A tool to assure the geographical origin of local food products (glasshouse tomatoes) using labeling with rare earth elements

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Abstract

BACKGROUND: Trace element fingerprinting has been widely used for identification of provenance of regional food. In the case of products from conventional agriculture, it is expected that the elemental composition will comply with that of the commercially available substrate of the plants. Therefore, for products without a direct relationship with the regional soil the region-specific differences in elemental composition are no longer recognizable. The idea of this work is the labeling of tomatoes with rare earth elements (REE) in the ultra-trace range for food authentication.

RESULTS: Labeling of tomatoes was carried out either by watering the soil with Nd- and Er-spiked water or by adding these elements as solid oxides to the soil. In both cases enrichment of Nd and Er relative to the control group was detected in tomato fruits and leaves using inductively coupled plasma–mass spectrometry. Tomato plants rapidly absorb the dissolved REE from the irrigation water, and watering for a short period just before ripeness is sufficient to induce REE labels.

CONCLUSION: Labeling with trace amounts of REE could potentially be used to assure the provenance of tomatoes of local origin and separate these from products of foreign origin.

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Keywords: food authentication; tomatoes; rare earth elements; chemical labeling; ICP-MS

INTRODUCTION

The globalization of food markets and, consequently, the ease in the circulation of foodstuffs may be associated with an eventual loss of the geographic origin of foods. This fact may expose consumers to risks because imported products often come from countries where quality and safety rules are less stringent than those adopted in countries where EMEA (European Agency for the Evaluation of Medicinal Products) and FDA (US Food and Drug Administration) directives are followed.1 Consumers increasingly ask for regional products and demand a precise indication of origin on the individual items. The reasons for this increasing interest of consumers are varied, following the global trend for organic and healthy products to a concern about animal welfare and environmentally safe methods of production. The trend is towards local products, in order to reduce the energy footprint and pollution through transportation. As a result, local products around the world have regained an appreciation and are bringing wealth to local producers.2

Authentication of food products is of primary importance for consumers, honest farmers and producers. For consumers, confirming the geographical origin assures quality and organoleptic and nutritional characteristics. From an economic point of view, product authentication is fundamental to prevent unfair competition, which can affect regional and even national economies.3 A lack of scientific methods to verify the geographical denomination is an essential reason why some large producers can disguise the origin or can afford to label products incorrectly.

The growing concern of consumers stimulated the development of chemical analytical methods for determining the geographical origin of food and other agricultural products. These new methods are able to improve the current method of controlling the origin by the examination of written documentation and to effectively guarantee the origin of regional products.

Trace and rare earth element fingerprinting, especially in combination with stable and/or radiogenic isotope signatures, has been widely used for identification of provenance of regional food products. This use of a trace element fingerprint, combined with statistical techniques such as multivariate data analysis, was successfully applied for the classification of products such as dairy products, beverages, wine, meat, vegetable oils, honey, fruit and

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vegetables, peas, grain, etc., according to their origin. This holds especially true for those products that have a direct relationship with the autochthonous soil, and have undergone no or little further processing. In these special cases, the region-specific distribution of the trace elements, transmitted from the soil into the plant, is reflected in the products. Furthermore, the fingerprint is passed on to animals fed by locally or regionally grown pasture. It has been proven that plant products reflect the composition of the trace elements of the soil on which they are grown or cultured.

Additionally, trace element availability depends on various factors, e.g. soil pH, humidity, clay mineralogy and humic complexes. Consequently, the bioavailable nutrients underlying the soils can give us direct information about their geographical origin. Based on this observation, a procedure taking advantage of multi-elemental compositional regional variations was developed for the Austrian regional specialty product ‘pumpkin seed oil’. Also, in recent years, many studies have focused on differences in the elemental composition between ‘organic’ and conventional food products.

