlaps. The working isotopes were as follows: ¹⁶³Dy, ¹⁴⁰Ce, ¹⁶⁶Er, ¹⁵³Eu, ¹⁵⁵Gd, ¹⁶⁵Ho, ¹³⁹La, ¹⁷⁵Lu, ¹⁴⁶Nd, ¹⁴¹Pr, ¹⁴⁷Sm, ¹⁵⁹Tb, ¹⁶⁹Tm, ⁸⁹Y, and ¹⁷²Yb.

Results and discussion

The work consisted of designing an experimental plan to analyse the samples of edible mushrooms. Mushrooms are chosen and collected as food crops because they are able of absorbing the foreign substances to a large extent from the environment, are not obtainable by common agricultural technologies and also, because of the fact that there are no legislative limits for the REE content. The work includes the optimization of sample preparation before analysis and with appropriate analytical procedure for monitoring REE (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, and Yb). The results obtained are intended to be subsequently statistically processed and evaluated with respect to Gd anomaly.

Method optimization

To design a method for REE and analysis of mushroom samples, well-established procedures commonly used in our laboratory were used. Also, a long-term experience of our laboratory staff with the determination of REE could be exploited. Due to the very low REE concentrations expected in the mushroom samples, the actual analysis of the mushroom samples had to be performed by using ICP-MS. Because of the same reason, the temperature programme of microwave digestion, as well as composition of a mixture of chemicals — the digesting agents (nitric acid and hydrogen peroxide) —, were optimized accordingly.

The operating conditions of the ICP-MS analysis were checked and, if necessary, adjusted before each analysis to obtain a compromise between the highest possible signal intensity and resolution, so these parameters differed slightly in each analysis. The measurement conditions were based on the work of Mišíková et al. (2021) [24].

Method validation

The ICP-MS method was validated by analysing the selected certified reference materials CRM GBW 10052 Green Tea (GBW, China), GBW 07603 Bush Twigs and Leaves (GBW, China) and BCR 670 Aquatic Plant (Duck Weed) (IRMM, Belgium). Long-term repeatability, recovery, and reliability of the analysis were monitored and instrumental detection limits and detection limits of the method determined; the corresponding values being given in Table 3. Concentrations of the monitored elements were measured (in $\mu\text{g kg}^{-1}$) and compared with values for CRMs given in certificates.

As found, experimentally obtained values corresponded to the certified values declared by the manufacturer. The recovery for CRM GBW 10052 Green Tea varied between 79–96 %, for GBW 07603 Bush Twigs and Leaves between 66–105 % and for BCR 670 Aquatic Plant between 82–96 %.

The long-term repeatability and recovery of ICP-MS analyses were verified by the analysis of calibration standards S4, S5 and S6 (see Table 1). The results of the evaluation of the repeatability and recovery of the ICP-MS method are shown in Table 3. The recovery of the analysis results is expressed as the ratio of the found and theoretical concentration and ranged between 94–114 % for ICP-MS. A long-term repeatability expressed as RSD was in an interval of 0.2–8.9 %.

Table 3 Instrumental LODs and method LODs of selected isotopes of the elements together with the recovery and long-term repeatability of ICP-MS method

Isotope	LOD _I [ng L ⁻¹]	LOD _M [μg kg ⁻¹]	A* 0.5 μg L ⁻¹ , B* 0.1 μg L ⁻¹		A* 1 μg L ⁻¹ , B* 0.2 μg L ⁻¹		A* 5 μg L ⁻¹ , B* 1 μg L ⁻¹	
			Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]
¹⁶³ Dy	0.033	0.002	97–105	1.2–6.1	97–103	1.1–4.6	96–105	0.8–3.4
¹⁴⁰ Ce	0.020	0.001	98–108	0.4–2.5	97–103	0.5–3.6	98–108	0.6–2.1
¹⁶⁶ Er	0.202	0.015	100–106	2.1–3.9	98–103	1.9–4.7	95–105	0.8–2.0
¹⁵³ Eu	0.075	0.005	100–108	1.2–3.5	100–104	1.7–3.2	97–103	0.2–2.6
¹⁵⁵ Gd	0.350	0.025	99–101	2–3.2	96–100	0.5–5.0	94–100	0.9–1.8
¹⁶⁵ Ho	0.037	0.003	99–106	1.6–2.8	98–102	0.4–1.0	96–104	0.7–1.4
¹³⁹ La	0.075	0.005	97–114	0.4–2.5	97–111	0.4–1.6	95–107	1.0–2.3
¹⁷⁵ Lu	0.055	0.004	99–105	0.8–1.4	97–100	0.4–1.8	95–104	0.6–2.3
¹⁴⁶ Nd	0.280	0.020	100–106	0.4–3.1	100–102	0.6–2.3	97–101	0.2–1.7
¹⁴¹ Pr	0.017	0.001	101–104	0.3–1.4	99–100	0.3–1.0	98–103	0.4–1.7
¹⁴⁷ Sm	0.340	0.024	100–107	1.7–8.4	99–104	0.5–8.9	97–107	1.0–2.5
¹⁵⁹ Tb	0.037	0.003	100–102	1.1–2.0	98–101	0.8–1.3	96–103	1.0–2.5
¹⁶⁹ Tm	0.086	0.006	100–105	0.7–2.7	99–103	0.6–2.1	95–104	0.3–1.4
⁸⁹ Y	0.427	0.031	103–113	2.6–4.0	102–106	0.4–5.2	100–102	0.4–1.2
¹⁷² Yb	0.415	0.030	100–103	4.4–7.6	97–102	0.5–5.0	95–104	0.8–2.5

