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Levels of rare earth elements on three abandoned mining sites of bauxite in southern Italy: A comparison between TXRF and ICP-MS

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ABSTRACT

The essential utilization of rare earth elements (REEs) for the production of several electronic devices is making the demand for them being increased all the time. This extensive use of these elements has also increased concern about human and environmental health. Previous studies have shown that REE levels are higher in environmental samples near mining sites, and they are highly possible to be transferred to biota. In this study, REE levels were determined in environmental samples collected from three abandoned mining sites of bauxite (Gargano, Otranto, and Spinazzola) in the region of Puglia, Southern Italy. The samples were digested and analyzed by two different techniques, Total X-Ray Fluorescence (TXRF) and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) to investigate which technique is the most suitable for analysis of the REE content in samples from abandoned mining sites of bauxite. Only 6 REEs could be detected by TXRF, while all REEs were detected in all the samples by ICP-MS. Spinazzola is the richest site and Ce the most abundant REE in all three regions. REE levels are correlated between the soil and biota samples in many cases, although the calculation of the bioconcentration factor showed that REEs are not bioaccumulative. ICP-MS seems to be a more suitable technique for analysis of the whole REE content in environmental samples from abandoned mining sites of bauxite.

1. Introduction

The rare earth elements (REEs) is a group of metals consisting of the 15 lanthanides [Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (*Pm*), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu)] plus Scandium (Sc) and Yttrium (Y) [1]. Since the manufacturing of several electronic devices relies on their application, the global demand for these elements is continuously increasing [2–4]. The major part of REEs in European Union is imported by China, which is since ever the top extractor of these elements. Due to that, attention has been given over the last years to the potential discovery of new sources of REEs inside EU, in order to become independent from other countries, and so the exploration of new sites for the potential extraction of REEs is of a big interest [5].

Previous studies investigated the REE content in environmental matrices from mining sites that are either active or abandoned or on the areas near these sites. REE levels were found to be higher in a mine tailing composed by sludge and gravimetric waste [6], in a coal mine drainage [7], in acid mine drainages [8–11], in a rare earth mining area [12], in an U-REE mining site [13], in stream waters of a Cu–Pb–Zn mining area [14], in an inactive Zn–Pb mine [15] in coal mine drainages [16,17], or the areas close to abandoned mining sites [18–22].

Due to the aforementioned extensive use of REEs, concerns about their safety have been raised, not only for human [23,24] but also for

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environmental health [25,26]. Except for the elevated levels of REEs on areas near the mining sites, several studies evaluated the environmental risk of REEs and showed that they could be transferred from soil to plants [13,27–29] or from water to clams [30]. Other studies showed that REEs can be very hazardous to several living organisms [31–34].

For all the above reasons, in this study the potential existence of REEs was investigated in abandoned mining sites that were not studied before concerning the levels of these crucial elements. More specifically, environmental samples were collected from three abandoned mining sites of bauxite in the region of Puglia, Southern Italy. Each site is in the regions of Gargano, Otranto, and Spinazzola. Samples of soil, sediment, rock, water, and biota were collected and the REE content was analyzed by two different techniques, Total Reflection X-Ray Fluorescence (TXRF) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). These two techniques were compared for determining which one is the most ideal for the analysis of the REE content in such environmental samples from abandoned mining sites of bauxite. Thus, the advantages and disadvantages of the two techniques were elaborated upon for practical application in the measurement of such environmental samples. The correlation of the REE levels between the soil and biota samples from the same sampling, as well as the bioconcentration factor were also calculated.

2. Materials and methods

2.1. Sampling campaign

For determining the REE levels, samples of soil, sediment, rock, water, and biota were collected from three abandoned mining sites, each one in the areas of Gargano, Otranto and Spinazzola in the Puglia region, Southern Italy (Fig. 1).

Each area of sampling was tracked on Google maps on the scale of 50 m and was divided into 20 smaller areas. Ten of these areas were selected randomly for sample collection. Supplementary material 1 includes the figures (Figs. S1–S6) showing how each sampling site was divided and the coordinates of each point chosen for sample collection.

Table 1 shows the number of each type of samples collected from each area.

The lower number of sampled matrices was due to their absence in the areas selected for sampling, and moreover some sampling areas were not possible to be reached.

Table 1
Number of each type of samples collected from each area.

Site	Soil	Sediment	Rock	Biota	Water
Gargano	9	3	4	5	–
Otranto	8	4	5	9	1
Spinazzola	10	–	9	9	2

The temperature, pH, dissolved oxygen, % of O_2 saturation and conductivity of the water samples were measured at the time of sampling (Table 2).

Sub-surface soil and sediment samples were collected using a small shovel for removing the surface part. Rock, water, and biota samples were collected on the surface of the areas. All samples were collected in sterilized plastic bags except for the water samples which were collected in plastic bottles. Biota samples were stored at −20 °C until arriving in the laboratory for further digestion and analysis, while the rest of the samples were stored at 4 °C.

2.2. Sites of sampling

The Apenninic (NW-SE trending) and *anti*-Apenninic (NE-SW trending) tectonic deformation, which divided the region into three main structural blocks: Gargano promontory, Murge area, and Salento Peninsula, has an impact on the structure of the Apulia region [35]. Typically referred to as the “Apulian foreland” or the “Southern Apennine foreland,” this area is a vast foreland domain of the Apenninic and Dinaric orogens. Ephemeral sub-aerial exposures regularly interrupted carbonate accumulation. Albian-Cenomanian and Turonian are two important regional intra-Cretaceous unconformities that were created as a result of early tectonic deformation of the carbonate platform in this

Table 2
Characteristics of the water samples collected.