However, products – in particular from conventional agriculture or mass production (glasshouse vegetables, milk, chicken, eggs, or lamb meat) – are not expected to exhibit region-specific differences. Glasshouse vegetables grown on a commercial substrate lack the typical soil/plant relationship suitable as fingerprint for tracing the origin. Similarly, animals brought up on commercial animal feed lose the regional context. Thus it is not possible to guarantee the origin of such products based on a region-specific trace element fingerprint. Nevertheless, knowledge of the origin of conventionally grown vegetables is of great interest to consumers, especially since most vegetables such as tomatoes, bell peppers and cucumbers come from glasshouses from any climate zone. Particularly in these cases, it is important to guarantee the regionality of the products in order to ensure transparency and allow an informed choice for the consumer.

The objective of the present study was to develop a chemical analytical method to secure the authenticity of glasshouse tomatoes grown locally, where there is no direct connection between regional soil and fruit. The focus of this pilot project was to examine the possibility of securing the food origin by a potential marking with trace elements, as used in this case, with rare earth elements (REE). It is of utmost importance to choose a marker with low natural background levels in order to be able to induce a specific and detectable label. REE are well suited for the labeling of food products due to their low toxicity and the low amount required for labeling because of the generally low concentration level in food. In the literature only a few studies are mentioned that have investigated the feasibility of using REE to label fish. Atlantic salmon scales were successfully labeled by supplementation of REE to the fish diet for a short period of time, even though the mechanism of their uptake remains unclear.

We wanted to investigate whether spiking the soil with low concentrations of selected trace elements would show up in the tomato plant (leaves and fruit). We were also interested in determining in which form (dissolved or solid) the REE could be introduced into the soil and also what concentration levels were necessary to achieve a significant enrichment in the samples. Since the concentrations of REE in food are very low, the expected range of REE in food is in the μg kg⁻¹ or ng L⁻¹ range, only the most sensitive analytical techniques can be used to determine these low element concentrations. Inductively coupled plasma–quadrupole mass spectrometry (ICP-QMS) is one of the most commonly used techniques for the determination of REE mass fractions in biological samples because of its ability to carry out rapid multi-element detection over a wide concentration range with low detection limits.

The measurement procedure developed within this project could provide a simple and inexpensive tool for distinguishing between local food products and products from other regions, especially from abroad.

EXPERIMENTAL

Chemicals

Neodymium(III) oxide (Nd₂O₃) and erbium(III) oxide (Er₂O₃) (99.99%; Johnson Matthey Co., UK) were used for all labeling experiments. Sub-boiling distilled nitric acid (HNO₃) (≥65%, puriss p.a.), used to digest all samples, was from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). The water used throughout the sample preparation was deionized (DI) water prepared by the Ultra Clear™ System (18.2 MΩ cm, Siemens Water Technologies AG, Germany). Because the REE concentrations in soils and plants are not evenly distributed (concentrations of light REE are higher than heavier REE, and concentrations of even-numbered elements are higher than odd-numbered elements, according to the Oddo–Harkins rule), a custom-made calibration solution was ordered having a distribution pattern similar to continental crust. This solution (REE multi-element standard AHR-CAL-7, Inorganic Ventures, NJ, USA) has the following concentrations of REE: 1000 μg mL⁻¹ Ce, 500 μg mL⁻¹ La, Nd, Y, 100 μg mL⁻¹ Pr, 150 μg mL⁻¹ Th, 50 μg mL⁻¹ Dy, Gd, Sm, U, 20 μg mL⁻¹ Er, Eu, Yb, 10 μg mL⁻¹ Ho, Tb, and 5 μg mL⁻¹ Lu, Tm in 7% (m/v) HNO₃. A 50 ng mL⁻¹ stock solution (calculated for La, Nd, Y) was prepared and diluted accordingly with 1% m/v HNO₃ for a calibration range from 0 to 10 ng mL⁻¹. A 100 ng mL⁻¹ In and Re internal standard solution was prepared from 1000 mg L⁻¹ single-element standard solutions purchased from Merck KGaA (Darmstadt, Germany).

