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Multivariate Strategy for Understanding Soil Features from Rare-Earth Element Profiles: A Focus on Data Normalization

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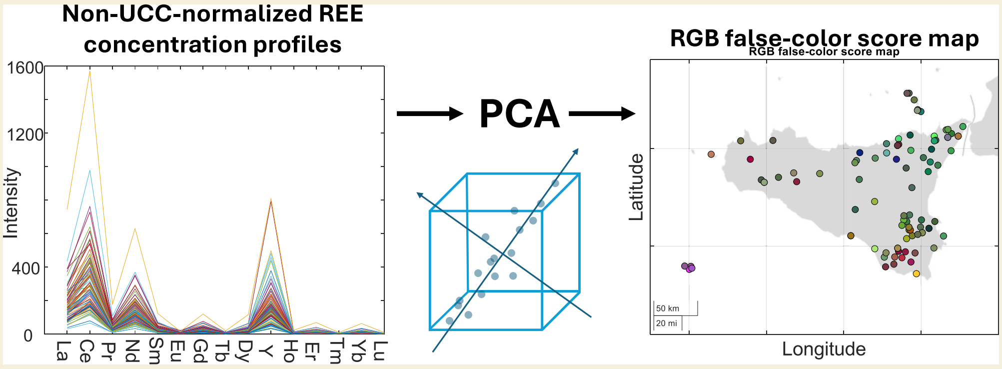

ABSTRACT: The interest in assessing the behavior of rare-earth elements (REE) in the natural environment is constantly increasing due to their numerous applications in both environmental and technological fields. However, current methodologies for analyzing REE distributions are based on normalization of REE concentration profiles to lithological values, potentially resulting in different outcomes depending on which lithological values are used for normalization, affecting the interpretability of the data. The present work proposes an alternative approach for analyzing REE concentration profiles by applying principal component analysis (PCA) to create REE chemometric maps. The data compression allows the visualization of the REE distribution using a red-green-blue (RGB) color scale (PC1 = red channel; PC2 = green channel; PC3 = blue channel) directly on a geographical map, reflecting the chemical properties of rare-earth elements. This highlights similarities and differences in the compositional REE distribution of natural soils, facilitating the interpretability of REE data and potentially leading to new insights related to seemingly unrelated samples. Additionally, PCA applied to soil variables correlates with REE patterns and provides deeper insights into soil properties in an unsupervised manner, enhancing the interpretation of soil characteristics and implementing the ability to monitor environmental changes and study soil evolution processes. Of particular significance is the fact that applying the proposed methodology to non-normalized data yields results that are consistent with those derived from normalized data sets. Therefore, this approach not only overcomes normalization challenges but also supports the classical approach from a new methodological perspective, paving the way for broader applications.

KEYWORDS: *rare-earth elements (REE), data normalization, chemometrics, principal component analysis (PCA), score maps, World Reference Base for Soil Resources (WRB)*

INTRODUCTION

Lanthanides together with lanthanum (La), scandium (Sc), and yttrium (Y) are known as rare-earth elements (REE), 17 elements with remarkable characteristics. Nevertheless, scandium (Sc) is often excluded from the list due to its different chemical properties,[1,2] and promethium (Pm) does not have any stable isotope in nature, making it *de facto* irrelevant in analytical chemistry problems.[3] Therefore, discussion of REE usually focuses only on the remaining 15 elements.

These elements can be classified in two different ways. The first is based on the electron configuration of each rare-earth element, where f^0 (no f-subshell electrons), f^7 (half-filled), and f^{14} (fully filled) configurations are considered more stable. These configurations define the boundaries for classification, with cerium (Ce) to gadolinium (Gd) plus lanthanum (La) categorized as light rare-earth elements (LREE) and terbium (Tb) to lutetium (Lu) as heavy rare-earth elements (HREE).[2,4,5]

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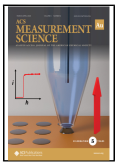

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Gadolinium (Gd) is an intermediate element of REE's series, classified in several literature works as both LREE and HREE.[2,5,6] The second possible classification separates them depending on their atomic weight into three groups: the LREE (La to Nd), the medium rare-earth elements (MREE) (Sm to Gd), and the HREE (Tb to Lu).[7] Yttrium (Y) is always classified in the heavy rare-earth element group due to its chemical similarities with Ho even if it has a lower atomic weight.

In their natural state, these elements, with atomic numbers ranging from 57 to 71, are generally trivalent and exhibit similar electronic configurations ($[Xe]4f^n5d^16s^2$). This characteristic remains consistent throughout the filling of the 4f orbital (with an increase from 0 to 14), which occupies an inner position in the atomic structure from La to Lu. Therefore, the ionic radius of REE decreases linearly with an increasing atomic number, a phenomenon known as lanthanide contraction, even though the variations in effective ionic radii are minimal, only 18.7% from La^{3+} to Lu^{3+}[8] and merely 0.8−1.5% between two consecutive elements.

Since ion chemistry is predominantly controlled by the charge and ionic radius, these minimal variations explain both the consistency in chemical behavior of trivalent REE and the inability of natural processes to separate one of these elements from its neighbors. Consequently, in nature, the abundance of two neighboring trivalent REEs is generally highly correlated. However, the specific decoupling of particular elements from the other REE is naturally possible on Earth. For instance, cerium exhibits exceptions in oxidizing environments ($Ce^{3+} \rightarrow Ce^{4+}$), while europium does so under reducing conditions ($Eu^{3+} \rightarrow Eu^{2+}$),[1,9] determining potentially distinct behaviors in Earth's systems.

