Research article

Improved organic and pesticide-free rice (*Oryza sativa* L.) authentication based on multiple stable isotope ratio analysis and rice milling state

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A B S T R A C T

This study looked at the application of multiple bulk stable isotope ratio analysis to accurately authenticate organic rice and counteract organic fraud within the expanding global organic market. Variations of δ^{13}C, δ^{15}N, δ^{18}O, and δ^{34}S in organic, pesticide-free, and conventional rice were assessed across different milling states (brown, milled, and bran). Individual stable isotope ratio alone such as δ^{15}N demonstrated limited capacity to correctly differentiate organic, pesticide-free, and conventional rice. A support vector machine model—incorporating δ^{13}C, δ^{15}N, δ^{18}O, and δ^{34}S in milled rice—yielded overall predictability (95%) in distinguishing organic, pesticide-free, and conventional rice, where δ^{18}O emerged as the pivotal variable based on the feature weights in the SVM model. These findings suggest the potential of multi-isotope and advanced statistical approaches in combating organic fraud and ensuring authenticity in the food supply chain.

1. Introduction

The European Union (EU) delineates organic production as an environmentally sustainable agricultural system that prioritizes animal welfare and encompasses all facets of the food supply chain. Organic farming practices within the EU encompass crop rotation and impose prohibitions on genetically modified organisms, chemical pesticides, and synthetic fertilizers [1]. Consequently, organic products are often perceived as possessing superior quality, enhanced health benefits, greater safety, and an eco-friendlier profile. Accordingly, consumers are often willing to pay a premium price for organic products [2,3].

In 2020, the global organic market was valued at over 120 billion euros with the United States contributing 49.5 billion euros and constituting 41% of the global market. Successive rankings were held by Germany, France, and China contributing 15.0 (12.5%), 12.7 (10.6%), and 10.2 billion euros (8.5%), respectively [4]. As the global market continues to expand, organic fraud continues to escalate with losses amounting to nearly USD 3.7 trillion in 2014 [5]. Recently, organic grain fraud has been reported in the United States where non-organic or conventionally produced products were sold as organic, resulting in financial losses of $71 and $46 million in South Dakota (2020) and Minnesota (2022), respectively [6]. Consequently, the need for accurate organic authentication to counteract fraud or the mislabeling of non-organic products as organic has become paramount across all phases of the food supply chain, encompassing production, trade, and sale [2,7,8].

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Bulk stable isotope ratio (SIR) analysis is a promising tool for discerning organic authenticity in various produce categories. This technique has been effectively applied to differentiate vegetables [3,7,9], fruits [10,11], and cereals [12–15], either as a supplementary or alternative approach to pesticide residue screening. The SIR methodology primarily capitalizes on the discernible isotopic value disparities between applied fertilizers and the isotopic fractionation inherent in different production modes. Furthermore, the efficacy of bulk SIR-multielement analysis and compound-specific isotope analysis has been enhanced to refine the power of organic authenticity discrimination, particularly in cereals and vegetables cultivated using legume-based green manure [16–18].

To distinguish organic rice from conventional counterparts, the $\delta^{15}N_{bulk}$ threshold of >3 ‰ was proposed in Japan [14]. Furthermore, a four-year field trial study conducted in China [2] demonstrated that organic rice could be accurately differentiated

Table 1
Detailed information of organic (OR), pesticide-free (PFR), and conventional rice (CR) samples examined in this study.