The accuracy of the analytical measurements was checked using blank samples and two commercially supplied certified reference materials: GBW07603 (Gsv-2) Bush Twigs and Leaves (Institute of Geophysical and Geochemical Exploration, China, approved by General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic China) and BCR®-670 Aquatic Plant (Institute for Reference Materials and Measurements, Geel, Belgium).

Preparation of REE markers

In order to label the tomatoes by irrigating the soil with specific REE in dissolved form, two stock solutions (REE 1 and REE 2) containing different concentration levels of Nd and Er were prepared. Neodymium and erbium were chosen as labeling elements for this study in order to test the suitability of both light (Nd) and heavy (Er) REE for this purpose. In addition, economic factors were considered, which are of greater importance if REE are used for labeling on a larger scale. Because REE oxides are poorly soluble in water, Nd and Er oxides were weighed and dissolved with concentrated HNO₃ and subsequently diluted to 50 mL in a volumetric flask. The resulting solutions were diluted to a final volume of 10 L with purified water. REE 1 solution contained 12.5 g Nd and 1.25 g Er in 10 L water, while REE 2 solution contained 2.5 and 0.25 g in 10 L, respectively. For the spiking of water for 10 plants, 200 mL REE 1 or REE 2 solutions was split into 20 mL portions – one for each plant. Hence 0.025 g Nd and 0.0025 g Er were added to the soil by spiking with REE 1 solution per day per plant, and 0.005 g and 0.0005 g when REE 2 solution was applied.
Alternatively, solid oxide spikes were added directly to the soil in which the tomato plants were cultivated. For easier handling during the mixing process of the soil and the spike, portions of Nd and Er oxides were mixed with an REE-poor rock powder (harzburgite). Each portion consisted of ~1.25 g Nd and 0.125 g Er oxides. The ingredients were homogenized in a ball-mill (MM200, Retsch, Germany) at a frequency of 15 Hz for 1 min. The powder was then directly added to the soil (either one or two portions) and well mixed in before planting the tomato scion. The addition of one single portion (~1 g Nd and 0.1 g Er) to ~4.4 kg soil corresponded to an approximately fivefold enrichment relative to an average soil content.

Cultivation of tomato plants
Experiments concerning the cultivation and picking of the tomato plants were conducted from 15 May to 26 September 2013. During 19 weeks, 60 tomato plants were cultivated in the glasshouse on the premises of the agricultural school (Höhere Lehranstalt für Land- und Ernährungswirtschaft des Schulvereins der Grazer Schulschwestern). The cultivation of tomatoes is ideally done in a glasshouse, as the temperature and water supply are automatically controlled through adjustable windows and an irrigation system, respectively. The tomato scions of the 'Diploma' variety (F1 hybrid) were planted in plastic pots with a capacity of 15 L. ‘Diploma’ is a high-yield early-ripening variety and is considered to be very resistant to disease. The tomato fruit is uniformly red, round and large. The plant prefers a warm, sunny location with a loose, humus-rich and moist soil. This cultivar is well suited for planting both in polytunnels and outside. Each pot was filled with about 4.4 kg potting soil. As a growing medium a tomato soil ('Bio pot substrate CRH 50'; Patzer GmbH & Co. KG) was used. The soil is made up of natural clay, peat, wood fiber, bark humus and organic fertilizer. The pH of the soil was 5.5–6.5, and it contained <3.0 g L\(^{-1}\) sodium chloride, 250–450 mg L\(^{-1}\) phosphate, 200–300 mg L\(^{-1}\) nitrogen and 300–900 mg L\(^{-1}\) potassium. As an additional organic fertilizer, horn shavings, containing 130–140 g kg\(^{-1}\) nitrogen, and Osmocote® (ICL Specialty Fertilizers, Geldermalsen, Netherlands), containing 150 g kg\(^{-1}\) nitrogen, 90 g kg\(^{-1}\) phosphate and 20 g kg\(^{-1}\) magnesium oxide, were added to ensure an optimal supply of nutrients for the tomato plants. A drip irrigation system to each single tomato plant was installed. The plants were individually tied to a string system for support.