Region	Otranto	Spinazzola	
Sampling point	**D3**	**B3**	**E2**
Temperature (°C)	22.3	20.3	19.1
pH	7.88	8.01	7.80
Disolved oxygen (mg/L)	8.71	7.20	6.21
% O_2 saturation	104	91	70
Conductivity (mS/cm)	1157	303	284

Fig. 1. Map of Italy and location points of the three abandoned mining sites in the region of Puglia.

region.

The Late Cretaceous exposure events resulted in the formation of the Gargano karst bauxite deposits. On the karstified limestone, the Gargano promontory bauxite (Cenomanian-Senonian) is found as lenticular, irregular bodies. Up to the 1970s of the previous century, this deposit was mined underground (Fig. S1 A and B).

Allochthonous bauxite, also known as Salento or Terra d'Otranto, is a mineral that grows in the southern Apulian Foreland [36]. According to the stratigraphical classification of Bosellini and Parente [37], the Melissano Limestone beneath the Campanian-lower Maastrichtian Santa Cesarea Limestone is the lowest unit of the late Cretaceous in this area. The Ciolo Limestone, which is the topmost unit in the succession, has a latest Maastrichtian age at its type section. Schlüter et al. [38] discovered that the Ciolo Limestone has an age range from the middle Campanian to the latest Maastrichtian based on the $^{87}Sr/^{86}Sr$ dating of rudist shells. The Melissano Limestone Formation in the southeast of the ACP is comparable to the Altamura Limestone Formation [39].

The bauxite of the Salento-type deposits is made up of bauxitic fragments that resulted from previous deposits' weathering and erosion [40]. The late Oligocene succession, which developed in alternating freshwater, lagoonal, and emergent habitats at the Otranto site, was sandwiched between the underlying, severely weathered late Cretaceous limestone and the detritus. A debris layer several meters thick makes up the bauxite deposit, which today faces a small lake (Fig. S3 A and B). The debris has a reddish-yellow hue and is filled with several sizable bauxite pebbles that were once part of a healthy bauxite deposit.

The Spinazzola group of bauxite deposits are situated in the northern portion of the Murge district of Apulia, in southern Italy (40.986812762416804, 16.181751378099847) [41]. A 3-km-thick succession of Cretaceous shallow-water limestones and dolomites dominate this region, which is a portion of the southern Apennines foreland. These rocks form a monocline that dips from southwest to southeast and is gently deformed by folds and crosscut by subvertical normal and *trans*-tensional faults. In the interior of the Mesozoic Apulia Carbonate Platform (ACP), a shallow-water environment with limited energy development is where the carbonate succession was formed. The ACP suffered deformation brought on by the propagation of intraplate stress during the early stages of the Alpine Orogeny as a result of the beginning of the collision between Africa and Eurasian in the middle to late Cretaceous. Two significant regional intra-Cretaceous unconformities that show evidence of prolonged subaerial exposures during the Albian-Cenomanian and Turonian are the result of the carbonate platform's tectonic deformation. According to a new plate tectonic model put out by Ref. [42], the ACP was located between tropical latitudes between 20° and 30° during the Cretaceous. The ACP only documents the Turonian exposure event, and in the Murge region, bauxite formed as vertical masses filling large voids that resembled canyons and were surrounded by steep walls. Most of these are small, karstification-related sliding planes. But many of the bauxite deposits in the Murge area's sub-parallel east-west arrangement points to a structural control and the existence of a fault system that supports the development of karst cavities. The bedrock that has been karstified is made of Valanginian-Cenomanian limestone (Calcare di Bari Formation), which has been severely distorted by the Cenomanian tectonism that has elevated the entire region. Using biostratigraphic and chronostratigraphic data, uplift has been dated to 4 Ma (early Turonian-Santonian). The Valanginian-Cenomanian carbonate footwall and the transgression, shallow-water Coniacian-Campanian limestones (Calcare di Altamura Formation) at the hanging wall are both preserved in the 20-m-thick bauxite deposit at the Spinazzola sampling site. Just below the hanging wall separating the bauxite from the underlying carbonate, there is also a conglomerate level with a clay matrix and carbonate clastics. A distinct normal fault clearly borders the right and left sides of the bauxite deposit's typical canyon-like structure (Fig. S5 A, B, and C).

2.3. Digestion of samples

Rock samples were rinsed with ultra-pure water, dried overnight, at 70 °C, and then pulverized by FastPrep-24 5G (MP Biomedicals, Germany). Soil and sediment samples were dried overnight at 70 °C and then pulverized with the use of a mortar. Usually, samples are dried at 105 °C. However, for technical reasons it was not possible to dry at 105 °C, but in order not to create mistakes in the interpretation of the results, all the samples were dried in the same way at 70 °C. All three types of samples were digested by a microwave digestion system (MARS 6, CEM, Bruker, Germany) using the US EPA method 3051a. Briefly, about 0.5 g of dry sample was weighted, followed by the addition of 9 mL HNO_3 (69 %, v/v) and 3 mL HCl (37 %, v/v). The digestion protocol was as follows: heating for 5:30 min up to 175 °C, remaining at 175 °C for 4:30 min, and then cooling down to room temperature. The samples were then transferred in 50 mL falcon, filtrated by Fisherbrand™ Grade 600 cellulose general purpose filter paper and ultrapure water was added up to a final volume of 20 mL.