Type[a]	Producer	Cultivar	Sample collection		Rice producing region (Latitude, °N/ Longitude, °E)	Ecofriendly certification number	Ecofriendly certification body	Pesticide residue (mg·kg^{-1}, dry weight base)[b]
			Rep, n	kg/ rep				
Organic Rice (OR)	**OR1**	**Mixed**	3	4 kg	Jeonnam Muan (35°21′/126°23′)	14600053	Seongnong Corp.	nd
	OR2	**Mixed**	3	1 kg	Jeonbuk Namwon (35°26′/127°25′)	14100236	Jirisan certification Corp.	nd
	OR3	**Mixed**	3	2 kg	Republic of Korea, (non-specified)	11600006	Korea organic certification Corp.	nd
	OR4	**Mixed**	3	2 kg	Gyeongnam Sancheong (35°46′/127°54′)	17600323	Yenong Corp.	nd
	OR5	**Mixed**	3	2 kg	Gyeongnam Yeongam (35°12′/126°36′)	15101810	Enviroment-friendly certification center Corp.	nd
	OR6	**Mixed**	3	2 kg	Gyeongbuk Uljin (37°12′/129°24′)	12600398	Global Agricultral Foods Certification	nd
	OR7	**Mixed**	3	4 kg	Jeonnam Shinan (35°01′/125°43′)	10600612	Korea organic certification Corp.	nd
Pesticide-free Rice (PFR)	**PFR1**	**Mixed**	3	2 kg	Gyeonggi Yeoncheon (38°06′/126°59′)	10303895	Korea organic certification Corp.	nd
	PFR2	**Mixed**	3	4 kg	Jeonnam Shinan (35°01′/125°43′)	12600359	Global Agricultral Foods Certification Corp.	nd
	PFR3	**Mixed**	3	2 kg	Jeonnam Shinan (35°01′/125°43′)	16600339	Eco-Leaders Certification Co., Ltd.	nd
	PFR4	**Mixed**	3	2 kg	Chungbuk Goesan (37°10′/127°50′)	12600007	Konkuk ECO Certification Agency Corp.	nd
	PFR5	**Mixed**	3	2 kg	Gyeonggi Yeoncheon (38°06′/126°59′)	10306099	Korea organic certification Corp.	nd
	PFR6	**Mixed**	3	4 kg	Republic of Korea, (non-specified)	10600640	Green Eco-Friendly Corp.	nd
	PFR7	**Mixed**	3	2 kg	Jeonbuk Sunchang (35°25′/127°05′)	14302083	Jirisan certification Corp.	nd
Conventional rice (CR)	**CR1**	**Mixed**	3	2 kg	Republic of Korea, (non-specified)	–	–	Hexaconazole (0.008) Thiacloprid (0.009)
	CR2	**Mixed**	3	2 kg	Republic of Korea, (non-specified)	–	–	Ferimzone (0.022) Hexaconazole (0.017) Tricyclazole (0.048)
	CR3	**Mixed**	3	2 kg	Republic of Korea, (non-specified)	–	–	Tricyclazole (0.06)
	CR4	**Mixed**	3	4 kg	Republic of Korea, (non-specified)	–	–	nd
	CR5	**Mixed**	3	2 kg	Republic of Korea, (non-specified)	–	–	nd
	CR6	**Mixed**	3	2 kg	Republic of Korea, (non-specified)	–	–	Ferimzone (0.012) Propiconazole (0.008)
	CR7	**Mixed**	3	2 kg	Republic of Korea, (non-specified)	–	–	nd

[a] OR is defined the rice cultivated with none of organosynthetic pesticides and chemical fertilizers, while PFR is the rice produced with maximum a third of the recommended level of chemical fertilizers, but none of organosynthetic pesticides in South Korea (Chung et al., 2017).

[b] In this study, OR and PFR samples as the state of a brown rice were certified by a pesticide residues test at an inspection body that specializes in certification and comprises manpower and facilities, appointed by the National Agricultural Products Quality Management Service in Korea.The Korea maximum residue limit (MRL, mg·kg^{-1}) of the pesticides detected in rice samples are ferimzone (2.0 mg kg^{-1}), hexaconazole (0.3 mg kg^{-1}), thiacloprid (0.1 mg kg^{-1}), tricyclazole (0.7 mg kg^{-1}), and propiconazole (0.7 mg kg^{-1}), respectively (MFDS, 2023).

from both green and conventional rice with 100% accuracy using bulk SIR (δ^{13}C, δ^{15}N) and multielement analyses. However, the discrimination accuracy between green and conventional rice was observed to be 85.33%, notably with variations in δ^{13}C and δ^{15}N in rice predominantly influenced by interannual fluctuations rather than specific fertilizer practices aligned with production modes. Additionally, a previous model study [12] centered on bulk %C, %N, δ^{13}C, and δ^{15}N in milled rice available in retail markets in Korea, proposed a $\delta^{15}N_{bulk}$ threshold exceeding 5‰ for distinguishing organic from conventional rice. This model achieved an overall accuracy of approximately 83%, albeit with an approximate 85% misclassification rate of pesticide-free rice as conventional or organic rice.

Rice, a staple supporting over half of the global population, plays a pivotal role by providing essential energy and nutrients. Notably, brown rice—in comparison to milled rice—has a higher nutritional content, encompassing proteins, lipids, and minerals. This variance in nutrient composition can consequently yield differences in bulk SIRs within rice grains due to the milling process. Against this backdrop, our current study investigated bulk SIR (δ^{13}C, δ^{15}N, δ^{18}O, δ^{34}S) variations across organic (OR), pesticide-free (PFR), and conventional rice (CR) grains contingent upon the milling state (brown and milled rice and rice bran). Our objective extended to enhancing the efficacy of the organic authenticity model for OR, PFR, and CR concerning milling processes, predicated on the analysis of multiple bulk SIRs. Furthermore, we evaluated the potential and limitations of pesticide residue screening in OR, PFR, and CR samples as a tool for assessing organic authenticity, in conjunction with a bulk SIR-based discrimination model.

2. Materials and methods

2.1. Rice samples

The classification of ecofriendly rice in Korea is based on whether chemical/synthetic fertilizers and pesticides are used during the rice cultivation period. Ecofriendly authentication, such as that used for OR or PFR, was certified based on documented history as well as pesticide residue analysis by an official inspection body approved by the National Agricultural Products Quality Management Service [19]. Grown in 2021, the rice samples (OR, PFR, and CR), as a form of brown rice, were obtained from seven certified eco-friendly or conventional rice producers or retail markets in South Korea (Table 1), with each sample composed of triplicates ($\geq$1 kg/replicate). In total, 63 brown rice samples ($n = 21$ per OR, PFR, and CR) were lyophilized at $\leq$70 °C for 2 days and were polished to prepare milled rice (degree of milling >10) and bran samples. Thereafter, each brown rice, milled rice, and bran samples were pulverized to $\leq$400 μm for bulk δ^{13}C, δ^{15}N, δ^{18}O, and δ^{34}S analyses.