Labeling with REE
For labeling of the tomato plants Nd and Er oxides were used according to the procedure described above. Because the oxides are insoluble in water, it was not clear whether the plants would be able to take up these indicator elements directly from the soil as oxides or if they had to be added in dissolved form through watering. The estimation of a suitable concentration range and whether elements were to be added directly to the soil or to the water as a solution were important issues in the design of the experiment. Sixty tomato plants were subjected to the experimental conditions, as set out in Table 1. The absolute amounts of Nd and Er added in dissolved form (aqueous solution) or in undissolved form (solid oxides) were 0.085–2 g and 0.0085–0.2 g per plant, respectively.

The plants of group 1 (control group) were irrigated during the complete experimental period with tap water only, and thus without REE addition.

In groups 2, 3, 4, and 5 REE were added in dissolved form to the irrigation water with no addition of REE to the soil. It should be noted that in order to determine a possible stagnation or even decline in the REE content in the tomatoes, group 2 was subdivided into two subgroups (2a and 2b) with five plants each after 14 weeks of receiving portions of REE1. While the plants of subgroup 2a continued to receive REE1, portions the plants of subgroup 2b received only plain water from then on.

Group 3 received irrigation water containing stock solution REE2 during the full experimental period.

The tomato plants of groups 4 and 5 were irrigated with tap water until the first picking. From then on, which was approximately 9 weeks after the start of the experiment, REE 1 and REE 2 solutions, respectively, were added through irrigation. This was done to test whether a short-term addition of small quantities of REE before harvesting was sufficient to significantly label the fruit. In the subgroups 6a and 6b, the soil of the tomato contained solid Nd and Er oxides at two different concentration levels. Additionally, tap water was added throughout the entire period through an automated drip irrigation system on demand.

Sampling and sample preparation for measurement
Tomato leaves and fruits were picked weekly: tomato leaves beginning 3 weeks after start of experiment (a total of 13 times), and tomato fruits after 11 weeks (a total of seven times). Composite samples from the 10 subsamples of each group were prepared: two leaves each from every plant in a group were combined for the leaf sample and one ripe tomato of each of the 10 plants in the group was harvested and then combined for the fruit samples. The tomato leaves were thoroughly washed in the laboratory with deionized water. After drying in a lab oven at 60 °C for 1 day the leaf samples were ground in an agate mortar. The tomatoes were washed, halved and pureed in a blender, dried at 65 °C for 4 days and also ground in an agate mortar. In order to determine

| Group | Kind of spiking | Added amount (g per plant) |
|-------|----------------|--------------------------|
|       | Solid addition to substrate | Nd | Er |
| Group 1 (control group) | – | – | – |
| Subgroup 2a | – | Water + REE 1 | 0.6 | 0.06 |
| Subgroup 2b | – | Water + REE 1 | 0.45 | 0.045 |
| Group 3 | – | Water + REE 2 | 0.12 | 0.012 |
| Group 4 | – | Water + REE 2 | 0.425 | 0.0425 |
| Group 5 | – | Water + REE 2 | 0.085 | 0.0085 |
| Subgroup 6a | 1 g Nd + 0.1 g Er | Water | 1 | 0.1 |
| Subgroup 6b | 2 g Nd + 0.2 g Er | Water | 2 | 0.2 |
the distribution of REE in different parts of the tomato fruits, composite samples of skin, pulp and seeds, respectively, from the 10 tomato plants of group 2 (picked 12 weeks after the start of the experiment) were prepared. The tomato fruits were cut into halves and one half of each fruit was separated into skin, pulp and seeds, dried and analyzed subsequently. The second half was used for the composite sample of tomato fruit of the corresponding week.

