



Communication Unravelling the Concentrations of Five Rare Earth Elements in Two Vineyard Red Soils

Raimundo Jiménez-Ballesta ^{1,*}, Francisco J. García-Navarro ², José A. Amorós ², Caridad Pérez-de-los-Reyes ² and Sandra Bravo ²

- ¹ Department of Geology and Geochemistry, Autónoma University of Madrid, 28049 Madrid, Spain
- ² High Technical School of Agricultural Engineers of Ciudad Real, University of Castilla-La Mancha, 13001 Ciudad Real, Spain

* Correspondence: profe.raimundojimenez@gmail.com

Abstract: The La Mancha region is a primary food production area in central Spain, with extensive zones used as vineyards. This article aims to present information about rare earth elements' (REEs) contents and deals with their distribution in two representative soil profiles (Alfisols) in this area. The presence of carbonates and a semiarid climate are its main characteristic environmental factors. Lanthanum (La), Cerium (Ce), Neodymium (Nd), Scandium (Sc) and Yttrium (Y) concentrations were determined using X-ray fluorescence spectroscopy (XRF). The results revealed the following maximum REEs' contents (mg·kg⁻¹): Ce 93.3, La 46.8, Nd 38.6, Y 25.5 and Sc 13.0. The REEs' concentrations in the two soil profiles were in the following order: Ce > La > Nd > Y > Sc. The application of fungicides and the addition of fertilisers in vineyards can increase the soil concentration of rare earths up to this region's normal background levels. According to the Geo-Accumulation Index (Igeo), soil samples were non-contaminated or slightly contaminated by REEs.

Keywords: lanthanides; contamination; calcareous soils; red soils; distribution; REE enrichment; pedogenesis



Citation: Jiménez-Ballesta, R.; García-Navarro, F.J.; Amorós, J.A.; Pérez-de-los-Reyes, C.; Bravo, S. Unravelling the Concentrations of Five Rare Earth Elements in Two Vineyard Red Soils. *Pollutants* **2023**, *3*, 114–122. https://doi.org/10.3390/ pollutants3010010

Academic Editor: Saddam Hussain

Received: 5 December 2022 Revised: 13 December 2022 Accepted: 5 January 2023 Published: 8 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

1. Introduction

It is generally understood that "soil contamination" refers to the presence in soil of a chemical or substance that is out of place and/or present at a higher-than-normal concentration that has adverse effects on any untargeted organism [1]. However, soil pollution cannot often be directly assessed or visually perceived, and it is sometimes controversial to establish its hidden origin.

Yaalon and Yaron [2] argue that human-induced changes in soil-forming processes should be considered to be an integral independent factor. This should be included as another recognised forming factor (the sixth one), termed metapedogenesis, which is the result of anthropogenic activity in soil. In line with this, and in addition to soil genesis, contamination processes can substantially deplete or enrich soil mineral metrics that originally derived from parent material.

Rare earth elements (REEs) is a term used to name a group of elements that, according to the International Union of Pure and Applied Chemistry (IUPAC), integrates a group of 15 elements with similar chemical characteristics from Lanthanum (La) to Lutetium (Lu), as well as Scandium (Sc) and Yttrium (Y). Sc and Y are considered to be rare earth elements since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. Due to the similar chemical properties of their trivalent ions, they act coherently in geochemical processes and are used as geochemical tracers [3,4], as well as in soil genesis [5].

Several soil parent materials are natural sources of certain elements, such as rare earth elements which, at high concentrations, can pose a risk to the environment and human health. It has been stated that REEs' contents in soils is largely influenced by bedrock and its physico-chemical properties [6]. However, in a broad sense, centuries of anthropogenic activities have resulted in a widespread soil contamination problem around the world [7–9]. The literature reports that REEs can be easily enriched by anthropic activities, such as mining, fertilisers and industrial activity [10,11]. Using pesticides not only causes environment impact [12] and heavy metals accumulation [13], but also increases the REE accumulation in agricultural soils. In this way, the contamination potential depends on dose and frequency of application and crops' ability to accumulate these contaminants, among other factors.