Biota samples were rinsed with ultrapure water, dried overnight at 70 °C, and digested following the method of [43]. Briefly, about 4 g of dry sample were weighted and incinerated at 550 °C overnight. The next day, the ash was dissolved by the addition of 1.5 mL HCl (37 % v/v), was let stand for 30 min, and then 15 mL of ultrapure water were added. The samples were then filtrated using Millipore Millex syringe filter, pore size 0.22 μm by Merck.

Water samples were digested by MARS6 by CEM (Bruker, Germany) using the method US EPA 3015a. Briefly, 5 mL of HNO_3 (69 %, v/v) were added in 45 mL of water sample. The properties of the digestion were the following: Heating for 10 min up to 170 °C, remaining at 170 °C for 10 min, and then cooling down to room temperature. The samples were then transferred in 50 mL falcon, filtrated by Fisherbrand™ Grade 600 cellulose general purpose filter paper.

It should be noted that the filtration increases the possibility of losing an amount of the analyte, however, the digestion procedure showed good recovery rates.

2.4. Analysis by TXRF

Multielement analysis by TXRF was performed with a benchtop TXRF spectrometer (Picofox S2, Bruker, Germany) operating with a molybdenum X-ray source at 50 kV. The experimental conditions are given in Table S1. Reusable quartz sample carriers (4 × 30 mm) were employed for all measurements. The sequence of the sample preparation was the following: the digested samples were prepared in a 2 mL reaction caps (Eppendorf) containing 10 mg/L of Gallium as internal standard and were homogenized on a vortex for 10 s. A drop of 10 μL of the sample was pipetted on the center of the surface of the carrier and dried at 60 °C on a hot scale.

A gain correction was performed before each series of measurements. Samples were measured for 1000 s. All volumes were controlled gravimetrically by weighing. Spectra were analyzed with the Bruker Spectra Picofox V 6.2.0.0 software. Corrections were made for the escape peak and for pile ups. The background was corrected by a maximum of 1000 stripping cycles with a step width of 50.

2.5. Analysis by ICP-MS

Multi-elemental analysis by ICP-MS was performed by ICP-MS Aurora M90 (Bruker, Germany). The experimental conditions are given in Table S2. The analysis was performed in high-sensitivity mode. All standards and samples were prepared in HNO_3 solution (2 %, v/v). Calibration curves for determining REEs ranged from 0.005 to 100 μg/L (Table 3) and were constructed daily by analysis of standard solutions prepared immediately before analysis. The internal standard was ^{115}In for both the calibration curve and sample analysis.

The working range was evaluated by analyzing one blank and nine

Table 3
Calibration range for each REE during analysis by ICP-MS. All values are expressed in μg/L.

REE	Calibration range (μg/L)
^{89}Y	0.010–10
^{139}La	0.010–10
^{140}Ce	0.010–10
^{141}Pr	0.010–10
^{146}Nd	0.010–10
^{149}Sm	0.010–10
^{153}Eu	0.010–10
^{157}Gd	0.010–10
^{159}Tb	0.005–10
^{163}Dy	0.005–10
^{165}Ho	0.010–10
^{166}Er	0.005–10
^{169}Tm	0.005–10
^{172}Yb	0.010–10
^{175}Lu	0.005–10

standards at different concentrations, and the linearity was tested verifying the linear regression coefficient (R^2) of the calibration curve. The linearity was acceptable, with R^2 value equal or greater than 0.996.

To confirm REE contamination of all materials utilized for each batch, a blank for reagents and a blank for the digestion procedure were carried out, and the instrumental sequence was validated every 10 samples. For every 20 samples, at least two control standards were confirmed with an acceptance criterion of 10 % compared to the true value.

2.6. Limits of detection (LOD)

LOD values on ICP-MS Aurora M90 were determined according to Eurachem Guide [44] with the determination of 10 replicate measurements of blank samples containing only HNO_3 solution (2 %, v/v). LOD was calculated as 3*s*, *s* being the standard deviation of the measured concentrations.

On Picofox S2, every time that a sample is analyzed a LOD value is also received depending on several parameters [45]. According to Espinoza-Quiñones et al. [46] the LOD value of a specific element in TXRF is proportional to at least three times the square root of the integrated area of background or three-sigma background fluctuation. Within such a statistical estimation, the concept of 3*s* detection limits conveys an exploitation of the minimum concentration in TXRF analysis through the true confirmation of a detectable X-ray when its peak area is at least three times the background signal fluctuation. On TXRF, LOD values for only six elements (Y, La, Ce, Nd, Yb and Lu) were already determined by the manufacturer.

2.7. Statistical analysis

Statistical analysis was elaborated in SPSS Statistics v20. Values of REEs below the limit of detection (LOD) were replaced by 0, due to the different LOD values between TXRF and ICP-MS. Independent samples *t*-test was used to compare REE concentrations analyzed by the two different methods. Significant differences between the results from the two methods were determined by Welch's *t*-test. Differences were considered significant when $p < 0.05$.

Correlation of matrix was used to investigate the correlation of REE levels between soil and biota sample from the same sampling point. The existence of correlation was considered when Pearson $r > 0.7$.

Percentage (%) of the bioconcentration factor (BCF) was calculated by dividing the REE concentration in biota to this in soil from the same sampling point, multiplied by 100.