All types of samples were digested in closed digestion vessels with a high-pressure asher (HPA-S; Anton Paar, Graz, Austria). For this purpose ~400 mg of the dried and ground sample was weighed into 50 mL quartz glass digestion vessels. The vials were sealed after the addition of 5 mL sub-boiling distilled concentrated HNO₃. For ICP-QMS measurement on a hotplate at 50–70 °C and a pressure of ~125 bar. The remaining colorless solutions were transferred into 15 mL round-bottomed PFA vials and dried. In addition, two quality control samples (GBW7603 and BCR®-670) and total procedural blanks containing the same amount of concentrated HNO₃ that was used for sample decomposition, all prepared in the same way as the samples, were analyzed. Digestion vessels were washed with concentrated nitric acid and rinsed with purified water.

**ICP-MS measurement**

The REE concentrations in tomato leaves and fruits, as well as in different parts of tomato fruit (skin, pulp and seeds) were determined using an Agilent 7500ce ICP-QMS (Agilent Technologies, Tokyo, Japan) equipped with a 100 μL PFA nebulizer and a quartz glass spray chamber cooled to 2 °C. The instrument was externally calibrated with acid matrix-matched calibration solutions. The signal intensities of the analytes were corrected for intensity drift with 115In (light elements including LREE) and 185Re (heavy elements including HREE). In order to minimize interference of REEs of the LREE on the HREE, the instrument was tuned until the level of oxide formation (CeO²⁻/Ce³⁺) in the plasma was smaller than 1.0%. Where possible, in order to detect interferences two isotopes per element were measured. Y, Pr, Tb, Ho and Tm are mono-isotopic elements. 140La and 175Lu isotopes occur with a relative isotopic abundance of 99.91% and 97.4%, respectively, and their mass fractions were quantified using these isotopes only. The following isotopes were used for quantifications: 89Y, 115In, 139La, 142Ce, 141Pr, 145Nd, 146Nd, 147Sm, 148Sm, 151Eu, 153Eu, 157Gd, 159Tb, 160Gd, 161Dy, 163Dy, 165Ho, 166Er, 167Er, 166Tm, 172Yb, 173Yb, 175Lu, 185Re, 232Th and 238U.

RESULTS AND DISCUSSION

Validation results

The determination of REE concentrations was validated for precision and accuracy through replicate analyses of CRM GBW07603 (Bush Twigs and Leaves) and BCR®-670 (Aquatic Plant). Each value given is the mean of 13 replicates for each material, carried out by ICP-QMS in this work, and the precision is expressed in terms of standard deviation for GBW07603 and in terms of confidence interval for BCR®-670. Table 2 shows a comparison of the results from this study with certified and literature values. Spalla et al.²⁹ published REE concentration values in BCR®-670 achieved by digestion procedures with a closed oven and with an open system and