2.2. Pesticide residue screening test

Based on the Ministry of Food and Drug safety Notification No. 2021–27 (2021.3.25) in Korea, a total of 548 types of pesticide residues were examined in each OR, PFR, and CR pooled sample by LC-MS/MS (273 residues) and GC-MS/MS (275 residues). Detailed analytical conditions including multiple reaction monitoring information of pesticides examined here are available in the Supplementary Tables S1–S4. The instrument detection limits for LC-MS/MS and GC-MS/MS were 0.5 and 5 μg L^{-1}, respectively. The recovery of five pesticide residue types detected in this study are shown in the range of 96.0–109.8% at a concentration of 50 μg kg^{-1} (Table S5), and the representative multiple reaction monitoring ion chromatograms of pesticide residues detected in CR samples are available in Supplementary Fig. S1.

2.3. δ^{13}C and δ^{15}N analysis

δ^{13}C and δ^{15}N measurements in the samples were performed using an Elementar Vario EL Cube elemental analyzer interfaced with an Elementar VisION isotope ratio mass spectrometer (IRMS, Elementar Analysensysteme GmbH, Langenselbold, Germany). Initially, 4.5 mg of rice powder was encapsulated in a tin capsule (3.5 × 17 mm; IVA Analysentechinik e. K., Dusseldorf, Germany). The encapsulated samples were then combusted at 950 °C in a reactor packed with chromium oxide and silvered copper oxide, and oxygen was introduced to ensure complete combustion. After combustion, residual oxygen and nitrogen oxides were removed by passing the samples over reduced copper at 650 °C, and water was trapped by magnesium perchlorate and phosphorous pentoxide. An aliquot of CO_2 and N_2 separated from the samples was directed to the IRMS for measurement [20,21].

Quality control (QC: amaranth flour and keratin) and assurance materials (QA: nylon, chitin, alfalfa flour, glutamic acid, enriched alanine, and caffeine) were calibrated against international reference materials (i.e., IAEA-600, USGS40, USGS41, USGS42, USGS43, USGS61, USGS64, USGS65), which were directly traceable to the primary isotopic reference materials (i.e., Vienna Pee Dee Belemnite for δ^{13}C and Air for δ^{15}N). The provisional isotopic values of the sample peaks were initially calculated against a pure CO_2 or N_2 reference gas. Subsequently, in-house reference materials (nylon powder, chitin, and alfalfa flour) were used to adjust isotopic values for changes in linearity and instrumental drift. Finally, the measurements were scale-normalized to the primary reference materials using in-house reference materials (glutamic acid, enriched alanine, and caffeine). The final sample values were calculated as:

$$\delta, ‰ = [(R_{unknown} - R_{standard}) / R_{standard}], \tag{1}$$

where $R_{unknown}$ and $R_{standard}$ are the stable isotope ratio (i.e., ^{13}C/^{12}C, ^{15}N/^{14}N) of the sample and the primary isotopic reference materials, respectively [22].

Based on several replicate measurements (n $\geq$ 6) of the QC/QA materials, the precision ($\pm$ mean standard deviation (SD)) was

determined to be ±0.09 ‰ for δ^{13}C and ±0.08 ‰ for δ^{15}N, and the mean absolute accuracy was within ±0.06 ‰ for δ^{13}C and ±0.07 ‰ for δ^{15}N. The limit of quantification (LOQ), based on peak area, was 100 µg C for δ^{13}C and 20 µg N for δ^{15}N.

2.4. $\delta^{18}O$ analysis

δ^{18}O measurements in the samples were carried out using an Elementar vario PYRO cube elemental analyzer interfaced with an Elementar VisION IRMS. Rice powder (0.2 mg) was encapsulated in a silver capsule (3.5 × 5.0 mm; Elemental Microanalysis, Oke-hampton, UK) and thermally decomposed to CO in a glassy carbon reactor filled with glassy carbon, graphite felt, and lamp black at 1450 °C. CO was then isolated from interfering N_2 by an adsorption trap, heated to release CO for analysis. An aliquot of the analyte gas was then directed to the IRMS for measurement [20,21].

Provisional values for the samples and references were established based on reference gas peaks introduced to the IRMS with each sample. Thereafter, drift correction, scale normalization, and linearity correction of these values were performed using QC (e.g., nylon, alanine, IAEA-600, and USGS-35) and QA (e.g., cellulose and chitin) reference materials. All in-house reference materials were calibrated against international reference materials (i.e., IAEA-V9, IAEA-600, USGS-42, USGS-43, and USGS-35). The final delta (δ) value, δ^{18}O, was expressed relative to VSMOW. Based on several replicate measurements (n ≥ 8) of the QC/QA materials, the precision and accuracy for δ^{18}O were determined to be ±0.36 ‰ (± mean SD) and within ±0.13 ‰ (mean absolute accuracy), respectively. The LOQ was 50 µg O for δ^{18}O.