Thanks to these unique characteristics, REEs have received considerable attention over the past decades both as tracers for pedogenesis evolution and petrological studies,[10−13] as well as biogeochemical tracers for food origin[14−22] or anthropogenic activities.[23,24]

Regardless of the field of interest, the classical method for studying REE's behavior involves the use of normalized patterns, where each element's concentration is divided by its corresponding concentration in a lithological reference,[25] thus minimizing the natural variability of REE. Indeed, REE concentrations in the environment can vary by two or three orders of magnitude, reflecting the Oddo−Harkins effect,[26] whereby elements with an even atomic number greater than 6 tend to have higher abundances than their immediate odd-numbered neighbors.

However, several classical references are available, such as the upper continental crust (UCC),[27] north American shale composite, chondrites,[28] postarchean Australian shale,[29] and European shale composite.[9] Although the choice of reference is crucial for the subsequent interpretation of REE behavior in geochemical systems,[30] one of the main challenges lies in comparing distributions, which becomes even more complex with large numbers of samples.[31]

Moreover, regardless of the type of normalization chosen, the classical data processing approach to distinguish the unique behavior of specific elements compared with their neighboring counterparts is typically univariate. This distinction, in fact, is usually evaluated by examining the ratio X/X^*, where X represents the normalized concentrations of one element and X^* is the geometric mean of normalized concentrations of neighboring elements. However, this results in anomalous values that can be very different from one study to another and cannot be compared.[32] Furthermore, a significant limitation is that this approach may work well for flat profiles, while its suitability significantly decreases for curved profiles.[31,32] The use of raw data is crucial, for example, in environmental assessments, particularly for understanding spatial-temporal evolution. In this context, the implementation of chemometric tools offers valuable methods for simplifying complex data sets across various fields of application. In the literature, chemometrics, particularly through principal component analysis (PCA), has already been proven to be beneficial on REE analysis. For instance, PCA has been used on REE concentrations and soil parameters to differentiate between various land usages[33] and to recognize uranium ore deposits.[34] PCA has also been used by Sarparandeh and Hezarkhani[35] to individuate relationships between elements, and, with a similar idea, Sadeghi et al. showed in two successive studies[36,37] that PCA can be used to reveal correlations and anomalies in REE distributions and that PC scores can be exploited to build color composites of PC maps to study soil composition and orogen. Although these studies effectively apply PCA as a tool, none of them have proposed a method to compare REE distributions *a priori*, either from raw or normalized data. The main challenge in describing REE patterns lies in the high correlation between variables, which is directly addressed in this work using appropriate preprocessing strategies. However, given the high intercorrelation of REE data, using appropriate preprocessing strategies before the application of chemometric tools is crucial. In particular, row preprocessing should be employed to avoid global intensity effects. In this context, "sum100" is a preprocessing with the goal of correcting for global intensity effects within data, reaching a constant sum (in this case, 100) of the values of variables used to describe a specific sample, and is elsewhere referred to as constant sum normalization (CSN),[38] row profile (RP),[39] or total ion current (TIC) normalization when applied in mass spectrometry context.[40] An advantage of this procedure is that it does not require any additional information to be available since it uses only data-derived parameters. This possibility makes sum100 row preprocessing a highly promising tool, enabling the possibility of efficiently normalizing REE profiles in a totally unsupervised way, without any requirement for external information that might introduce bias in the data.

This work aims to propose a method capable of identifying similar or dissimilar REE distributions without prior information (by applying suitable mathematical pretreatments), ensuring objectivity and addressing the issue of high variable correlation. By applying PCA directly to concentration profiles, the proposed approach aims to create REE geographical distribution maps. The obtained maps allow a straightforward evaluation of similarities and differences in the geographical region under study and enable visual monitoring of REE variations over time. The proposed strategy applied to REE profiles of soils not only provides an easy-to-read color output but also improves the chemical interpretability of results, allowing a global evaluation of possible REE pattern variation. A further application of PCA on pedological variables allows us to rule out the relationships both within those variables and REE, reaching a wider understanding on the studied region. Such a joint evaluation can expand the analysis of REE distribution also in relation to a broader range of soil characteristics, giving potential implications for studying soil evolution processes and environmental changes over time.

Finally, a fundamental step of the present study is the confirmation of the proposed strategy directly on non-normalized data. Results obtained were consistent with those derived from the normalized data, delineating for the first time the power of the proposed strategy for a direct processing of raw REE profiles, which overtakes the normalization step.

■ MATERIALS AND METHODS

Experimental Setting

The experimental system consists of 92 soil samples of diverse geographic origins in Sicily (Italy) characterized by different lithological origins and varying land use (Table S1). Full details are available at https://zenodo.org/record/7072306. Routine soil data (i.e., pH, organic carbon, total carbonates, texture, clay, silt, and sand) and REE concentrations were analytically determined on soils sampled at depths ranging between 0 and 30 cm. Data are presented in Table S2 (Supporting Information).

Sample Preparation for REE Determination

REE analysis can be performed using two different types of digestion: total and pseudototal. Total digestion utilizes hydrofluoric acid to completely decompose the samples through the digestion of aluminosilicates, reflecting the lithological composition. In contrast, pseudototal digestion uses nitric acid and hydrogen peroxide, enabling the mineralization of the organic fraction of the soil and partial extraction from the mineral fraction, thus determining the labile fraction. Since the distribution of REE in surface soils varies according to several factors, including properties of the parent material, weathering, leaching, state of the soil, content of organic matter and clay minerals, and anthropogenic activity,[6] REE topsoil concentrations may differ significantly, even when the underlying lithological origin is similar.[6] Therefore, to evaluate variations in REE profiles that may be relevant for predicting potential pollution or correlating with soil characteristics, the present study focused on the pseudototal fraction rather than the total content. This approach targeted the REE content in carbonates, sulfates, oxides, and other less labile phases while minimizing their release from the immobile fraction.[17,41]

Nitric acid (65%) and hydrogen peroxide (30%) ultrapure reagents (Merck, Milan, Italy) were used throughout the study.[33] A 1000 ± 5 mg L^{-1} standard solution containing REE and rhenium as an internal standard were purchased from BDH International (East Yorkshire, UK) and CPI International (Santa Rosa, CA, USA). Ultrapure water at 18.2 MΩ cm was produced by an EASYpureII (Thermo, Milan, Italy) ion-exchange system.