Bearing this fact in mind, it is worth wondering how we can discern one source or another to the enrichment in certain REEs in soil; that is, what importance can the different factors that may intervene in the enrichment/loss of these elements have? Therefore, the objectives of this study were to explore the content of REEs in two representative soil profiles in La Mancha (central Spain) and their distribution in vineyard land use to, in turn, shed light on this frequently hidden problem.

2. Materials and Methods

2.1. Study Site and Soil Sampling

The study site was located in the Mancha region in the Ciudad Real province (central Spain), (Figure 1). The area is far from cities and industrial operations, and agriculture is the main activity there. Of the most widespread and representative crops, vineyards are worth mentioning. It is also true that a potential mining deposit of REEs had been identified in a relatively close area (approximately 30 km) which, for various reasons, was not operational. The climate in this region is "dry Mediterranean"; the average annual temperature in the area is 14 °C, with an average rainfall value of 450 mm per year. According to the Köppen–Geiger classification, the climate in this region is of the Csa type, a "temperate" climate, with a markedly dry summer.





Figure 1. Location map of study area and partial view of the vineyard landscape (Moral de Calatrava, Ciudad Real).

The soil profiles examined in this study were part of the well-developed soil profiles of the region, represented mainly by Alfisols, although Inceptisols and Entisols were also present in large proportions [14]. The two soil profiles were dug from under land used as vineyards (Figure 2), for full descriptions and sampling in January 2011.



Figure 2. Soil profile photographs. (a) Profile 1, (b) profile 2.

The main pedological features of the two investigated soil profiles are shown in Table 1, along with their classification according to the FAO System [15] and Soil Taxonomy [16].

Table 1. General and pedological characteristics of the investigated soil profiles. Soil type according to [15] and Soil Survey Staff 2014 [16].

| Profile | Location (Coordinates) | Parent Material | Slope | Drainage | Morphology | Soil Type (FAO/Soil Taxonomy) |
|---------|--|--|----------------------|----------------------------|--------------------|--|
| 1 | Moral de Calatrava 38°43'47.6″ (N) 03°35'06.4″ (W) | Quarcitic and calcareous sediments | Slightly inclined 4% | Moderately well-drained | Ap-Bt-Bt/ Ck-Ck | Calcic Luvisol (Profondic, Rhodic)/ Calcic Rhodoxeralf |
| 2 | Moral de Calatrava 38°43'23.7" (N) 03°34'50.3" (W) | Fluvial sediments | Flat 1% | Imperfectly drained | Ap-Bt-C | Haplic Luvisol (Profondic, Novic)/ Typic Haploxeralf |

2.2. Analytical Procedures

Soil samples were air dried at room temperature, homogenised and sieved (<2 mm). Then, samples were pulverised with an agate mortar and pestle, and sieved again to separate a 0.063 mm size to obtain a homogenous fraction with which REEs were associated (also Ti and Zr elements). Portable X-ray fluorescence spectroscopy (XRF) was applied because it has been used to study the contents of chemical elements in various media, particularly soils [17,18]. pH was potentiometrically measured in 1:2.5 soil:water suspension, and in KCl (1 mol/L) solution at the 1:2.5 rate [19]. Clay proportions were determined using the hygrometer method [20]. Organic matter was determined via dichromate oxidation [21]. Finally, calcium carbonate was determined using a calcimeter [22].

3. Results and Discussion

3.1. General Parameters Data

The analytical data of the examined samples are presented in Table 2. The result obtained from soil samples determined that the pH range was between 8.2 and 8.7 in Profile 1, and between 8.2 and 8.3 in Profile 2, which fall in the slightly alkaline soils category. Soil electrical conductivity was a measure of soluble salt ions, with values of samples ranging from 0.06 to 0.17 dS/m. Hence, there was no concentration of salts. Organic matter is an important parameter that affects soil quality and agriculture sustainability; contents hardly varies and is low at <2.9%, as befits a semi-arid region. In such regions, calcium carbonate accumulation is a common process, and one frequently accompanied by argillic horizon formation (especially at stabler levels). The contrasts observed along the two profiles in the carbonate and clay contents determined the appearance of calcic and argillic horizons.