2.5. $\delta^{34}S$ analysis

δ^{34}S measurements in the samples were conducted using an Elementar vario ISOTOPE cube elemental analyzer (Elementar Ana-lysensysteme GmbH, Langenselbold, Germany) interfaced with an Elementar PrecisION IRMS (Cheadle Hulme, Cheadle, England). The sample (20 mg) was placed in a tin capsule (9 × 10 mm; Costech Analytical Technologies Inc., Valencia, CA, USA) for δ^{34}S analysis and then at 1150 °C in a reactor packed with tungsten oxide. Subsequently, the sample gases were reduced with elemental copper at 880 °C and passed through a buffering reactor filled with quartz chips held at 900 °C. SO_2 and CO_2 were then separated by adsorption col-umns, the SO_2 adsorption trap was heated, and the sample SO_2 passed directly to the IRMS for measurement [20,21].

Sample and reference provisional values were established based on reference gas peaks introduced to the IRMS with each sample. These values underwent further, including drift/linearity corrections and scale normalization, using QC (e.g., hair and Mahi-Mahi muscle) and QA (e.g., taurine, whale baleen and cysteine) reference materials.

All in-house reference materials were calibrated against internationally recognized reference materials (i.e., IAEA-S-1, IAEA-S-2, IAEA-S-3, NBS-127, IAEA-SO-5, and IAEA-SO-6). The final delta (δ) value, δ^{34}S, was expressed relative to VCDT, an international primary reference material. The precision and accuracy for the δ^{34}S measurement were ±0.54 ‰ (± mean SD) and within ±0.44 ‰ (mean absolute accuracy), respectively, and the LOQ was 10 µg O for δ^{34}S.

2.6. Statistical analysis

Each OR, PFR, and CR group was composed of 21 replicates in this study, then a total of 63 rice samples were used to all statistical analysis and create discriminating models. All measured data were initially subjected to statistical analysis using the general linear model in the statistical analysis program SAS (version 9.2; SAS Institute Inc., Cary, NC, USA). The least significant difference test at a probability level of 0.05 was conducted and the results presented as mean ± SD.

Additionally, the same data were utilized for linear discriminant analysis (LDA) to construct a classification and predictive model for OR and PFR authentication against CR using IBM SPSS statistics version 28. For grouping variables of equal size (OR, PFR, and CR) or unequal size (ecofriendly and CR), all independent factors (δ^{13}C, δ^{15}N, δ^{18}O, and δ^{34}S) were subjected to LDA using Wilks' lambda. Further, cases with no user- or system-missing values for any predictor variable were used. A binary-classifier model (ecofriendly vs CR) was assessed by calculating the cutting score, sensitivity, and specificity through a receiver operating characteristic (ROC) curve analysis at a probability level of 0.05 using SPSS. Furthermore, cross-validation using the leave-one-out method was performed to evaluate the accuracy of the discrimination model developed here.

Finally, a support vector machine (SVM) with a radial kernel trick was employed to enhance the performance of the discrimination model for OR and PFR against CR using the high-dimensional isotopic data obtained here [20,23]. The parameters of radial basis kernel were set as gamma (0.25, 1/number of independent variables), degree (3), and coeffecient (0). The additional parameters were set as epsilon (0.1) and nu (0.5), and also cases with missing values were excluded to create models in this study.

3. Results and discussion

3.1. Pesticide residue screening in OR, PFR, and CR

Table 1 shows pesticide residue screening results in OR, PFR, and CR samples as a form of brown rice. None of the pesticide residues were detected in all OR and PFR measured here. Four CR samples detected five pesticide residue types such as ferimzone (≤0.022 mg kg^{-1}), hexaconazole (≤0.017 mg kg^{-1}), propiconazole (0.008 mg kg^{-1}), thiacloprid (0.009 mg kg^{-1}), and tricyclazole (≤0.06 mg kg^{-1}) (Table 1, Fig. S1); however, all were present at below the Korean maximum residue limit allowed for rice [24]. Notably, the propiconazole detected is usually applied as an insecticide over rice cultivation periods, and ferimzone, hexaconazole, thiacloprid, and

tricyclazole are used as fungicides [24]. As a result, pesticide residue screening, a common and popular organic certification tool, was effectively able to discriminate ecofriendly rice (OR and PFR) from CR; however, it is not suitable for discrimination between OR and PFR as a standalone. Therefore, here, multiple bulk SIR analyses combined with chemometric models were conducted in OR, PFR, and CR to examine the potential for detecting organic fraud or avoiding mislabeling of pesticide-free as organic and/or conventional counterparts.

3.2. $\delta^{13}C$ variation in OR, PFR, and CR depending on rice milling state

The mean $\delta^{13}C$ value ranged from -30.09 to -27.42 ‰ across different rice types and milling states (Table 2). Rice bran exhibited lower $\delta^{13}C$ values in comparison to both brown and milled rice samples (Fig. S2a). Notably, the $\delta^{13}C$ values were significantly different only among milled rice samples of OR, PFR, and CR, rendering them inadequate for discriminating the OR and PFR authenticity in brown rice and rice bran samples (Table 2). The primary factor leading to bulk $\delta^{13}C$ differences in plants is the type of photosynthesis, such as C3, C4, or CAM plants. Furthermore, abiotic (e.g., temperature, drought, fertilization regime, light intensity, soil moisture) and genetic factors that influence photosynthesis also affect bulk $\delta^{13}C$ characteristics [25,26].