A*: Y, Yb, Ce, La, Nd, Pr; B*: Dy, Er, Eu, Gd, Ho, Lu, Sm, Tb, Tm

Statistical evaluation of results

In Table 4, the obtained results of REE in mushroom samples are presented as minimum, maximum, median, arithmetic mean and the standard deviation. The concentrations of REE found in fungal samples are in the range from 0,17 to 87,7 (in $\mu\text{g kg}^{-1}$). An exception is represented by 4 samples with the concentrations higher than $1000 \mu\text{g kg}^{-1}$. In our study, an average concentration of Gd was found $33.7 \mu\text{g kg}^{-1}$ (with a minimum at $1.41 \mu\text{g kg}^{-1}$, and a maximum $361.00 \mu\text{g kg}^{-1}$).

Table 4 Determination of concentrations of REE (in $\mu\text{g kg}^{-1}$) found in mushroom samples analyzed by ICP-MS, a survey and statistics

Element	Minimum	Maximum	Mean	Median	SD
Dy	0.27	178	13.3	3.35	34
Ce	3.97	5780	393	62.2	1160
Er	0.85	81.7	7.34	2.21	15
Eu	0.17	87.8	6.72	1.86	17
Gd	1.41	361	33.7	6.61	80
Ho	<LOD	30.7	2.38	0.67	5.6
La	2,47	2810	194	34,9	559
Lu	0.03	8.80	1.13	0.35	2
Nd	0.78	1370	92.5	13.4	277
Pr	0.40	544	36.6	5.94	108
Sm	0.67	358	24.6	4.62	71
Tb	<LOD	39.4	2.87	0.77	8
Tm	<LOD	9.80	0.92	0.30	2
Y	2.41	866	71.3	21.6	160
Yb	0.18	61.5	6.44	1.81	12

Compared to the study of Fiket et al., who have monitored the REE in the Prašník area, where the bedrock naturally contains a higher concentration of REE [22], the concentrations in mushroom samples found in this work are lower than those in the previously mentioned publication. In contrast, the average concentrations ascertained for the whole mushroom samples by Falandysz et al. [25] had reached almost all REE values lower than the average concentrations found out in this work. Compared to the data obtained in this study, a multi-year study conducted by Siwuski et al. reports on higher concentrations of REE in the species of *Boletus edulis* and *Imleria badia*. In contrast, the concentrations of REE found in *M. procera* were lower than those revealed in the samples within this study [23]. For comparison, the data from publications are given in Table 5.

Table 5 Mean concentrations of REE in mushroom samples (in $\mu\text{g kg}^{-1}$) given in selected publications

Author	Samples	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Fiket [22]	location 1	1370	4140	530	2140	470	100	300	60	290	60	160	30	150	30
	location 2	520	1060	120	470	90	30	80	20	60	10	30	10	30	10
Falandyżs [25]	mushroom body	130	280	28	96	17	4.6	16	2.5	14	3.2	9	1.4	10	1.5
	pileus	83	180	17	63	12	2.7	11	1.8	10	2.3	7	1.1	7.3	1.1
Borovička [27]	ectomycorrhizal	23.1	42.1	5.56	19.9	4.06	0.68	2.35	0.59	2.16	0.42	1.28	0.17	1.26	0.13
	saprobic	13.4	21.8	2.53	10.9	2.46	0.68	1.37	0.27	1.24	0.21	0.79	<LOD	0.87	0.1
Siwulski [23]	<i>Boletus edulis</i>	75	361	130	186	28	44	175	–	234	–	–	22	61	46
	<i>Imleria badia</i>	216	384	171	268	27	42	199	–	192	–	–	80	63	48
	<i>M. procera</i>	9	70	31	30	25	5	24	–	165	–	–	11	25	31