Table 2. Physico-chemical properties of the studied soil profiles.

| Profile | Horizon | Depth (cm) | pH H ₂ O (1:2.5) | pH KCl (1:2.5) | CaCO ₃ (%) | E.C. (dS/m) | O.M. (%) | Clay (%) | Ti/Zr |
|---------|---------|---------------|--------------------------------|-------------------|--------------------------|----------------|-------------|-------------|-------|
| 1 | Ар | 0–12 | 8.2 | 7.5 | 8.0 | 0.12 | 2.9 | 12.2 | 11.9 |
| | Bt | 12-42 | 8.3 | 7.5 | 5.5 | 0.09 | 1.3 | 38.2 | 12.4 |
| | Bt/Ck | 42-81 | 8.6 | 7.9 | 30.7 | 0.15 | 0.2 | 31.4 | 13.2 |
| | Ck | >81 | 8.7 | 7.8 | 40.7 | 0.14 | 0.0 | 36.2 | 16.2 |
| 2 | Ар | 0–31 | 8.3 | 7.7 | 0.8 | 0.08 | 1.9 | 14.2 | 14.5 |
| | Bt | 31–4 | 8.2 | 7.4 | 3.6 | 0.06 | 1.3 | 32.2 | 12.7 |
| | С | >74 | 8.2 | 7.4 | 10.2 | 0.17 | 0.2 | 32.2 | 15.1 |

3.2. Contents and Distribution of the Five REEs Analysed in Depth in the Two Soil Profiles

The average contents and vertical distributions of the REEs in two soil profiles are presented in Figure 3; they specifically varied within ranges (expressed as $mg \cdot kg^{-1}$): Ce 83.6–43.3, La 43.9–32.0, Nd 23.0–38.6, Y 19.2–14.8 and Sc 11.3–10.8 in one soil profile; Ce 93.3–83.3, La 46.8–41.7, Nd 16.2–13.3, Y 25.5–21.1 and Sc 13.0–8.0 in the other soil profile. Vertically, REEs' contents (except for Sc) tended to decrease in depth in both soil profiles; that is, REEs' contents in soil profiles decreased with the depth from surface horizons to deeper horizons.

Several studies have shown that REEs' contents in soils is influenced by parent material, pedogenic processes and soil characteristics such as texture, organic matter and clay mineralogy [4,23]. In the study case, as organic matter content was low in both soil profiles, its effect seemed negligible. Clay content was very high. In addition, several other sources can be involved in explaining the different REEs' contents in soils. Aide and Aide [5] stated that there are numerous pathways for REE migration that involve (1) plant uptake; (2) erosion; (3) the leaching of REE inorganic complexes in percolating water; (4) organic complexation, which may result in either REE mobilisation or immobilisation; (5) lessivage (eluviation–illuviation of clay with co-adsorbed REEs); (6) the removal of REEs from percolating water being attributed to precipitation reactions; (7) REE adsorption via inorganic colloids (phyllosilicates and oxyhydroxides).

It has been revealed that REEs are mobile during soil formation and weathering processes [6,24]. For this reason, the degree of the uniformity of the pedological materials in soil profiles was first established. In this way, the use of stable minerals (or the chemical elements they contain) are considered to resist weathering in soils, and have been used to estimate the degree of uniformity material. In this sense, Alexander et al. [25] and Chapman and Horn [26] proposed Zr and Ti. The results that appear in Table 2 suggest a similar Ti/Zr ratio in each profile and, therefore, allochthonous contribution was irrelevant [27].



Figure 3. Vertical variation in REE concentration in each soil profile.