Bulk $\delta^{13}C$ values alone are not significant when differentiating production modes (organic vs conventional) in rice [15], barley [27], tomato [28], and wheat/vegetables [7]. Furthermore, despite the statistical difference in $\delta^{13}C$ between production modes, its narrow range often poses challenges in determining a correct organic authenticity [29]. In general, in comparison to conventional rice paddy fields, organic rice paddy fields can be much lower in $\delta^{13}C$ due to isotopic fractionation resulting from microbial decomposition of applied organic fertilizers such as manure and compost [2,15]. However, in a recent four-year field trial study [2], $\delta^{13}C$ values of organic, green, and conventional rice were largely affected by genotype and interannual climate variations (temperature, precipitation, and light intensity), rather than production modes linked to fertilization regimes. Another study [12] also concluded that there were no statistically significant differences in the mean $\delta^{13}C$ (~-27.0 ‰) of milled rice grains among production modes (OR, PFR, and CR) over a five-year study at the retail market level. Notably, the five-year-annual $\delta^{13}C$ variation (~0.8 ‰) across all rice samples was considerably larger than that attributed to production modes (≤0.1 ‰).

Here, the $\delta^{13}C$ range (-28.04 to -27.42‰) observed in brown and milled rice samples was comparable to that from the four-year field trial (-29.0 to -26.0 ‰) [2] and the five-year retail market level (-27.5 to -26.7‰) studies [12]. Particularly, the lower $\delta^{13}C$ values in rice bran could be linked to variations in constituents based on plant parts—higher lignin or lipid content may result in lower $\delta^{13}C$ values. Interestingly, our current study indicated that the mean $\delta^{13}C$ in milled rice could serve to differentiate production modes, with a maximum difference of 0.58 ‰ (Δ_{PFR-CR}). Nevertheless, this difference remained smaller than the previously reported interannual $\delta^{13}C$ variations of ~1.7 ‰ (from paddy fields) and ~0.8 ‰ (from the retail market), suggesting that it is insufficient as a sole indicator of organic authenticity.

3.3. $\delta^{15}N$ variation in OR, PFR, and CR depending on rice milling state

Taking into consideration the milling state (brown and milled rice and rice bran), it was observed that OR exhibited higher $\delta^{15}N$ values in comparison to CR, while no significant difference was found between OR and PFR ($p < 0.05$, Table 2). Furthermore, as shown in Fig. S2b, $\delta^{15}N$ did not show a significant correlation with the milling state. However, a previous study noted that unpolished rice grain (ranging from 5.3 to 7.1 ‰) exhibited slightly higher $\delta^{15}N$ values than polished rice grain (ranging from 4.6 to 6.1 ‰), contingent upon the use of synthetic or organic fertilizers [30]. Notably, due to the distinct $\delta^{15}N$ ranges of fertilizers used in conventional and organic farming, $\delta^{15}N$ is often regarded as the most promising isotope fingerprint for identifying the production mode [31]. Chemical/synthetic fertilizers used in conventional farming exhibit $\delta^{15}N$ ranges of -3.9 to 5.7 ‰, whereas organic fertilizers show a wider $\delta^{15}N$ range of 2.5–45.2 ‰. However, the use of legume-based green manure in organic farming poses challenges in differentiating organic authenticity from conventional counterparts, as its $\delta^{15}N$ value is as low as 0 ‰, akin to the $\delta^{15}N$ range of chemical fertilizers.

In the four-year field trial study [2], organic rice exhibited a $\delta^{15}N$ range of 4.5–6.2 ‰, conventional rice showed a $\delta^{15}N$ range of

Table 2
Variation in bulk $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ of rice samples as a function of the milling state (brown, polished, bran) and rice type (CR, OR, PFR).

	Type, $n = 21$ per each	$\delta^{13}C$, ‰	$\delta^{15}N$, ‰	$\delta^{18}O$, ‰	$\delta^{34}S$, ‰
Brown rice	CR	-28.04 ± 0.45^{ns}	4.38 ± 0.49^{b}	22.10 ± 0.66^{b}	-8.84 ± 3.47^{a}
	OR	-27.98 ± 0.21	5.17 ± 0.94^{a}	22.94 ± 0.72^{a}	-12.92 ± 1.90^{c}
	PFR	-27.92 ± 0.35	4.90 ± 0.85^{a}	22.45 ± 0.63^{b}	-11.09 ± 1.98^{b}
LSD$_{0.05, \text{ for brown rice}}$		0.22	0.48	0.42	1.58
Milled rice	CR	-28.00 ± 0.45^{c}	4.49 ± 0.55^{b}	22.15 ± 0.75^{b}	-16.78 ± 2.22^{b}
	OR	-27.69 ± 0.17^{b}	5.29 ± 0.96^{a}	22.84 ± 0.64^{a}	-16.37 ± 2.85^{b}
	PFR	-27.42 ± 0.32^{a}	4.79 ± 0.89^{ab}	22.40 ± 0.60^{b}	-13.08 ± 2.53^{a}
LSD$_{0.05, \text{ for polished rice}}$		0.21	0.50	0.41	1.57
Rice bran	CR	-30.03 ± 0.60^{ns}	4.27 ± 0.46^{b}	20.66 ± 0.88^{b}	-8.73 ± 1.88^{b}
	OR	-30.09 ± 0.24	5.12 ± 0.82^{a}	21.12 ± 0.51^{a}	-5.95 ± 2.90^{a}
	PFR	-29.81 ± 0.45	4.84 ± 0.83^{a}	21.16 ± 0.51^{a}	-6.02 ± 1.13^{a}
LSD$_{0.05, \text{ for rice bran}}$		0.28	0.45	0.42	1.36