Soils were dried at 105 °C, gently crushed, and sieved (mesh width, 0.5 mm). Then, an aliquot of 250 mg was transferred to PFA microwave vessels and digested in a closed Mars Xpress microwave (CEM, Bergamo, Italy), with 4.5 mL of a 2:1 v/v mixture of HNO_3:H_2O_2. The temperature was increased from 20 to 200 °C in the first 10 min and then held at 200 °C for 50 min. After digestion, the samples were quantitatively transferred into graduated polypropylene tubes and diluted with 100 mL of ultrapure water. Reagent blanks containing only Milli-Q water, nitric acid, and hydrogen peroxide were measured to control the suitability of the reagents. Standard Reference Material (NIST SRM 2711a) Montana Soil II (CRM, distributed by the "National Institute of Standards and Technology" (NIST), Gaithersburg, USA) was processed in the same manner as soil samples.

Chemical Measurements

An Agilent Technologies 7500ce ICP-MS series spectrometer was selected for REE determinations adopting the following operative conditions: power, 1550 W; nebulizer gas flow, 1.00 L min^{-1}; auxiliary gas flow, 0.85 L min^{-1}; plasma gas flow, 15 L min^{-1}. The acquisition time was 180 s for each determination, which was made in triplicates. The better tuning conditions were determined on a solution containing ^{7}Li, ^{59}Co, ^{89}Y, ^{140}Ce, and ^{205}Tl isotopic masses, obtaining a minimal precision of 2%. Analysis of rare-earth elements requires careful management of interferences. Specifically, interferences may occur for ^{151}Eu, ^{153}Eu, ^{159}Tb, ^{157}Gd, ^{158}Gd, ^{160}Gd, ^{161}Dy, ^{166}Er, ^{171}Yb, ^{172}Yb, and ^{175}Lu. For Dy and Er, ^{163}Dy and ^{167}Er isotopes were chosen because they are practically free from interferences.[42] ^{171}Yb and ^{175}Lu are primarily interfered by BaC^{1+} species.[42] In this study, this type of interference was prevented by avoiding the use of hydrochloric acid. However, when all ions are interfered with, as in the case of gadolinium (^{157}Gd due to $CeOH^{+}$ and PrO^{+}; ^{158}Gd due to CeO^{+} and NdO^{+}; ^{160}Gd due to NdO^{+} and Dy^{+}) and europium (^{151}Eu and ^{153}Eu due to $^{135}Ba^{16}O^{+}$ and $^{137}Ba^{16}O^{+}$), it is not possible to completely eliminate the interferences. Nevertheless, it is possible to minimize them by controlling the formation of oxides and doubly charged species.[43−45] Collision cell technology was utilized to overcome spectral interferences using pure helium gas at a flow rate of 3.5 mL min^{-1}, and a kinetic energy discrimination (KED) barrier of 2 V was applied to minimize polyatomic interferences in the determination. Oxide and doubly charged ion interferences were monitored and controlled by maintaining CeO^{+}/Ce^{+} and Ce^{2+}/Ce^{+} ratios <0.5−1%. Similar strategies were adopted by Mnculwane,[46] Aceto et al.,[47] and Prohaska et al.[45]

It was challenging to ensure analytical validation for REE analyses because certified materials are only available for the total REE fraction, while there is a lack of certified materials for the pseudototal fraction. To assess data quality, an in-house reference material (RM) was prepared by adding a known quantity of REE to SRM 2711a, Montana II Soil. Repeatability and the degree of agreement between the expected and measured REE quantities were evaluated. The related results are reported in the Supporting Information (Table S3). REE determination was accomplished by measuring ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{158}Gd, ^{159}Tb, ^{163}Dy, ^{89}Y, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb, and ^{175}Lu isotopic masses, while ^{187}Re served as the internal standard. Each set of analyses was monitored by analyzing, within each batch, a reagent blank (mineralization mixture) and a quality control (QC) sample (RM). Data were considered acceptable when the REE levels in the reagent blank were below the limit of quantification (LOQ, values provided in the Supporting Information, Supplementary Methods, Table S3). RM values were acceptable if the REE concentration did not deviate by more than 10% from the expected RM value (reported in the Supporting Information, Supplementary Methods, Table S4).

Characterization of Soils

Soils were described according to the World Reference Base (WRB) guidelines.[48] All soil samples were collected in compliance with ISO 18400-201:2017,[49] air-dried, and passed through a sieve (2 mm mesh width) for laboratory analysis. Particle size distribution was determined with the pipet method, without the removal of carbonates. Soil pH was measured in 1:2.5 w/v soil/water mixtures.[50] Organic carbon was measured through the sulfochromic oxidation method,[51] while total carbonates were determined volumetrically.[52]

Data Processing

REE Data Normalization. REE distribution patterns were normalized according to the lithological reference, specifically the UCC, commonly used in soil studies.[17,18,27,53−59] Normalization was carried out using the following equation:[10,58]

$$[\mathrm{REE}^{*}]_{\mathrm{soil}} = \frac{\mathrm{REE}_{\mathrm{soil}}}{\mathrm{REE}_{\mathrm{UCC}}} \quad (1)$$

where REE* represents the normalized distribution, REE_{soil} is the concentration detected in the soil, and REE_{UCC} is the concentration in the upper continental crust.