3. Results and discussion

3.1. LOD values

Table 4 shows the LOD values obtained for TXRF and ICP-MS, respectively. LOD values of ICP-MS were about 1000 times lower than the LOD values of TXRF. LOD values on TXRF ranged from 2 μg/L to 16 μg/L, while LOD values of ICP-MS ranged from 0.001 μg/L to 0.004 μg/L.

On TXRF, LOD values of the 9 REEs (Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm) couldn't be received by the manufacturer and it was not possible to determine them due to spectral interferences due to the high concentrations of other trace metals in the analyzed samples. However, due to the fact that these elements occur together in all their common minerals, any of the most common REEs can serve as an indicator for the presence of REEs.

3.2. Analysis by TXRF and ICP-MS

Supplementary material 2 includes all the results concerning the concentrations of each REE, on each type of sample, from each sampling point, and analyzed by each technique (Tables S3–S26).

3.2.1. Analysis by TXRF

No REE was detected in any water sample when analyzed by TXRF. Tables 5–7 show the mean concentrations of each REE in each type of sample collected from the regions of Gargano, Otranto, and Spinazzola, respectively, after elemental analysis by TXRF.

In the region of Gargano, Y, La and Ce were detected in all types of samples; Nd was detected in rocks and biota, Lu was detected in sediments and rocks, and Yb only in rocks. The most abundant REE was Ce in soil, sediments, and biota, and Yb in rocks.

In the region of Otranto, Y, La and Ce were detected in all types of sample collected; Nd was detected in rocks and biota, and Yb and Lu were detected in sediments and rocks. The most abundant REE was Ce in soil, sediments and biota, and Y in rocks.

In the region of Spinazzola, Y, La Ce and Nd were detected in all types of samples collected, while Lu was detected only in soil. The most abundant REE was La in all three types of sample.

3.2.2. Analysis by ICP-MS

Tables 8–10 show the mean concentrations of each REE in each type of sample collected from the regions of Gargano, Otranto and Spinazzola, respectively, after elemental analysis by ICP-MS.

All REEs were detected by ICP-MS in all types of samples collected from all three regions. The most abundant REE was Ce, followed by La, in all types of sample from all regions. The only exception were the biota samples from Spinazzola region, in which La was the most abundant

Table 4
LOD values of TXRF and ICP-MS. Values are expressed in μg/L.

Element	LOD TXRF	LOD ICP-MS
^{89}Y	2	0.003
^{139}La	16	0.003
^{140}Ce	16	0.003
^{141}Pr	–	0.003
^{146}Nd	16	0.004
^{149}Sm	–	0.003
^{153}Eu	–	0.002
^{157}Gd	–	0.003
^{159}Tb	–	0.001
^{163}Dy	–	0.002
^{165}Ho	–	0.002
^{166}Er	–	0.001
^{169}Tm	–	0.001
^{172}Yb	12	0.002
^{175}Lu	3	0.002

Table 5
Mean values of each REE in each type of sample from Gargano region, after analysis by TXRF. Values are given in mg/kg dry mass.

Sample type	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Soil	13.5 ± 4.88	66.1 ± 40.6	111 ± 45.7	–	< LOD	–	–	–	–	–	–	–	–	< LOD	< LOD
Sediments	8.80 ± 7.39	40.1 ± 46.7	75.1 ± 22.3	–	< LOD	–	–	–	–	–	–	–	–	< LOD	2.18 ± 3.78
Rocks	3.13 ± 6.00	5.16 ± 7.02	15.4 ± 28.2	–	0.37 ± 0.73	–	–	–	–	–	–	–	–	19.1 ± 28.2	6.51 ± 10.5
Biota	5.87 ± 4.80	3.60 ± 3.00	12.1 ± 7.24	–	1.21 ± 1.11	–	–	–	–	–	–	–	–	< LOD	< LOD

Table 6
Mean values of each REE in each type of sample from Otranto region, after analysis by TXRF. Values are given in mg/kg dry mass.

Sample type	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Soil	17.7 ± 13.0	69.6 ± 19.5	117 ± 125	–	< LOD	–	–	–	–	–	–	–	–	< LOD	< LOD
Sediments	14.6 ± 6.32	51.5 ± 22.9	93.4 ± 95.8	–	< LOD	–	–	–	–	–	–	–	–	1.57 ± 3.14	12.6 ± 25.2
Rocks	8.71 ± 10.2	5.11 ± 6.89	7.47 ± 12.7	–	0.31 ± 0.69	–	–	–	–	–	–	–	–	6.65 ± 14.9	4.41 ± 6.04
Biota	3.83 ± 3.27	4.43 ± 2.03	8.02 ± 4.08	–	0.45 ± 1.12	–	–	–	–	–	–	–	–	< LOD	< LOD

Table 7
Mean values of each REE in each type of sample from Spinazzola region, after analysis by TXRF. Values are given in mg/kg dry mass.

Sample type	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Soil	34.1 ± 37.6	159 ± 72.0	156 ± 58.5	–	42.4 ± 74.4	–	–	–	–	–	–	–	–	< LOD	3.40 ± 4.40
Rocks	15.1 ± 12.8	59.8 ± 18.8	31.8 ± 36.5	–	12.6 ± 17.3	–	–	–	–	–	–	–	–	< LOD	< LOD
Biota	8.42 ± 10.3	8.78 ± 10.4	5.18 ± 5.56	–	7.60 ± 12.6	–	–	–	–	–	–	–	–	< LOD	< LOD

Table 8
Mean values of each REE in each type of sample from Gargano region, after analysis by ICP-MS. Values are given in mg/kg dry mass.