| Table 2. Trace element concentration and precision (n = 13) values in certified reference materials GBW07603 (Bush Twigs and Leaves) and BCR®-670 (Aquatic Plant) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Element         | GBW07603 (mg kg⁻¹) | This work   | BCR®-670 (mg kg⁻¹) | This work |
| Ce              | 2.2 ± 0.1        | 1.93 ± 0.23    | 0.99 ± 0.04       | 0.860 ± 0.018  |
| Dy              | (0.13)           | 0.118 ± 0.016  | 0.079 ± 0.007     | 0.0674 ± 0.0011 |
| Er              | 0.0614 ± 0.0097  | 0.0440 ± 0.0028 | 0.0371 ± 0.0012  |                |
| Eu              | 0.0299 ± 0.0045  | 0.0232 ± 0.0015 | 0.0223 ± 0.0006  |                |
| Gd              | 0.133 ± 0.020    | 0.098 ± 0.008  | 0.0764 ± 0.0011  |                |
| Ho              | 0.0226 ± 0.0032  | 0.0158 ± 0.0018a | 0.0132 ± 0.0002  |                |
| La              | 0.978 ± 0.120    | 0.487 ± 0.020  | 0.439 ± 0.005    |                |
| Lu              | 0.0074 ± 0.0015  | 0.0063 ± 0.0005 | 0.0006 ± 0.0001  |                |
| Nd              | 0.846 ± 0.111    | 0.473 ± 0.015  | 0.414 ± 0.005    |                |
| Pr              | 0.221 ± 0.028    | 0.121 ± 0.006e | 0.104 ± 0.001    |                |
| Sm              | 0.160 ± 0.024    | 0.094 ± 0.007  | 0.0837 ± 0.0028  |                |
| Tb              | 0.0202 ± 0.0028  | 0.0140 ± 0.0011 | 0.0119 ± 0.0004  |                |
| Th              | 0.342 ± 0.037    | 0.159 ± 0.018  | 0.115 ± 0.009    |                |
| Tm              | 0.0085 ± 0.0015  | 0.0057 ± 0.0003e | 0.0053 ± 0.002  |                |
| Yb              | 0.616 ± 0.079    | 0.46 ± 0.06e   | 0.407 ± 0.009    |                |
| U               | 0.0052 ± 0.0105  | 0.040 ± 0.004  | 0.0315 ± 0.0007  |                |
|                 | 0.116 ± 0.017    | 0.082 ± 0.008  | 0.0772 ± 0.0026  |                |

• Data ± SD. Data in parentheses are proposed values.
• Number of laboratory average data contributing to the statistical analysis was not less than six sets. Two or more reliable analytical methods without obvious bias based on different principles were used.
• Data ± half-width of 95% confidence interval.  
• Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values are traceable to the SI.  
• Certified values are traceable to determinations by ICP-MS.
Table 3. REE concentration range and median value (on dry basis) in tomato fruits and leaves during the whole experiment period

|        | µg kg⁻¹ | La  | Ce  | Pr  | Nd* | Nd  | Sm  | Eu  | Gd  | Tb  | Dy  | Ho  | Er* | Er  | Tm  | Yb  | Lu  |
|--------|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Fruits |         |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Minimum| 0.92    | 2.19| 0.26| 2.41| 3.39| 0.18| 0.08| 0.13| 0.07| 0.11| 0.12| 0.02| 0.12| 0.35| 0.01| 0.07| 0.02|
| Maximum| 18.3    | 22.9| 2.96| 13.6| 78.9| 2.48| 3.62| 1.38| 0.67| 1.63| 0.42| 1.65| 17.1| 0.22| 0.59| 0.64|
| Median  | 2.84    | 6.58| 0.89| 4.51| 32.0| 0.82| 0.42| 0.66| 0.14| 0.46| 0.08| 0.52| 3.68| 0.05| 0.28| 0.11|
| Leaves |         |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Minimum| 22.8    | 36.9| 3.30| 23.1| 39.0| 1.85| 1.52| 2.79| 0.23| 1.62| 0.28| 3.11| 3.41| 0.02| 0.43| 0.08|
| Maximum| 226     | 429 | 48.8| 293 | 1954| 35.4| 11.0| 33.3| 5.68| 26.5| 4.77| 36.2| 306  | 2.35 | 10.0| 1.63|
| Median  | 93.5    | 162 | 18.9| 96.4| 210 | 13.8| 5.06| 14.1| 2.17| 11.0| 1.99| 7.86| 23.8 | 0.83 | 5.01| 0.80|

Measurands Nd* and Er* are the respective concentrations in group 1 (n = 31 for leaves and n = 14 for fruits), Nd and Er those in all labeled groups (n = 194 for leaves and n = 89 for fruits), and the remaining REE in all groups tested (n = 225 for leaves and n = 103 for fruits).