Normalized patterns were plotted from La to Lu according to the increasing atomic number *Z*. Since the reference also reflects the Oddo−Harkins effect, the normalization cancels the effect out, resulting in a smooth curve that allows graphical identification of small differences in the fractionation of one REE from another.[27] This allows the visualization of the distribution patterns of individual REE,[54] facilitating comparisons of REE patterns graphically between sites.[56]

Chemometric Data Processing. Data were initially organized into data matrices having the 92 samples on the rows and the concentration of the 15 analyzed REEs (variables) on the columns, thus making 92 × 15 matrices. Two such matrices were prepared, one containing concentration normalized according to the UCC reference, as previously described, and one containing non-normalized data. Both normalized and non-normalized data were subjected to sum100 as the preprocessing strategy. Values for preprocessed variables $v_{i,\mathrm{p}}$ were computed as shown in the following equation:

$$v_{i,\mathrm{p}} = \frac{v_i}{\sum_{i=1}^{n} v_i} \times 100 \tag{2}$$

where v_i is the value for the ith variable and n is the total number of variables.

Principal Component Analysis. After preprocessing, data underwent chemometric analysis by means of PCA, a multivariate strategy used to identify the directions of maximum variability within a multivariate data set and thus condensate the information into few new variables called principal components (PCs).[60] The obtained variables result from a linear combination of the original variables, whose weight is indicated as loading. Loading interpretation provides an understanding of correlations between the original variables, making it possible to rule out patterns between variables themselves. The coordinates of the original samples in the PC space are described by the scores. Scores can be observed as such or used to plot the so-called score plot, a Cartesian graph with different PC scores on the axes representing the original samples projected in the PCA space through their score coordinates. This type of plot can be used to visualize clustering and trends between samples by projecting a multivariate data set onto a bivariate surface.

In the present study, PCA was initially applied on both normalized and non-normalized REE concentration profiles. The significant PCs were identified by observing the variance captured by progressive components (scree plot). Loadings of significant components were then analyzed as a tool to understand the correlations between elements and to infer anomalies of specific samples. Scores of principal components 1, 2, and 3 were then used to produce REE distribution maps where spots corresponding to the geographical coordinates of samples' collection are indicated by a dot colored according to its PC scores. The color is obtained by converting scores on the three lowest-order PCs into false-color red-green-blue (RGB) values. To do that, scores of each PC were first range-scaled between 0 and 1. Then, those values were used to create RGB triplets, with scores on PC1, PC2, and PC3 representing the intensity of the red, green, and blue colors, respectively. The so-obtained maps were then used to easily identify similarities and differences in REE distribution in various geographical areas. Afterward, PCA was applied on soil variables for some samples that had resulted in a similar color on the REE distribution map to observe whether comparable REE patterns correlated with similar soil conditions. In this case, the results were analyzed by means of a score plot.

RESULTS AND DISCUSSION

REE Normalized to UCC

Abundances of neighboring rare-earth elements appear to be highly correlated, preventing the use of the data as they are for chemometric data processing (Figure 1A,B). This apparent high correlation is due to a marked global intensity effect characterizing the REE patterns. Therefore, suitable mathematical pretreatments were applied to minimize the contribution of unwanted signal variations, which are not useful for the characterization of the system under study. The outcome of the preprocessing (Figure 1C) shows how the chosen strategy, i.e., sum100, enables the correction of the total intensity effect, giving the same importance to all samples within the data set. Moreover, the preprocessing enabled the individuation of correlation patterns within the data matrix, previously hidden (Figure 1D). In particular, LREE from La to Sm are positively correlated (correlation coefficient >0.5) between themselves, as underlined by the red color in the figure, and inversely correlated with HREE from Ho to Lu (correlation coefficient < −0.5), underlined by the blue color in the figure. HREEs from Ho to Lu are at the same time strongly positively correlated with themselves (correlation coefficient >0.6, red in the figure).

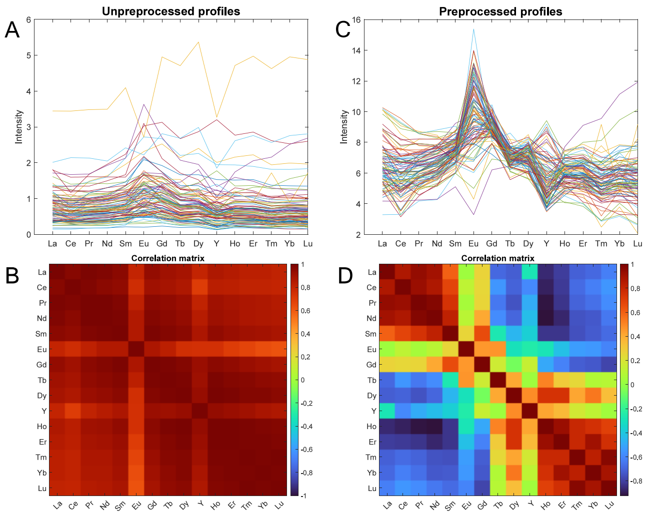

Figure 1. Effect of data processing. (A) UCC-normalized profiles before the application of row preprocessing. (B) Correlation matrix of UCC-normalized profiles before the application of row preprocessing. (C) UCC-normalized profiles after the application of sum100 preprocessing. (D) Correlation matrix of UCC-normalized profiles after the application of sum100 preprocessing.