Sample type	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Soil	35.1 ± 16.2	78.0 ± 32.2	309 ± 275	20.7 ± 8.09	74.1 ± 31.6	13.7 ± 6.07	2.97 ± 1.26	14.0 ± 6.36	1.78 ± 0.79	7.62 ± 3.36	1.31 ± 0.63	3.96 ± 1.76	0.43 ± 0.17	3.27 ± 1.16	0.40 ± 0.15
Sediments	20.4 ± 9.71	52.8 ± 17.5	120 ± 28.6	12.4 ± 3.17	41.7 ± 9.80	7.65 ± 1.74	1.45 ± 0.29	7.61 ± 1.43	0.93 ± 0.29	3.87 ± 1.61	0.64 ± 0.27	2.11 ± 0.89	0.23 ± 0.11	1.66 ± 0.64	0.22 ± 0.10
Rocks	20.6 ± 20.1	38.1 ± 56.4	98.7 ± 159	9.93 ± 15.3	34.7 ± 53.1	6.57 ± 9.44	1.62 ± 2.28	6.57 ± 9.09	0.91 ± 1.16	4.11 ± 5.30	0.76 ± 0.91	2.25 ± 2.86	0.25 ± 0.29	1.84 ± 2.29	0.23 ± 0.27
Biota	4.89 ± 3.27	10.7 ± 6.85	21.7 ± 15.0	2.59 ± 1.64	9.67 ± 6.11	1.85 ± 1.16	0.40 ± 0.24	1.59 ± 1.03	0.21 ± 0.13	1.07 ± 0.66	0.19 ± 0.12	0.51 ± 0.32	0.07 ± 0.04	0.43 ± 0.26	0.06 ± 0.04

Table 9
Mean values of each REE in each type of sample from Otranto region, after analysis by ICP-MS. Values are given in mg/kg dry mass for soil, sediment, rocks and biota samples, while in μg/L for water sample.

Sample type	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Soil	36.0 ± 17.4	66.3 ± 13.7	188 ± 72.7	15.8 ± 5.72	55.5 ± 21.6	10.9 ± 3.85	2.45 ± 0.91	11.2 ± 4.10	1.58 ± 0.61	6.99 ± 2.65	1.28 ± 0.55	3.91 ± 1.53	0.46 ± 0.20	3.61 ± 1.30	0.45 ± 0.21
Sediments	36.6 ± 33.7	45.0 ± 38.7	163 ± 223	11.3 ± 11.2	41.7 ± 40.0	8.22 ± 8.07	1.91 ± 1.76	9.09 ± 8.95	1.27 ± 1.22	6.09 ± 5.75	1.16 ± 1.09	3.53 ± 3.11	0.44 ± 0.38	3.18 ± 2.76	0.43 ± 0.40
Rocks	21.8 ± 18.4	28.8 ± 32.5	33.6 ± 35.5	4.96 ± 4.89	17.0 ± 16.1	3.72 ± 3.29	0.86 ± 0.68	3.67 ± 3.14	0.64 ± 0.54	3.25 ± 2.80	0.67 ± 0.60	1.96 ± 1.75	0.25 ± 0.22	1.87 ± 1.74	0.24 ± 0.23
Biota	3.21 ± 2.45	7.22 ± 3.51	13.9 ± 7.10	1.41 ± 0.79	5.04 ± 2.98	0.97 ± 0.59	0.21 ± 0.13	0.87 ± 0.57	0.12 ± 0.08	0.64 ± 0.44	0.12 ± 0.08	0.33 ± 0.24	0.04 ± 0.03	0.28 ± 0.20	0.04 ± 0.03
Water	0.28 ± 0.08	0.25 ± 0.05	0.60 ± 0.39	0.05 ± 0.03	0.17 ± 0.09	0.04 ± 0.03	0.02 ± 0.00	0.10 ± 0.00	0.01 ± 0.00	0.06 ± 0.02	0.01 ± 0.00	0.02 ± 0.01	<0.01	0.02 ± 0.01	<0.01

REE, followed by Nd.

3.2.3. *Comparison of the two techniques*

Supplementary material 3 includes the statistical analysis elaborated for comparing the results obtained from the two techniques.

An independent sample *t*-test (Welch) was elaborated for the investigation of significant differences ($p < 0.05$) between the REE levels obtained by TXRF and ICP-MS (Table S27). Only the levels of Y, La and Ce were used for comparing the results between the two techniques since they were the only elements detected in all samples by TXRF. Significant differences were observed for Y in the soil samples of Gargano and Otranto and in the rock samples of Spinazzola, and for Ce in the soil samples of Spinazzola. No statistically significant difference was observed for La in any type of sample. Figs. S7–S11 show the differences of the levels of Y, La and Ce after analysis by TXRF and ICP-MS, respectively.

Although there are studies that previously determined REE levels in environmental samples and elaborated a comparison of the results between TXRF and ICP-MS [47,48], to the best of our knowledge there is no study up to now to have elaborated a comparison between these two techniques when analyzing REEs in environmental samples from abandoned mining sites. This is of a great importance, since the

Table 10
Mean values of each REE in each type of sample from Spinazzola region, after analysis by ICP-MS. Values are given in mg/kg dry mass for soil, rocks and biota samples, while in μg/L for water samples.