Figure 1. REE patterns in tomato leaves and fruits normalized to control group (tomato leaves group 1 without spiking). Enrichments of Nd and Er can already be seen in first sampling of leaves (after 3 weeks) and in fruits after 11 weeks.

ICP-QMS measurement. The values observed in our experiment, with recoveries of 67–97% for GBW07603 and of 72–100% for BCR 670 are within the range reported, and the precision was also very satisfactory. The concentration average with confidence intervals of elemental traces in standard reference material Apple Leaves (NIST SRM 1515) by ICP-QMS after high-pressure asher digestion were published previously.31

REE distribution in tomato plants

In general, assessment of the distribution pattern of REE in the different parts of tomato plant provides information that improves knowledge of the soil uptake and plant translocation mechanisms for these elements. The enrichment of Nd and Er in dried tomato leaves and fruits during the whole test period in all tomato plants labeled is clearly visible in Table 3. The table reports the minimum, maximum and median concentration values of all REE found in all groups of tomato plants during the whole experimental period, except values of Nd* and Er* which are from group 1 (control group) only. The latter presents the respective average background levels for these two elements. It is worth noting that the concentrations of Nd and Er found in labeled leaves and fruits reflect the concentration ratio added to the irrigation water or the soil, which was 10:1 (Table 1).
The contents of REEs are in the ranges previously reported. The concentrations of Nd and Er in dried tomato fruits after labeling were very low – lower than those in leaves – and can be defined as in the range of no effect to health. The acceptable daily intake of REE for a person would be 0.1 – 2 mg kg\(^{-1}\) body weight, which would correspond to nearly 3000 kg labeled tomato fruit (total REE content 2.5 \(\mu\)g kg\(^{-1}\)) per day for a person of 70 kg.

**Enrichment of Nd and Er in tomato leaves**

Unlike tomato fruits the tomato leaves were sampled throughout the vegetation period (see details above). Due to the large amount of data, only some representative results are presented and discussed. It may be noted that the distribution of lanthanides in plants, as in tomatoes, and plant products is in accordance with the Oddo–Harkins rule, with the even-numbered nuclides being more abundant than the odd-numbered ones. In order to have flatter and smoother patterns for better comparison of the different samples and particularly for the detection of any anomaly in the pattern during the enrichment phase, the REE concentrations were normalized, dividing by the concentrations of a reference sample from control group.

The first sampling of leaves was carried out 3 weeks after the start of the experiment. Thus, for group 2 and 3, plants had already received three portions of spike through watering. The plants of group 6 received tap water as the soil was already spiked. The results with the enrichment of Nd and Er in the tomato leaves can be seen in Fig. 1. Enrichments of Nd and Er in the leaves of groups 2, 3 and 6 are already clearly visible after 3 weeks. The patterns after 7 weeks are even more pronounced and the total REE concentrations are also elevated, as the plant also absorbs as natural process the other REE from the soil.

The increase of Nd in the leaves during the whole experimental period of 19 weeks is presented in Fig. 2. The enrichment of Er in tomato leaves of the same groups is also well established and very similar to the Nd results (figures are not presented). For the rest of the discussion only Nd will be considered. The concentration of Nd in the leaves steadily increases, as can be seen in Fig. 2. As mentioned before, group 2 was subdivided after 14 weeks (subgroups 2a and 2b). The irrigation with REE solution to plants of subgroup 2b was stopped after 14 weeks. No clear difference in the enrichment of neodymium in the leaves between the two subgroups is evident. The differences in the amount of REE added (6b 2× higher than 6a) to the soil are also reflected in the accumulation in the leaves. The total amount of Nd added to subgroup 2a and 6a over the whole period of the experiment was 0.6 and 1 g respectively, and the Nd enrichment in both subgroups was comparable. The uptake and translocation mechanisms of the elements from soil through roots and other parts of the plant were not the main focus of this work. In any event, the results indicate that the poorly soluble REE oxides (in water)
Figure 3. Increasing accumulation of Nd in the tomato fruits of all groups during the 19 weeks observation period. Spiking conditions are described in Table 1. Subgroups 6a and 6b start at a higher level as the spike was added before planting. Open symbols in plot '2a and 2b' are subgroup 2b data.