After data preprocessing, the REE concentration profiles underwent PCA. Figure 2 shows the PCA scree plot, a graph depicting the percentage of explained variance (ordinate) as a function of the number of principal components (abscissa). From the figure, it is evident that the three lowest-order principal components contain the highest amount of variability and that after PC3, the variance explained by the components stabilizes. This is an indication that, after the third component, only nonstructured variability is modeled and, therefore, that subsequent PCs should be regarded as noninteresting.

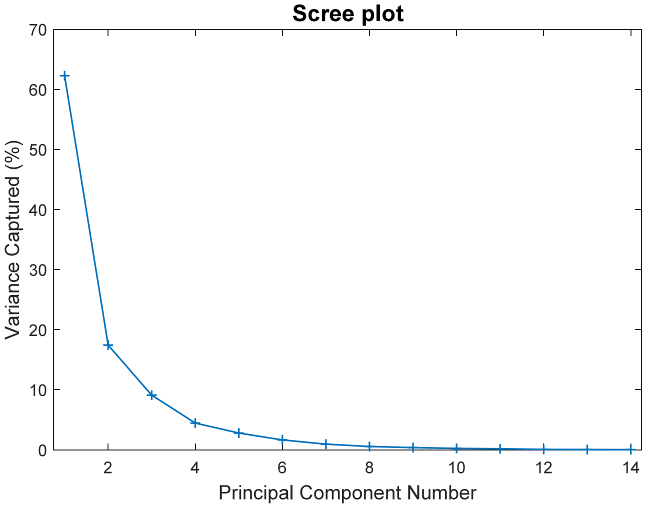

Figure 2. Scree plot: variance captured by the progressive principal components.

Figure 3 shows the relationships between the principal components (PCs) and the original descriptor variables encoded in the loading line plot. It can be observed that the loadings of the three lowest-order principal components

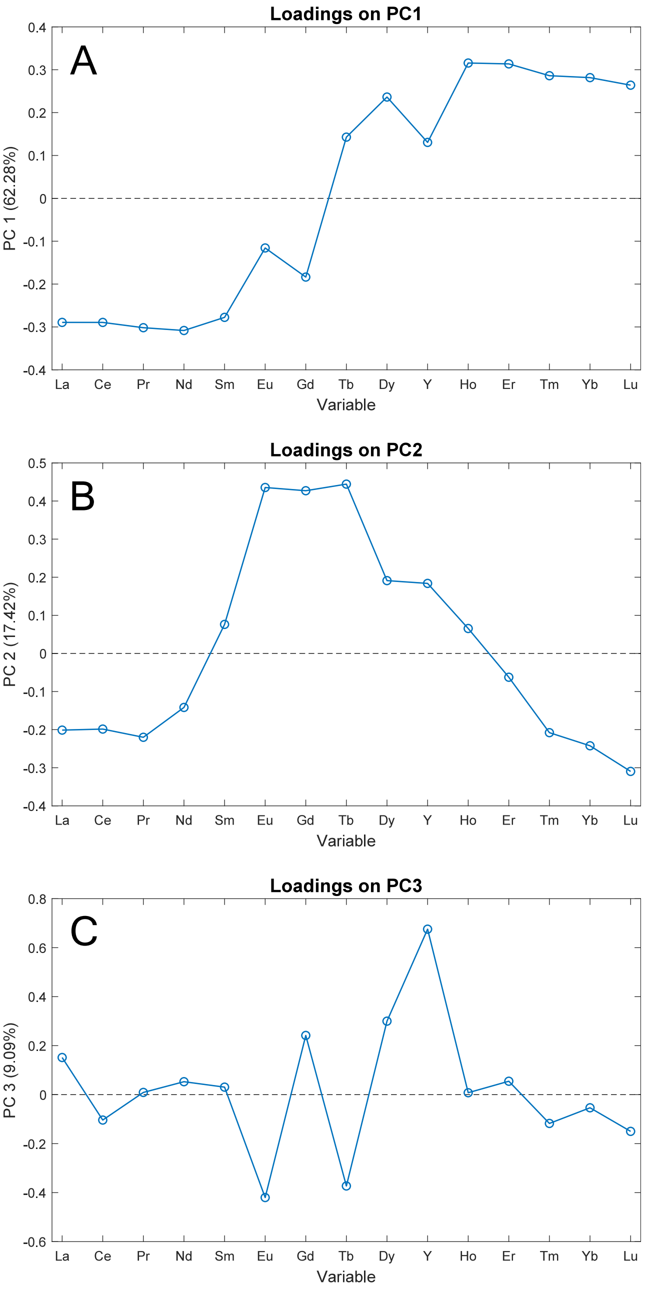

Figure 3. Loading line plots for the three lowest-order PCs (PC1−3 in plots A−C), which explain the 62.28, 17.42, and 9.09% variance, respectively.

consistently capture the trends associated with the variation of REE chemical properties. Specifically, PC1 describes the ratio between LREE and HREE, as evidenced by the fact that, on this component, all LREE have negative loadings, while all HREE have positive loadings. This means that samples whose LREE/HREE ratio is high, i.e., with a higher LREE relative concentration, will have negative scores on PC1; on the contrary, samples whose LREE/HREE ratio is low, i.e., with a higher relative concentration of HREE, will have positive scores in PC1. PC2 distinguishes the MREE group from the LREE and HREE groups. Indeed, for this component, loadings of MREE are positive, while those of HREE and LREE are negative. This means that samples with a higher relative abundance of MREE will show a positive value for the scores on PC2 and vice versa. Finally, PC3 highlights anomalies in Y, Eu, Gd, Dy, and Tb since those elements are the ones exhibiting the highest loading absolute values on this component. On the contrary, all other elements have loadings next to zero on PC3, and therefore, they will not have an influence on scores of this PC. Noteworthy, these results show for the first time that PCA is able to describe the REE profile reflecting their chemical properties, which are crucial for studying the unique behavior of REE in the environment. For example, enrichment or depletion of specific REE groups can serve as geochemical parameters to assess the influence of weathering processes and the mobility of elements in soils or groundwater.[10−12,53,61,62]