– Not measured elements

Gd anomaly

A positive gadolinium anomaly was monitored in fungal samples (see Table 6). To calculate this phenomenon, the measured REE values were normalized to the PAAS geological standard. The content of naturally occurring Gd was calculated according to the equation (1). The gadolinium anomaly was then calculated using the relationship (2) [14]. The profile of the normalised REE concentrations for mushroom samples is displayed in Figure 1.

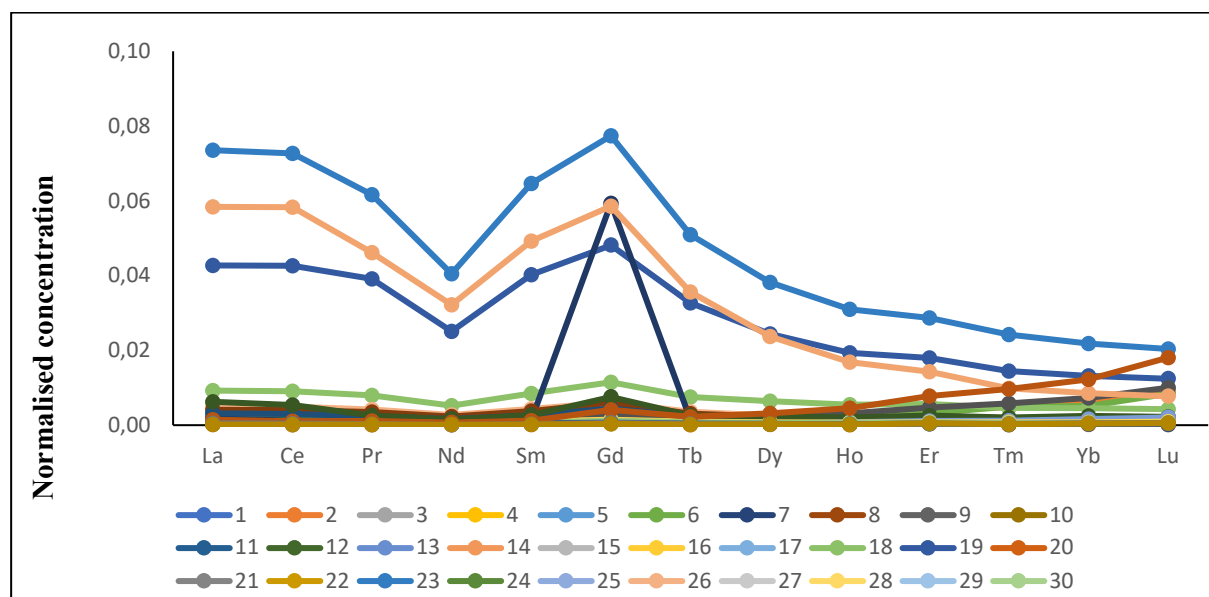


Fig. 1 Normalised REE concentrations for mushroom samples

From the normalized values, it is evident, that the representation of the individual REE in mushroom samples is almost identical. An evident exception is the sample 31 which, in addition to the significantly increased concentration of Gd compared to other REE, also contains a higher concentration of Eu. However, according to the recent studies, elevated Eu concentrations may be caused by polyatomic interferences that may be related to the presence of Ba. Several studies have already begun to address the issue of Eu and Ba interferences, especially of their oxides and hydroxide ions [26]. Due to these possible interferences caused by improperly set operating conditions, the Eu was not plotted in the normalized scale (Figure 1) to avoid possible overlap with the Gd anomaly.

According to Bau et al. [14], the threshold value for the Gd anomaly is 1.5. The average value for the Gd anomaly in the samples of mushrooms processed within this study was higher, when an average value of 2.9 was obtained.