were very effectively converted to a bioavailable form in the plant’s rhizosphere. Possible uptake mechanisms of REE from soil to plant are discussed in several papers.19,43 For application in practice a single addition of solid REE oxides to the soil at the beginning of tomato cultivation would reduce workload in comparison to watering with REE solution.

Enrichment of Nd and Er in tomato fruits
Labeling with Nd and Er of the tomato fruits was successful, both by enrichment of the soil with these marker elements in dissolved form (aqueous solution) or in undissolved form (solid oxides). The results of the first (11 weeks) and the last (19 weeks) sampling of tomatoes of different groups are shown in Fig. 1. In all groups, except the control group 1, a unique enrichment pattern of Nd and Er can be seen, even in the first samples. Thus even short-time irrigation (approximately 2 weeks before sampling) of mature tomatoes leads to visible labels (groups 4 and 5). A significant labeling of all groups with Nd (and Er) could be observed in the last sampling, with the exception of the control group. The increase of Nd in plants of the groups mentioned during the whole experimental period of 19 weeks is presented in Fig. 3. As shown in Fig. 3, different concentration levels (group 4 higher, group 5 lower) in irrigation water produce different concentrations in the tomato fruits. The highest and most prominent level of enrichment could be achieved by irrigation with REE 1 solution and addition of solid oxides to soil, exemplified by data of (sub-)groups 2a and 2b, 4, and 6a and 6b. The absolute amount of added Nd per plant was, in dissolved form, 0.60 and 0.45 g for subgroups 2a and 2b, respectively, 0.425 g for group 4, and in solid oxide form 1 and 2 g for subgroups 6a and 6b, respectively (Table 1). The possible effect of the termination of spike addition can be seen in the different slopes of subgroups 2a (solid points) and 2b (spiking stopped after week 17, open circles). The higher the added amount or the longer the plants are exposed to irrigation with REE, the more clearly the enhancement of REE can be detected in fruit. As the tomato plants rapidly absorb the dissolved REE by irrigation and these can be detected in the tomato fruits almost immediately, it does not seem to be necessary to add the spike during the entire vegetation period.

Another interesting outcome of this experiment was the enrichment of Nd and Er in different parts of the tomato fruits after labeling. All parts of the tomato fruits, i.e. the dried skin, seeds and pulp, were well labeled with Nd and Er in the following sequence: pulp > skin > seed. Therefore, each part of the tomato fruit is suitable for labeling with marker elements.

CONCLUSIONS
In summary, this experiment demonstrates that very low concentrations of REE can be added to the irrigation water of tomato plants for a short time period to induce a significant labeling in the tomato fruits. It is not necessary to add the marker during the entire vegetation period. Within this study it was also confirmed that tomato plants are able to dissolve and absorb the poorly soluble REE oxides directly from the soil. This has a positive effect on the cost and workload. It was also found that the distribution of labeling elements in different parts of tomato fruits was very similar, but enrichment of the elements in dried tomato pulp was somewhat higher than in skin or seeds. Knowledge about the distribution of marker elements in different parts of the tomato fruit is important.
for sampling and sample preparation, but could also be helpful for the identification of the origin of tomato juice, for example.

The present method could be applied to labeling tomato fruits from a certain region in order to distinguish them from unlabeled products of other origin. Another application could be to separate non-conventional (organic) products from unlabeled conventional agriculture products. To exclude fraud through imitation of the REE pattern the substrate in a glasshouse should be changed yearly and supplemented with other or different combinations of REE marker elements.

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