Sample type	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Soil	125 ± 148	247 ± 202	366 ± 166	63.7 ± 55.0	236 ± 212	42.1 ± 36.3	10.0 ± 8.78	42.1 ± 35.7	5.46 ± 4.33	23.1 ± 17.1	4.36 ± 3.31	12.6 ± 9.69	1.37 ± 1.27	8.94 ± 7.28	1.18 ± 1.03
Rocks	47.6 ± 30.4	66.0 ± 36.3	115 ± 182	17.7 ± 11.4	65.9 ± 40.5	12.4 ± 7.69	3.10 ± 1.80	13.2 ± 7.07	1.84 ± 0.95	8.67 ± 4.37	1.68 ± 0.96	4.75 ± 2.54	0.51 ± 0.26	3.35 ± 1.45	0.43 ± 0.19
Biota	7.75 ± 7.75	254 ± 518	130 ± 199	63.9 ± 130	253 ± 525	46.3 ± 95.3	11.1 ± 22.9	40.3 ± 82.8	4.67 ± 9.31	21.7 ± 41.9	3.34 ± 6.21	7.83 ± 13.8	0.89 ± 1.54	5.26 ± 8.94	0.72 ± 1.21
Water	19.8 ± 2.49	37.0 ± 22.3	46.1 ± 20.7	10.3 ± 5.57	32.4 ± 16.9	6.72 ± 4.05	1.51 ± 0.80	7.53 ± 3.98	0.74 ± 0.38	2.65 ± 1.16	0.51 ± 0.20	1.49 ± 0.59	0.16 ± 0.04	0.93 ± 0.26	0.13 ± 0.03

environmental contamination of REEs is expected to be higher in the areas from which they are mined. In addition, as talked before, the demand for REEs in continuously increasing and so a higher extraction and production of these elements is wished; therefore, the determination of which method is more suited for analyzing REEs in future potential mining positions is also crucial.

Our results are in accordance with the study of [49] in which they found similar or lower levels of REEs in soil samples when analyzed by TXRF Picofox S2, compared to ICP-MS. They referred as well to errors occurred during analysis by TXRF due to the line interferences by other elements, depending on the concentration of the interfering element. Only systematic errors, such as fluorescence radiation adsorption for the light elements, can be corrected in TXRF.

Previous studies investigated also the REE levels in soil samples from abandoned mining sites around the world, using different techniques of analysis. Purwadi et al. [22] analyzed the REE content in tailing samples from two abandoned tin mine tailings in Indonesia using inductively coupled plasma optical emission spectrometry (ICP-OES). Except for the very elevated Er levels found in their samples, their results are similar to our results from soil samples from Spinazzola region, after analysis by ICP-MS. Medas et al. [21] analyzed the REE levels in solid materials from an abandoned mining in Sardenia using ICP-OES, while Atibu et al. [18] analyzed the REE-content in soil samples near an abandoned mining site in Congo using ICP-MS. All REE levels in the samples from both studies were much lower than the REE levels in our soil samples from all three regions, after analysis by ICP-MS. Fernández-Caliani et al. [19] analyzed the REE content in soil samples from Tharsis abandoned mines in Spain using XRF. The levels of La and Ce in their soil samples were lower than in our soil samples, in all three regions, after analyzed by TXRF. All in all, compared to other studies, it seems that the REE content in the soil samples from the abandoned mining sites in the region of Puglia are at higher levels, making them ideal spots for a possible REE extraction.

The ICP-MS seems to be a more suitable technique for the analysis of REEs on such environmental samples. The analysis of the REE levels in these samples by TXRF compared to ICP-MS has two main disadvantages. The first is the much higher LOD values, about 1000 times, which means that REEs in much lower concentrations can be determined by ICP-MS, when they can not by TXRF. The second is the spectra interferences of some REEs by the spectra of other trace elements that exist in higher concentrations in the samples. While ICP-MS functions with a quadrupole and the ions can be separated according to their mass per ratio and be detected separately without any interferences, in TXRF the spectra of the whole sample must be analyzed (Fig. 2). After a sample is analyzed by Picofox S2, a fit has to be made in the computer program between the spectra received from the instrument and the spectra given from the program. Only by this way someone can be sure about the concentrations of the elements that are included in the sample analyzed. While analyzing the spectra of a sample by TXRF, some REEs are in the same range with other heavy metals that are in higher concentrations and so, the spectra of the latter cover the spectra of these REEs, making them impossible for determination. For example, as shown in Fig. 3, the main spectra of Gd, Tb, Dy, Ho, Er and Tm are covered by the spectra of Fe, and so, these elements are not able to be determined by TXRF.