[a–c] Values with different lower-case superscripts differed statistically ($p < 0.05$) as a function of rice types. The results are expressed in the form of a mean ($\pm$ standard deviation, $n = 21$). ns: non-significant.
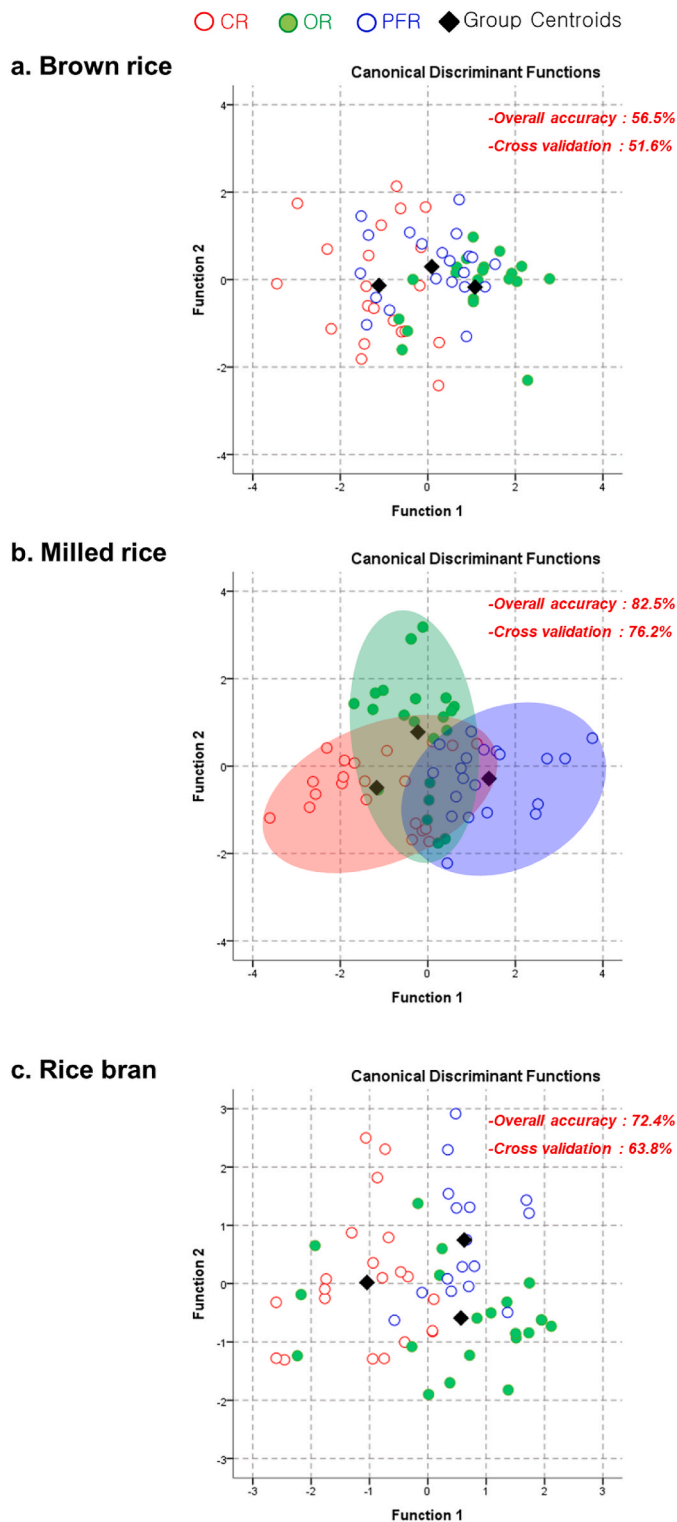
Fig. 1. Linear discriminant analysis (LDA)-based discriminative model of OR, PFR, and CR samples using bulk δ^{13}C, δ^{15}N, δ^{18}O, and δ^{34}S values as a function of the milling state (refer to Tables S6–S8 together).