From the obtained results, it can be established that there was an appreciable degree of uniformity between the soil materials in each profile. Specifically, in Profile 1, they varied between 11.9 and 16.2, and between 12.7 and 15.1 in Profile 2. However, the slight enrichment in certain horizons should partially be attributed to the incidence of a mixture of parent materials (rocks) with different contents. If we bear in mind that REEs can be absorbed in soils through clay type and content [28–32], then the preferential accumulation observed in more clayey horizons (Bt type) can be justified. Moreover, as the soil pH values for all of the samples were neutral to moderately basic, this could contribute to REEs' immobility and accumulation (as originally assumed). This statement agrees with Aide and Smith, [33], who investigated Paleustoll soils in south-central Texas and observed that

some REEs' concentrations were higher on argillic horizons than on surface horizons. They proposed that the clay fraction on the argillic horizon accumulated these REEs.

In light of this, the most important anthropogenic source of REEs entering soil for some authors has been associated with the manufacture and use of organic and mineral (especially phosphate) fertilisers [29,34,35]. Thomas et al. [4,36] revealed that a wide REE distribution depended on the application of REE-based pesticides and fertilisers while performing farming activities. So, in addition to natural factors, anthropogenic activities can also significantly influence REE distribution, especially on surface and subsurface horizons (Ap and Bt types). REEs are extensively applied in fertilisers given their function of improving crop quality and yields [29]. Thus, in agricultural areas, the external entrance of the main REEs can be caused by applying phosphate fertilisers [37,38]. This is an accepted notion that can occur because the composition of phosphatic rocks can present high REE concentrations.

The superimposition of allochthonous materials against differentiation by both weathering and pedogenetic processes imposes an extra difficulty for interpreting contrasting distributions of elements throughout a profile [39]. This is the case for Profile 2, located in the middle of a river valley.

Therefore, the distribution patterns of the REEs in the present study suggest that parent material and pedogenesis are more important factors than using REE-based fertilisers in the study area because fertilisers are probably used at low doses.

3.3. Environmental Evaluation

In order to evaluate possible REE contamination in the studied soils, the Igeo was determined for each sampling point using the equation described by Müller et al. [40]:

$$Igeo = Log_2 \frac{Cs}{1.5 \times Bn}$$

where *Igeo* is the geo-accumulation index; *Cs* is the measured concentration of REEs in soil and *Bn* is the background REE level. Factor 1.5 was used to correct possible variations in the background values. The regional geochemical background level established by Jiménez Ballesta et al. [41] was employed in the calculations. *Igeo* is classified as class 0 (*Igeo* < 0) non-contamination, 1 (0 < *Igeo* < 1) slight contamination, 2 (1 < *Igeo* < 2) low contamination, 3 (2 < *Igeo* < 3) moderate contamination, 4 (3 < *Igeo* < 4) heavy contamination, 5 (4 < *Igeo* < 5) high contamination and 6 (*Igeo* > 5) extreme contamination.

The contamination assessment (Table 3) showed none or slight enrichment in the REEs' contents of topsoils (Nd and La), which was why the ecological risk associated with REE contamination was considered to be nil or low.

| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | 50 |
|---|-------|
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | -1.63 |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | -1.61 |
| | -1.67 |
| Ck = -1.05 = -0.58 = -1.34 = -0.94 | -1.66 |
| Ap -0.01 -1.37 0.18 -0.41 | -2.10 |
| 2 Bt 0.05 -1.09 0.31 -0.16 | -1.40 |
| C -0.11 -1.34 0.15 -0.43 | -1.52 |

Table 3. The Igeo values obtained for each horizon.

Pedogeochemistry studies about soil-REE contamination related to agricultural inputs are relatively scarce, especially when compared with studies for some environmental trace elements [42,43]. Therefore, this work represents a new contribution in this line.