Coordinates of samples on the PCs (scores) were used to build a score map (Figure 4A) using an RGB false-color scale (PC1 = red channel; PC2 = green channel; PC3 = blue channel) directly overlaid onto a geographical map. This enables fast and easy visualization of the overall REE information, originally contained in 15 variables. After visual observation of the map, 5 pairs of samples with colors as similar as possible were visually chosen in different geographical areas to compare their REE patterns. In Figure 4B, it is possible to observe that the combination of the three lowest-order PC scores is sufficient to completely describe the REE pattern. Indeed, samples with similar colors are mirrored by comparable REE patterns. Moreover, the patterns are well-described by loadings, which can help in understanding the RGB coloring. For example, samples 89 and 90 (Figure 4B) present a pink/violet color derived from a combination of a high intensity for the red channel, a low intensity for the green one, and a medium intensity for the blue one. Red represents PC1, and, according to loadings, a high value on this channel refers to a pattern that presents higher values for HREE than for LREE. At the same time, according to the loadings on PC2, a low green intensity represents a sample with a concentration of MREE lower or

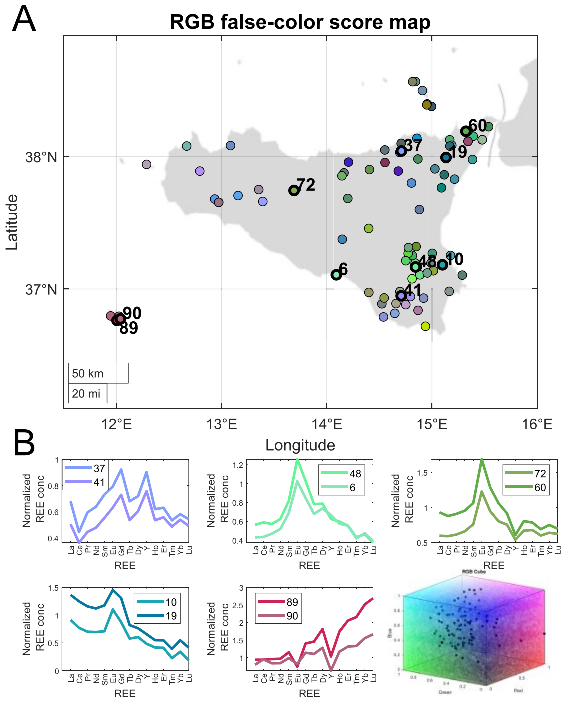

Figure 4. REE distribution geographical map (A) and REE concentration profiles of some exemplifying samples, chosen visually according to the color (B).

similar to that of LREE and HREE, while a medium blue intensity, according to loadings of PC3, suggests the presence of anomalies in Eu and Y. Indeed, all those characteristics can be observed in the REE patterns of the two samples reported in Figure 4B. Similar interpretations could be drawn for all selected pairs of samples. This underscores the effectiveness of treating the data as REE profiles using a multivariate unsupervised method while considering correlation patterns between all variables.

Figure 5 shows the score scatter plot obtained when PCA is applied to soil data on a subset of samples chosen according to chromatic similarities within the false-color score map (Figure 4A), as described above. The PCA identifies clusters with comparable colorations based on the similarity of samples in terms of REE profiles and soil characteristics. For example, the light green group shares the same parent material and exhibits an overall soil taxonomic uniformity.[48] Samples with blue-purple coloration, though differentiated on PC2, show a negative cerium anomaly, likely due to high organic matter values and a marl or limestone lithological origin, influencing Ce oxidation states. While these groups vary in carbonate content on PC2, they also exhibit slight LREE/HREE ratio differences, reflecting the varied complexing abilities of carbonate and organic matter with respect to REE.[6,10] In addition, PCA correlates samples (87, 88, 89, and 90 from Pantelleria and 85 and 36 from the Peloritani Mountains) that share similar REE patterns and agronomical features as a deficiency in carbonate and high sand content, despite their different geographical origins and lithological backgrounds. Notably, PCA easily identifies a subset of Pantelleria samples that share a common lithological lineage and distinctive agronomic parameters, characterized by a unique state shaped by centuries-old agricultural terracing resulting in soil taxonomic homogeneity as recognized by PCA.[48] However, the relationship with two samples from NW Sicily is less immediate, possibly due to parameters not considered in this study. Indeed, REE distribution can be affected by complexes with iron and manganese hydroxides and cycling by plants.[6,10,63,64]