3.0–4.8 ‰, and green rice showed an intermediate $\delta^{15}N$ range between OR and CR (3.9–5.3 ‰). The impact on $\delta^{15}N$ values in rice grain followed the order of interannual climate > fertilization practice > genotype over this four-year study in China. Consequently, the use of $\delta^{15}N$ as a sole isotope marker is often problematic when differentiating organic authenticity. Furthermore, in the five-year retail market study in Korea [12], the mean $\delta^{15}N$ in OR ranged from 5.4 to 6.6 ‰, relatively higher than that of 3.8–4.8 ‰ in CR. Notably, the overlapping $\delta^{15}N$ range in PFR (4.8–6.5 ‰) added to the challenges of differentiating OR from PFR. A recent study [13] established a case for a threshold $\delta^{15}N$ value widely employed by major European importers. In vegetables, $\delta^{15}N > 5$ ‰ was confirmed as a reliable indicator of proper organic practices with a high degree of confidence, whereas $\delta^{15}N < 2$ ‰ should not be considered indicative of organic practices. The middle zone (2–5 ‰) was suggested as requiring confirmation of refined organic authenticity through tracking mechanisms by official regulation bodies.

In our current study, ~65% of OR samples (41/63), ~37% of PFR samples (23/63), and ~11% of CR samples (7/63) exhibited $\delta^{15}N$ values > 5 ‰, irrespective of the milling state (data not shown). It indicated that applying the $\delta^{15}N$ criterion previously suggested was potentially misclassified OR of 35% as either PFR or CR samples. Furthermore, CR of ~11% as well as PFR of ~37% were possibly misclassified as OR. Therefore, unlike the aforementioned studies, the $\delta^{15}N$ criterion alone (>5 ‰) exhibited rather insufficient for determining rice organic authenticity. To overcome the limitations of using bulk $\delta^{15}N$ for organic authenticity, SIRA—combined with multi-element analysis such as K, Ca, and Mg—has been shown to improve accuracy by 100% for distinguishing organic from green or conventional rice [2]. Additionally, compound-specific isotope analysis [16,17] has enabled the classification of organic wheat (including animal and green manure vs conventional) as well as more refined rice classifications (OR, PFR, and CR).

3.4. $\delta^{18}O$ and $\delta^{34}S$ variations in OR, PFR, and CR depending on rice milling state

The mean $\delta^{18}O$ ranged from 20.66 to 22.94 ‰ across all samples measured. Notably, OR consistently displayed higher values compared to CR and PFR ($p < 0.05$, Table 2). Akin to $\delta^{13}C$, $\delta^{18}O$ values exhibited significantly lower values in rice bran compared to brown and milled rice (Fig. S2c). The mean $\delta^{34}S$ ranged from −16.78 to −5.95 ‰ across different rice types and milling states, with rice bran typically featuring higher values than brown or milled rice (Table 2, Fig. S2d). However, despite statistical significance ($p < 0.05$), $\delta^{34}S$ values in OR, PFR, and CR did not show a discernible trend (Table 2). Notably, owing to the substantial influence of geographical and climatic factors on bulk $\delta^{18}O$ and $\delta^{34}S$ in plants, these markers are typically more suited for distinguishing the geographical origin of foods rather than discerning production modes. Bulk $\delta^{18}O$ is not efficacious in discerning production modes in rice [15], barley [27], and field-grown vegetables [3,7].; however, organic or conventional production modes could potentially impact $\delta^{18}O$ values thorough
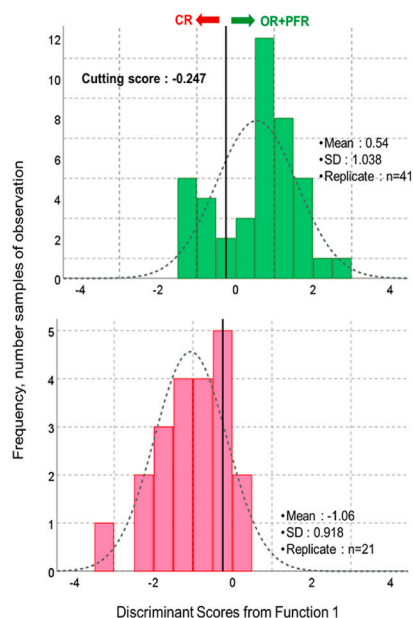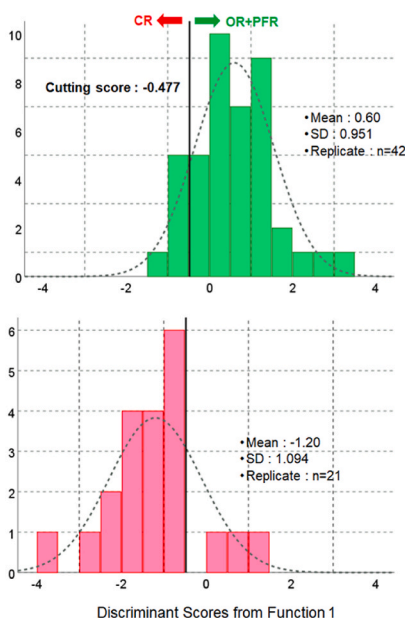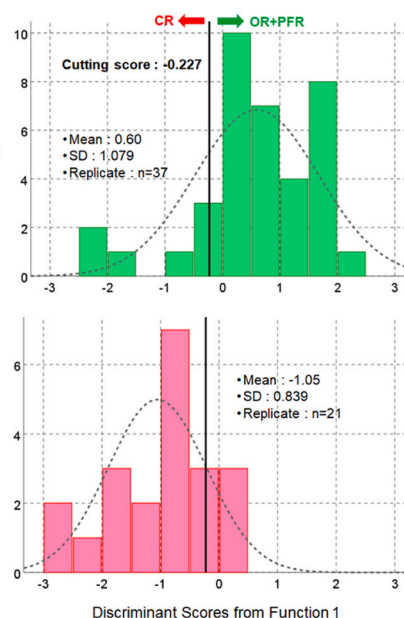