However, as demonstrated in Table 11, which is a summary of the advantages and disadvantages of each technique, TXRF possesses also some advantages compared to ICP-MS, being a less costly and time-

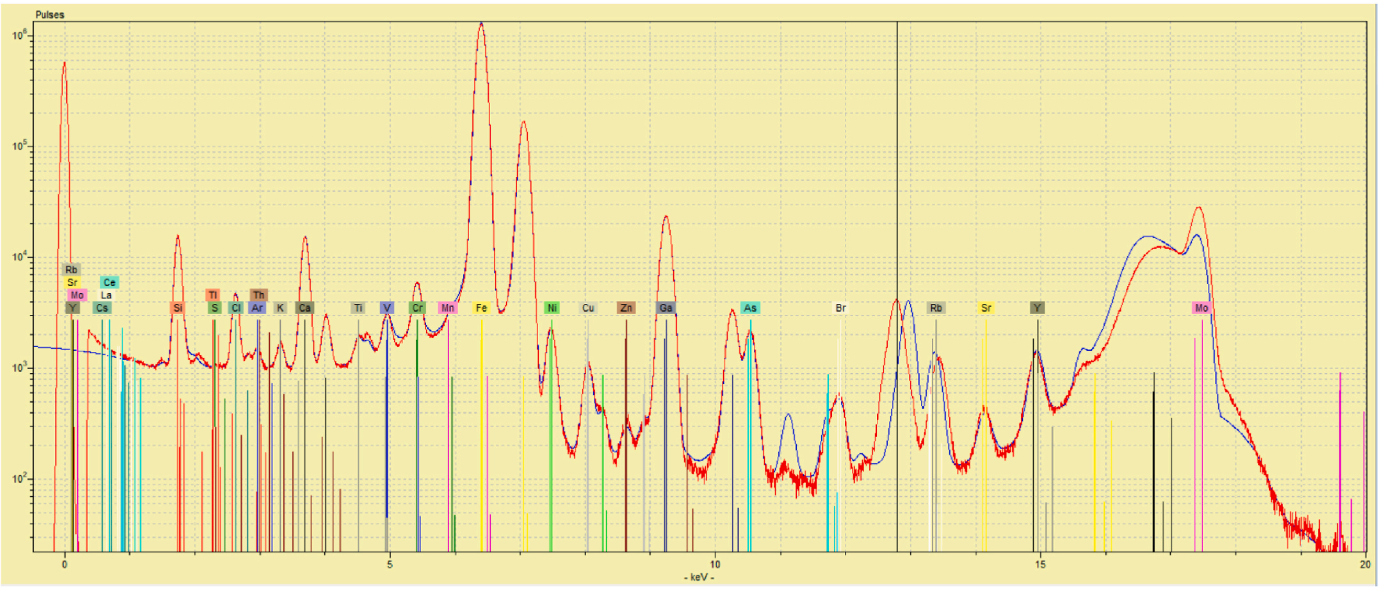

Fig. 2. An example of the whole spectra of a soil sample analyzed by Picofox S2.

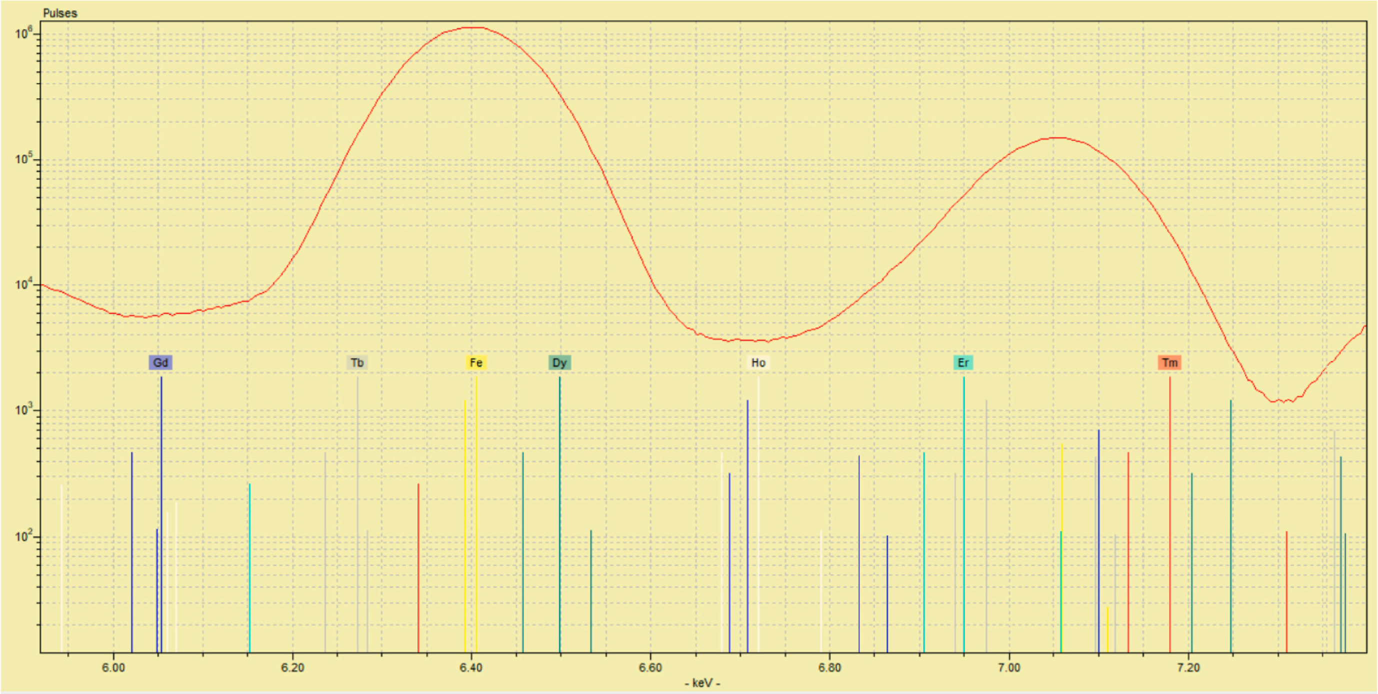

Fig. 3. The spectra of Fe after analysis of a soil sample by Picofox S2. This spectra is covering the spectra of Gd, Tb, Dy, Ho, Er, and Tm, making them impossible to be detected by this technique.