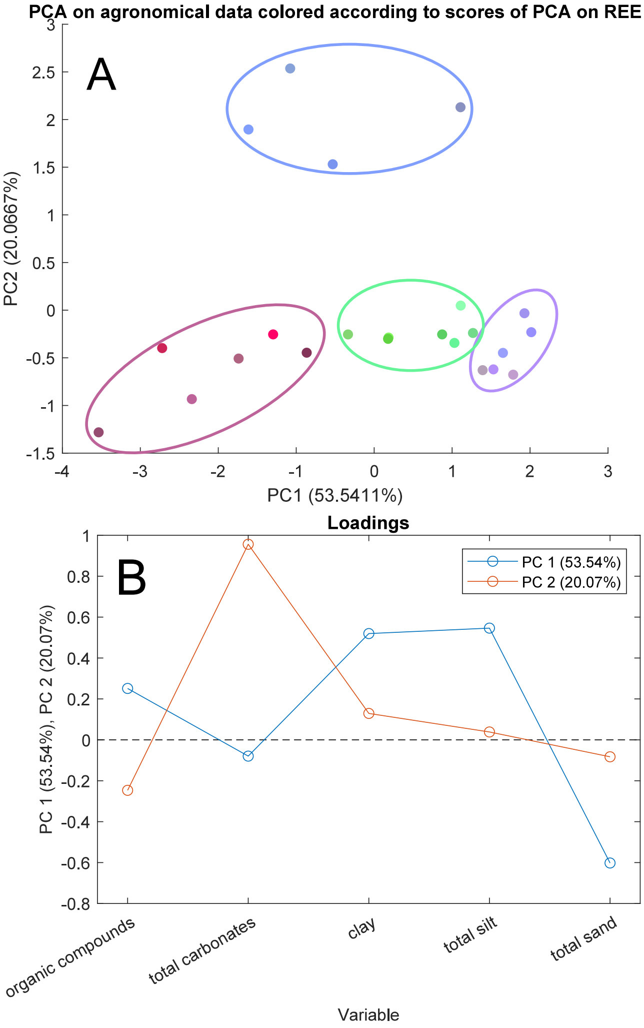

Figure 5. (A) Score scatter plots were obtained from PCA on soil data of a subset of data (REE profiles). Samples are colored according to the false RGB triplet obtained by the scores on PC1−3. (B) Loading profiles for soil variables on PC1 and PC2.

PCA results demonstrate that the proposed strategy facilitates the immediate recognition of distinctive features and that the color information is also related to agronomical variables to some extent, underscoring its effectiveness, even in the absence of prior knowledge. This suggests that under certain conditions, it is possible to identify characteristic areas estimating soil properties based on REE distribution. This may have important implications for studying soil evolution processes and environmental changes over time. Nevertheless, based on the evidence gathered so far, results of the present study demonstrate a significant potential to expand the analysis of REE distribution in relation to a broader range of soil characteristics, with potential implications for studying soil evolution processes and environmental changes over time.

REE Raw Data

As previously mentioned, one of the primary challenges in REE studies pertains to the interpretation based on the normalized distribution with respect to a lithological reference. To address this limitation, the feasibility of applying the proposed strategy to raw data was investigated. Figure 6 displays the loading line plot for the PCA performed on raw data after application of sum100 line preprocessing, revealing that it is still possible to differentiate the REEs based on their specific characteristics. Indeed, PC1 distinguishes the first four elements of the series, which are generally the most abundant, from the remaining ones. Therefore, samples with higher concentrations of these LREEs will present negative PC1 scores, and vice versa. Consequently, the behavior of PC1 scores obtained from raw data mirrors the tendency previously observed on the normalized data. On the other hand, PC2 focuses on LREE concentrations, which all have positive loadings, and differentiates them from Y, whose anomalies are described by this component, being the only REE with a negative loading. HREE does not affect this component, having loadings near to zero. Therefore, PC2 describes slightly different features when compared to the results on normalized data. PC3 again highlights anomalies in some of the REE, in particular Eu, Gd, and Y (Figure 6C). This component also shows positive loadings for HREE. Another interesting feature is that the amount of variance explained by the three lowest-order components results very similarly to what was observed when normalized data were processed, hence suggesting that PCA can individuate the distribution of the variability within the variables even in the absence of the normalization. Consequently, it can be concluded that the information contained in PC1, PC2, and PC3 obtained from raw data retains the structured information

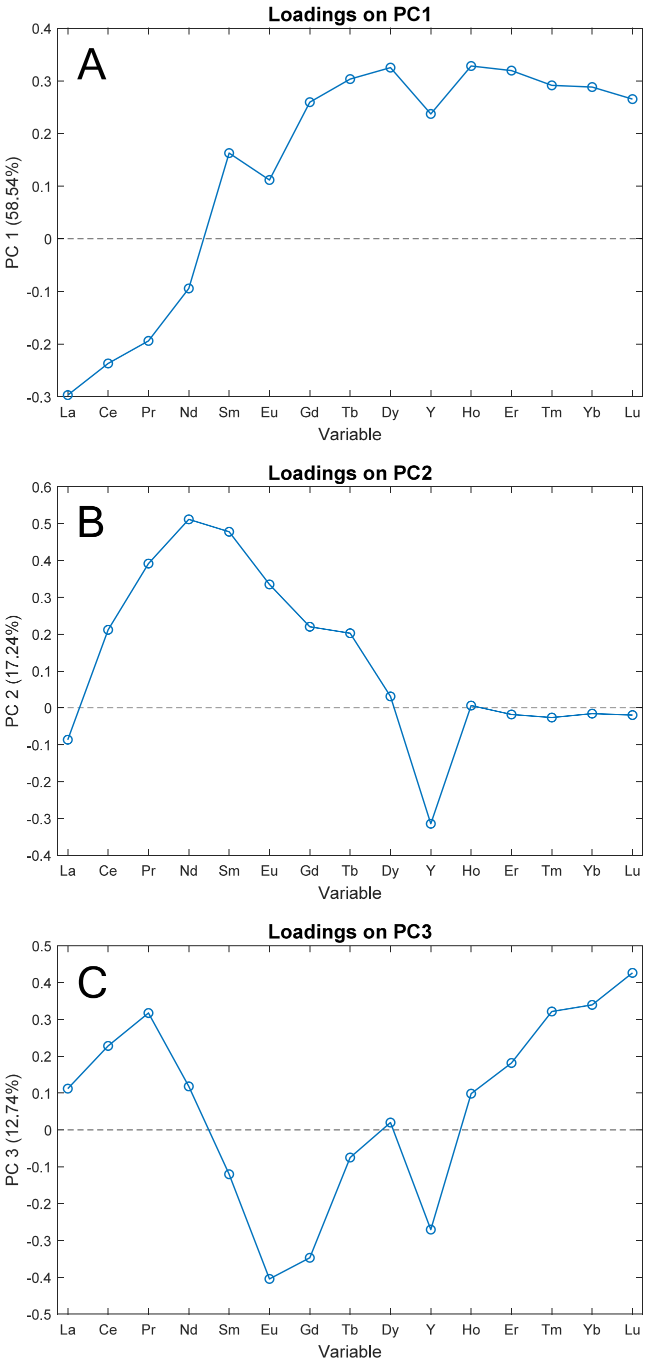

Figure 6. Loading line plots for the three lowest-order PCs (PC1−3 in plots A−C), which explain 58.54, 17.24, and 12.74% variance, respectively.