Exploring REEs' distributions in soil profiles is essential for understanding how natural and anthropogenic factors influence REEs' geochemical behaviours. This study examined the data of two representative soil profiles in La Mancha (central Spain) and revealed differences between the two profiles (and in vertical distribution) in total REE terms. The following maximum REEs' contents were found (expressed as $mg \cdot kg^{-1}$): Ce 93.3, La 46.8, Nd 38.6, Y 25.5 and Sc 13.0. The REEs' concentrations in the two soil profiles depend on the composition of source rocks, weathering and other pedological processes (e.g., increased clay content). It was found that the REEs' concentrations in the upper soil horizons were higher than in deeper soil horizons, which were probably affected by the application of fungicides and the addition of fertilisers to vineyards. Nevertheless, based on the Igeo, soil samples appeared to be either non-contaminated or slightly contaminated with REEs.

Author Contributions: R.J.-B. conceived and designed this study; F.J.G.-N., R.J.-B., C.P.-d.-l.-R. and J.A.A. participated in the collection of soil samples; software, S.B.; formal analysis, S.B.; writing—original draft preparation, R.J.-B. Writing—review and editing R.J.-B., F.J.G.-N. and S.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by "Denominación de origen Valdepeñas" (Denomination of Origin), grant number UCTR180065.

Data Availability Statement: The data and materials will be made available from the corresponding author(s) upon reasonable request.

Acknowledgments: The authors wish to acknowledge the financial support given by the "Denominación de Origen Valdepeñas", (Denomination of Origin).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Rodríguez-Eugenio, N.; McLaughlin, M.; Pennock, D. Soil Pollution: A hidden reality; FAO: Rome, Italy, 2018; p. 142.
- Yaalon, D.H.; Yaron, B. Framework for man-made soil changes-an outline of metapedogenesis. Soil Sci. 1966, 102, 272–277. [CrossRef]
- 3. Brookins, D.G.; Lipin, B.R.; Mckay, G.A. Geochemistry and mineralogy of rare earth elements. *Rev. Mineral.* 1989, 21, 201–225.
- 4. Laveuf, C.; Cornu, S.; Juillot, F. Rare earth elements as tracers of pedogenetic processes. *Compt. Rendus Geosci.* 2008, 340, 523–532. [CrossRef]
- 5. Aide, M.T.; Aide, C. Rare earth elements: Their importance in understanding soil genesis. ISRN Soil Sci. 2012, 1–11. [CrossRef]
- 6. Tyler, G. Rare earth elements in soil and plant systems—A review. Plant Soil 2004, 267, 191–206.
- Bundschuh, J.; Litter, M.I.; Parvez, F.; Román-Ross, G.; Nicolli, H.B.; Jean, J.-S.; Liu, C.-W.; López, D.; Armienta, M.A.; Guilherme, L.R.G.; et al. One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries. *Sci. Total Environ.* 2012, 429, 2–35. [CrossRef]
- European Environment Agency (EEA). Progress in Management of Contaminated Sites. 2014. Available online: https:// www.eea.europa.eu/data-and-maps/indicators/progress-in-management-of-contaminated-sites/progress-in-managementofcontaminated-1 (accessed on 12 November 2022).
- 9. SSR. Soil Contamination in West Africa | Environmental Remediation | Pollution. 2010. Available online: https://www.scribd. com/doc/71599035/SoilContamination-in-West-Africa (accessed on 12 November 2022).
- Wu, T.; Bi, X.; Li, Z.; Sun, G.; Feng, X.; Shang, L.; Zhang, H.; He, T.; Chen, J. Contaminations, sources, and health risks of trace metal (Loid)s in street dust of a small city impacted by artisanal Zn smelting activities. *Int. J. Environ. Public Health* 2017, 14, 961. [CrossRef]
- 11. Zhang, F.; Yamasaki, S.; Kimura, K. Rare earth element content in various waste ashes and the potential risk to Japanese soils. *Environ. Int.* **2001**, *27*, 393–398. [CrossRef] [PubMed]
- Arunrat, N.; Sereenonchai, S.; Chaowiwat, W.; Wang, C.; Hatan, R. Carbon, Nitrogen and Water Footprints of Organic Rice and Conventional Rice Production over 4 Years of Cultivation: A Case Study in the Lower North of Thailand. *Agronomy* 2022, *12*, 380. [CrossRef]
- Omeje, K.O.; Ezema, B.O.; Okonkwo, F.; Onyishi, N.C.; Ozioko, J.; Rasaq, W.A.; Sardo, G.; Okpala, C.O.R. Quantification of Heavy Metals and Pesticide Residues in Widely Consumed Nigerian Food Crops Using Atomic Absorption Spectroscopy (AAS) and Gas Chromatography (GC). *Toxins* 2021, 13, 870. [CrossRef]