Table 11
Comparison of the advantages and disadvantages between TXRF and ICP-MS.

Parameter	TXRF	ICP-MS
Matrix effects	Yes	Yes
Time-consuming	Less	More
LOD values	Higher	Lower
Precision and accuracy	Less	More
Cost	Less	More
Use of one internal standard	Yes	Yes
Multi-elemental analysis	Yes	Yes
Spectral interferences	Yes	No
Possible sample contamination and lose of elements due to digestion	Yes	Yes
Sample destruction	No	Yes
Risk of dilution errors	Less	More

consuming technique, with less risk of errors due to dilution factors. Therefore, in the end someone should consider also other parameters, except for the interferences, about which technique to be used.

3.3. Comparison of REE levels between the three sites after analysis by ICP-MS

Figures S13–S15 on Supplementary material 3 show the concentrations of each REE on soil, biota and rock samples, respectively, from the three abandoned mining sites, after analysis by ICP-MS.

Among all three sites, Spinazzola seems to be the richest site, containing higher concentrations of REEs with respect to Gargano and Otranto. As mentioned also above, Ce is the most abundant REE, followed by La, in all types of samples from all regions, except for the biota samples from Spinazzola region, where La was the most abundant REE, followed by Nd.

Soil, rock and biota samples from Spinazzola seem to contain a high amount of REEs, especially La and Ce. The mean concentration of Ce in soil samples was at 366 mg/kg, while in biota was at 130 mg/kg, and 116 mg/kg in rocks. On the same hand, the mean concentration of La was at 247 mg/kg, 66.0 mg/kg and 254 mg/kg in soil, biota and rock samples respectively. Therefore, the environmental samples from the abandoned mining site from Spinazzola region, seem to be exclusively ideal for a potential extraction of REEs.

The correlation analysis between the levels of each REE in the soil and biota samples from each sampling site after analysis by ICP-MS (Table S28), showed that there is correlation (Pearson r > 0.7) of the REE levels between the two types of samples for 13 REEs in Gargano, 11 in Otranto and 9 in Spinazzola.

The calculation of the bioconcentration factor (BCF) of the biota and soil samples from each sampling point (Tables S29–S31) revealed that no REE is bioaccumulative at any sampling point (>1000 L/kg), and so they do not seem to be considered as an environmental hazard in these areas.

The bioaccumulation of metals in biota from soil, depend on several factors, such as the soil properties, the types of extractants and the metals [50]. According to Ref. [51], the major factor governing metal availability to plants in soils is the solubility of the metal associated with the solid phase, since in order for root uptake to occur, a soluble species must exist adjacent to the root membrane for some finite period.

We have to highlight that the small number of soil (9 from Gargano, 8 from Otranto and 10 from Spinazzola) and biota samples (5 from Gargano, 8 from Otranto and 9 from Spinazzola) obtained for this research makes the results having a big bias. Therefore, we can only have some first indications about the REE levels and the correlation between soil and biota samples.

Last but not least, the potential environmental hazard should be mentioned. Since, these elements have been found in such high levels, and since they have been shown before to consist a potential threat for both human and environmental health, the risk assessment should be elaborated in future studies considering these environmental concentrations of REEs.

4. Conclusions

By analyzing environmental samples collected from the three abandoned mining sites, it can be concluded that REEs are not only present in traceable levels, but in levels that could be suitable for a possible extraction.

The analysis of the REE levels in these samples by TXRF compared to ICP-MS has two main disadvantages; the very higher LOD values, and spectral interference of some REEs by the spectra of other elements. Instead, ICP-MS technique allows the achievement of lower LOD values with less interferences for the analysis of REEs. This makes ICP-MS a more suitable technique for determining the whole range of REEs in environmental samples, even from areas with past mining activity, while TXRF is a suitable technique for making an initial screening of the REE content in the samples.

Cerium is the most abundant REE in all environmental samples from all three regions, except for the biota from Spinazzola, where La is the most abundant.

The correlation analysis revealed that REE levels are correlated between the biota and soil samples, while the calculation of BCF showed that REEs are not bioaccumulative at all.

Comparing REE levels between the three regions after analysis by ICP-MS, Spinazzola is the site containing higher levels of these elements making it the most interesting among all for a possible REE extraction.

REEs in environmental samples from abandoned mining sites in Southern Italy are still in traceable levels. Since several previous studies have shown that they might consist a threat for human and environmental health, more investigations should be elaborated about their concentrations either near or further from mining sites.

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CRediT authorship contribution statement

Antonios Apostolos Brouziotis: Writing – original draft, Formal analysis, Data curation, Conceptualization. **Susanne Heise:** Writing – review & editing, Supervision, Funding acquisition, Data curation. **Lorenzo Saviano:** Data curation. **Keran Zhang:** Data curation. **Antonella Giarra:** Writing – review & editing, Data curation. **Michael Bau:** Supervision, Funding acquisition. **Franca Tommasi:** Supervision, Funding acquisition, Conceptualization. **Marco Guida:** Supervision, Funding acquisition, Conceptualization. **Giovanni Libralato:** Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Marco Trifuoggi:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2024.126093.

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