observed from normalized data, even though it is slightly differently distributed among the principal components.

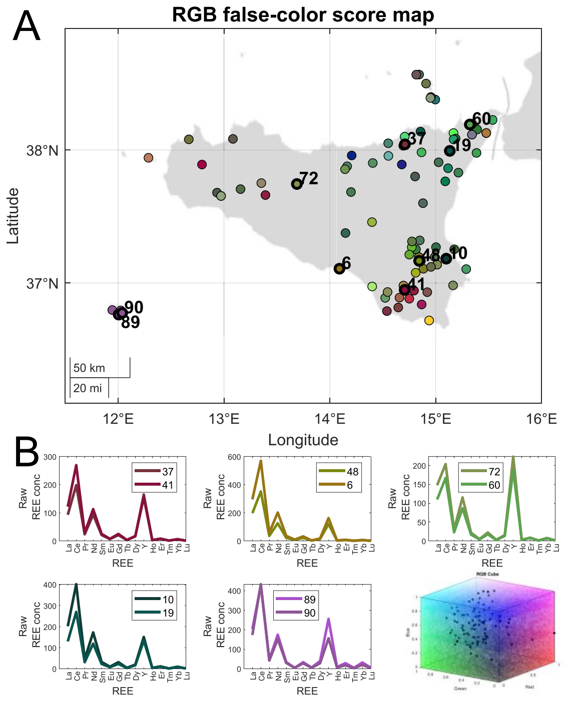

Figure 7. REE distribution geographical map (A) and REE raw concentration profiles of the exemplifying samples (B), chosen visually according to the color in Figure 4.

Also, in this case, scores were used to build a false-color RGB geographical map, shown in Figure 7A. Comparing it with Figure 4, even though color intensities and palettes are slightly different between the two figures (since the color depends on score numerical values), it is possible to observe that samples that presented the same color according to the PCA on normalized data maintain a similar coloration between each other also with this second processing. This is confirmed in Figure 7B, which represents the non-normalized REE patterns for the same samples previously selected for Figure 4B. Due to the huge difference in concentration among REE, slight changes are harder to be spotted when profiles of raw data are visually analyzed and compared to normalized profiles. However, it can be observed that samples with similar normalized patterns retain similar colors when they are not normalized, rendering, in practice, unnecessary the normalizing step when data interpretation is done directly from the map.

■ CONCLUSIONS

For the first time, it has been shown that PCA is a powerful tool for modeling and describing REE profiles, reflecting the chemical properties of these elements. This approach facilitates the description and interpretation of the distribution of the entire group, including the specific behavior of individual REE. The application of appropriate data preprocessing, namely, sum100, has an ancillary role in improving data interpretation and underlining correlations between variables.

Chemometric analysis of REE concentration profiles, both normalized and non-normalized, denoted that condensation of information into a few variables is beneficial in terms of interpretation and individuation of similarities and differences between samples. Data analysis of non-normalized data presents, in fact, similar results to normalized ones, even though normalization enhanced visual interpretation capabilities, accounting for systematic differences between REE concentrations. However, this feature should not be regarded as an issue since the use of chemometrics is proposed to avoid the visual interpretation stage. Indeed, the assessments made using normalized data are confirmed by non-normalized data, and this not only overcomes normalization-related issues but also supports the classical approach with a new methodological perspective.

In conclusion, the results presented in this study indicate that chemometric maps of REE enable a simple and direct evaluation of similarities and differences in the geographical region under study. Implementing an unsupervised system for differentiating REE distributions would facilitate the reconstruction of soil fingerprint maps based on their REE content. This will be crucial for REE traceability studies. Additionally, from an environmental perspective, establishing a reference system will enable assessment of potential changes over time, helping in distinguishing between natural and anthropogenic sources. This specific application also opens further research opportunities to explore how changes at particular points can be identified through color variations on these maps.

ASSOCIATED CONTENT

Data Availability Statement

All data will be made available upon request.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmeasuresciau.4c00084.

> (Table S1) Georeferencing of soil samples (latitude, LAT; longitude, LON) and description of pedological and lithological characteristics and land use extracted using Q-GIS software; (Table S2) REE values in soil samples and soil parameters (pH, organic carbon (OC), organic matter (OM), total carbonates (TCarb), clay, silt, and sand); REE* in the upper continental crust (UCC) from literature values (Wedepohl, 1995); (Supplementary Methods) data quality assurance for REE determination (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Marcella Barbera** data curation, formal analysis, investigation, writing - original draft; **Sara Gariglio** data curation, formal analysis, software, writing - original draft; **Cristina Malegori** conceptualization, methodology, supervision, writing - review & editing; **Paolo Oliveri** conceptualization, methodology, software, writing - review & editing; **Filippo Saiano** conceptualization, resources; **Riccardo Scalenghe** conceptualization, investigation; **Daniela Piazzese** funding acquisition, writing - review & editing.

Notes

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