Table 6 Values of the gadolinium anomaly and anthropogenic Gd for mushroom samples (in $\mu\text{g kg}^{-1}$)

Sample – location	Gd _{Anom}	Gd _{Ant}	Sample – location	Gd _{Anom}	Gd _{Ant}
1. Rohoznice	1.50	2.10	24. Lhota p. Libčany	1.85	5.16
2. Živanice	2.15	7.68	25. Česká Skalice	2.46	6.45
3. Kohoutov	1.21	0.64	26. Seč	1.60	10.5
4. Zvíčina	0.93	–	27. Albrechtice n. O.	2.54	3.41
5. Velké Karlovice	1.29	1.22	28. Těchlovice	1.81	2.59
6. Krkonoše	2.21	8.17	29. Hrádek	1.59	2.22
7. Přelouč	1.43	2.83	30. Nový Hr. Králové	1.74	1.09
8. Skála	1.56	1.16	31. Svatá Máří	42.6	270
9. Výsonín	1.47	2.11	32. Jevíčko	1.87	13.0
10. Polička	1.43	2.11	33. Pádolí	1.94	6.15
11. Radíkovice	1.23	1.08	34. Bučovice	2.39	0.97
12. Libčany	1.51	2.88	35. Bohdalov	1.86	9.55
13. Radostov	2.04	4.92	36. Jankovice	3.01	23.5
14. Albert supermarket	–	–	37. Kostomlaty n. L.	2.50	2.13
15. Neratov	2.21	2.91	38. Jankovice	1.46	86.1
16. Klentnice	1.68	4.57	39. Bohdalov	2.55	2.52
17. Nechanice	1.77	7.10	40. Česká Lípa	1.64	2.60
18. Dolní Přím	1.46	16.8	41. Malá Čermná	1.89	1.07
19. Hřibsko	1.37	60.6	42. Trutnov	1.77	2.29
20. Býšť	2.57	4.80	43. Dubové (SK)	1.57	1.05
21. Želí	2.01	2.09	44. Velký Vřešťov	2.21	10.3
22. Stěžery	2.24	1.56	45. Lesní hřbitov	2.44	1.60
23. Dlouhopolsko	1.40	102	46. Vysoká n. L.	2.21	0.77

The highest Gd anomaly was recorded for the sample 31. This is *Inonotus obliquus*, collected in the village of Svatá Máří in Šumava. The higher concentration of anthropogenic gadolinium is probably related to the locality. The R4 expressway is close to the collection site; the nearest town being Vimperk (3.4 km away from the collection site). In the vicinity, there are other 4 larger cities (Prachatice, Strakonice, Písek and České Budějovice), all having hospitals with MRI, as well as Vishay Electronic — one of the world's largest manufacturers of electrical and semiconductor components and integrated circuits — located in Prachatice. Regarding anthropogenic gadolinium, it enters the environment through the water system. There are several smaller watercourses in the vicinity of the village of Svatá Máří. A larger river is Volyňka that flows through Vimperk.

The lowest value of the Gd anomaly was recorded in the sample 4, which was a mixture of several edible mushrooms collected in the vicinity of the village Zvíčina in the district of Trutnov. Low values of the Gd anomaly may reflect the location with no significant industrial sources of Gd pollution nearby.

The only sample purchased from the Albert supermarket (sample 14) showed relatively low REE values. In this case, the Gd anomaly could not be calculated because the Tb concentration required for the PASS normalization in this sample was below the detection limit of the method. Otherwise, the low REE values indicate that the site of origin of this sample does not have naturally elevated REE levels and is not polluted with anthropogenic Gd.

Conclusions

In this study, the method for the ICP-MS analysis of rare earth elements (REE) in mushroom samples has been developed and validated. The parameters of the method complied with the low concentrations of REE in the analyzed samples. The REE were monitored to evaluate Gd of anthropogenic origin as the Gd anomaly. The values found in mushroom samples indicate the presence of Gd of anthropogenic origin. In the case of the monitored Gd, the minimum value found (in $\mu\text{g kg}^{-1}$) was 1.41, the maximum 361, and the average 33.7. The contribution of gadolinium of anthropogenic origin ranged from 0.77 to 270 $\mu\text{g kg}^{-1}$. Extreme values were obtained for samples 13, 23, 31 and 38, where the Gd anomaly was calculated; the average value being 2.92.

The work highlighted the growing use of REE and the related inclusion among potentially possible environmental contaminants. Gadolinium in the concentrations found in this work probably has no harmful effects on the health of the consumer (LD50 oral (rat) 3805 mg/kg body weight [28]). However, due to the ever-increasing number of MRI devices in medical facilities and diagnostics performed, it is appropriate to pay attention to the anthropogenic interventions in biogeochemical cycles of Gd and other REE, their fate, and movement in the environment and ways to the food chain.

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