- 14. Amorós, J.A.; Bravo, S.; García-Navarro, F.J.; Pérez-de-los-Reyes, C.; Chacón, J.L.; Martínez, J.; Jiménez-Ballesta, R. *Atlas de Suelos de Castilla-La Mancha*, 1st ed.; Globalcaja and Universidad de Castilla-La Mancha: Ciudad Real, Spain, 2015; p. 318.
- 15. IUSS Working Group WRB. World Reference Base for Soil Resources 2015. In *International Soil Classification System for Naming Soils and Creating Legends for Soil Maps;* World Soil Resources Reports No. 106; FAO: Rome, Italy, 2015; Available online: http://www.fao.org/3/i3794en/I3794en.pdf (accessed on 12 November 2022).
- Soil Survey Staff. Key to Soil Taxonomy, 12th ed.; USDA-Natural Resources, Conservation Service: Washington, DC, USA, 2014; p. 379.
- 17. Tepanosyan, G.; Norik, H.; Lilit, S. Revealing XRF data quality level, comparability with ICP-ES/ICP-MS soil PTE contents and similarities in PTE induced health risk. *Environ. Geochem. Health* **2022**, *44*, 1739–1750. [CrossRef] [PubMed]
- 18. Ravansari, R.; Wilson, S.C.; Tighe, M. Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method. *Environ. Int.* 2020, *134*, 105250. [CrossRef]
- Peech, M.; Alexander, L.T.; Dean, L.A.; Reed, J.F. Methods of Soil Analysis for Soil Fertility Investigations, 1st ed.; United States Department of Agriculture: Washington, DC, USA, 1947; p. 25.
- Gee, G.W.; Bauder, J.W. Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods, 2nd ed.; ASA-SSSA: Madison, WI, USA, 1986; pp. 383–411.
- 21. Nelson, D.W.; Sommers, L.E. Total Carbon, Organic Carbon and Organic Matter; ASA-SSSA: Madison, WI, USA, 1982; pp. 539–579.
- Loeppert, R.H.; Suarez, D.L. Carbonate. In *Methods of Soil Analysis. Part 3. Chemical Methods*; Sparks, D.L., Ed.; ASA and SSSA: Madison, WI, USA, 1996; pp. 437–474.
- 23. Laveuf, C.; Cornu, S. A Review on the Potentiality of Rare Earth Elements to Trace pedogenetic processes. *Geoderma* 2009, 154, 1–12.
- 24. Ohlander, B.; Land, M.; Ingri, J.; Widerlund, A. Mobility of rare earth elements during weathering of till in northern Sweden. *Appl. Geochem.* **1996**, *11*, 93–99.
- 25. Alexander, J.D.; Beavers, A.H.; Johnson, P.R. Zirconium content of coarse silt in loess and till of Wisconsin age in northern Illinois. *Soil Sci. Soc. Am. Proc.* **1962**, *26*, 189–191. [CrossRef]
- 26. Chapman, S.C.; Horn, M.E. Parent material uniformity and origin of silty soils in northwest Arkansas based on zirconium-titanium contents. *Soil Sci. Soc. Am. Proc.* **1968**, *32*, 265–271. [CrossRef]
- 27. García Navarro, F.J.; Amorós Ortiz-Villajos, J.A.; Sánchez Jiménez, C.; Jiménez Ballesta, R. Red Soil Geochemistry in a semmiarid mediterranen environment and its suitability for vineyards. *Environ. Geochem. Health* **2011**, *33*, 279–289. [CrossRef]
- 28. Alloway, B.J. Heavy Metals in Soils; Blackie Academic & Professional: Glasgow, UK, 1990.
- 29. Pang, X.; Li, D.; Peng, A. Application of rare-earth elements in the agriculture of China and its environmental behavior in soil. *Environ. Sci. Pollut. Int. Res.* 2002, 9, 143–148. [CrossRef]
- 30. Jones, D.L. Trivalent metal (Cr, Y, Rh, La, Pr, Gd) sorption in two acid soils and its consequences for bioremediation. *Eur. J. Soil Sci.* **1997**, *48*, 697–702. [CrossRef]
- 31. Piasecki, W.; Sverjensky, D.A. Speciation of adsorbed yttrium and rare earth elements on oxide surfaces. *Geochim. Cosmochim. Acta* **2008**, 72, 3964–3979. [CrossRef]
- Caspari, T.; Bäumler, R.; Norbu, C.; Tshering, K.; Baillie, I. Geochemical investigation of soils developed in different lithologies in Bhutan, Eastern Himalayas. *Geoderma* 2006, 136, 436–458. [CrossRef]
- 33. Aide, M.T.; Smith, C.C. Soil genesis on peralkaline felsics in Big Bend National Park, Texas. Soil Sci. 2001, 166, 209–221. [CrossRef]
- 34. Volokh, A.A.; Gorbunov, A.V.; Gundorina, S.F.; Revich, B.A.; Frontasyeva, M.V.; Pal, C.S. Phosphorus-fertilizer production as a source of rare-earth elements pollution of the environment. *Sci. Total Environ.* **1990**, *95*, 141–148. [PubMed]
- 35. Hu, Z.; Haneklaus, S.; Sparovek, G.; Schnug, E. Rare earth elements in soils. *Commun Soil Sci. Plant Anal.* 2006, 37, 1381–1420. [CrossRef]
- 36. Thomas, P.J.; Carpenter, D.; Boutin, C.; Allison, J.E. Rare earth elements (REEs): Effects on germination and growth of selected crop and native plant species. *Chemosphere* **2014**, *96*, 57–66.
- 37. Turra, C.; Fernandes, E.A.N.; Bacchi, M.A. Evaluation on rare earth elements of Brazilian agricultural supplies. *J. Environ. Chem. Ecotoxicol.* **2011**, *3*, 86–92.
- 38. Ramos, S.J.; Dinali, G.S.; Oliveira, C.; Martins, G.C.; Moreira, C.G.; Siqueira, J.O.; Guilherme, L.R. Rare Earth Elements in the Soil Environment. *Curr. Pollut. Rep.* **2016**, *2*, 28–50. [CrossRef]
- Price, J.R.; Velbel, M.A. Chemical weathering indices applied to weathering profiles developed on heterogeneous felsic metamorphic parent rocks. *Chem. Geol.* 2003, 202, 397–416.
- 40. Müller, G. Index of geo-accumulation in sediments of the Rhine River. *GeoJournal* 1969, 2, 108–118.
- 41. Jiménez-Ballesta, R.; Conde-Bueno, P.; Martín-Rubí, J.A.; García-Giménez, R. Pedo-geochemical baseline content levels and soil quality reference values of trace elements in soils from the Mediterranean (Castilla la Mancha, Spain). *Cent. Eur. J. Geosci.* **2010**, *2*, 441–454. [CrossRef]

- 42. Silva, F.B.V.; Nascimento, C.W.A.; Alvarez, A.M.; Araújo, P.R.M. Inputs of rare earth elements in Brazilian agricultural soils via P-containing fertilizers and soil correctives. *J. Environ. Manag.* **2019**, 232, 90–96.
- 43. Ferreira, M.D.S.; Fontes, M.P.F.; Bellato, C.R.; Marques Neto, J.D.O.; Lima, H.N.; Fendorf, S. Geochemical signatures and natural background values of rare earth elements in soils of Brazilian Amazon. *Environ. Pollut.* **2021**, 277, 116743. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.