Fig. 2. Binary classifier models for rice ecofriendly authentication based on LDA. The cutting scores were derived from receiver operating characteristic (ROC) curves using the discriminant scores resulting from the LDA. Binary models based on the (a) brown rice state, (b) milled rice state, and (c) rice bran state (refer to Tables S9–S11 together). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

intricate metabolic processes such as respiration, soil-plant water uptake, and transpiration driven by varying cultivation practices (e. g., plant density and growth rate) [7,13]. In a previous study, bulk $\delta^{18}O$ in lipids significantly distinguished between wheat production modes in Germany, revealing higher $\delta^{18}O$ values in organic wheat [13]. Our findings here similarly indicated significantly higher bulk $\delta^{18}O$ in OR compared to CR, regardless of rice milling states (brown, milled, or bran). Nonetheless, this marker did not prove useful in distinguishing PFR from OR or CR.

Moreover, different sulfate fertilizers applied in organic or conventional farming might also influence bulk $\delta^{34}S$ values in soil and plants [31,32]. Generally, organic S and elemental S (S°) are used in organic farming, while synthetic/manufactured sulfate fertilizers and S° are used in conventional farming practices, thereby potentially enabling distinguishing between production modes. However, regrettably, bulk $\delta^{34}S$ did not effectively discern different production modes in wheat [13] and vegetables [3,7]. Our results similarly demonstrated no distinct differences and patterns in bulk $\delta^{34}S$ for discerning amongst rice production modes. Consequently, bulk $\delta^{18}O$ and $\delta^{34}S$ exhibited limited discernment ability as isotope markers for distinguishing rice production modes (OR, PFR, CR), regardless of the rice milling state.

3.5. Evaluation of OR, PFR, and CR discrimination ability using LDA and SVM

Fig. 1 presents the LDA models of OR, PFR, and CR using bulk $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ values, contingent upon the milling state. Notably, the discriminant model based on milled rice exhibited superior classification accuracy for both original (82.5%) and cross-validated tests (76.2%) when compared to models utilizing brown rice or rice bran (Tables S6–S8). In particular, models based on brown rice showed poor classification accuracy of <60%, due to the misclassification of PFR as OR (33.3%) or CR (28.6%). The first two canonical discriminant functions of the models using milled rice showed an eigenvalue of 1.179 and Wilks' lambda of 0.346 ($p <$ 0.001), indicative of the relatively good discriminatory capability of the LDA model for OR, PFR, and CR groups (Fig. 1b). According to standardized coefficients, in the 1st function, $\delta^{13}C$ (0.941) and $\delta^{34}S$ (0.650) emerged as crucial variables for predicting the groups (OR, PFR, CR), whereas $\delta^{15}N$ (0.623) and $\delta^{18}O$ (0.640) played significant roles in predicting the groups within the 2nd function.

The binary classifier models (ecofriendly vs CR) enhanced the classification/prediction accuracy for brown and milled rice and rice bran (Fig. 2). The eigenvalue (0.741) and Wilks' lambda (0.574, $p <$ 0.001) indicated a notable discriminatory ability of the function within the binary classifier model (Fig. 2b). Consequently, the binary classifier model based on milled rice exhibited superior classification accuracy for both original (87.3%) and cross-validated tests (82.5%) in comparison to other models (Fig. 2). This model incurred a 7% misclassification of ecofriendly rice as CR in the original set; however, it erroneously predicted 14% of the ecofriendly rice as CR in the cross-validated set (Tables S9–S11). According to standardized coefficients, $\delta^{13}C$ (0.806), $\delta^{15}N$ (0.634), and $\delta^{34}S$ (0.438) emerged as the most pivotal variables for predicting the groups (ecofriendly vs CR) in the binary classifier model (Fig. 2b). Additionally, through ROC analysis, the cutting score value (−0.477), sensitivity (85.7%), and specificity (85.7%) were calculated for the milled rice-based binary classification model (Fig. 2b–Table 3).

Furthermore, in comparison to the LDA discrimination models (Fig. 1), the SVM exhibited improved overall predictability for OR, PFR, and CR authentication in milled rice (95.2%), brown rice (85.5%), and rice bran (93.1%) (Table 4). SVM is commonly employed to ascertain optimal predictability by determining a hyperplane that facilitates vector separation based on their respective classes [33]. In the SVM model of milled rice, the feature weight (−1.951) for $\delta^{18}O$ was relatively higher compared to $\delta^{13}C$ (−6.063), $\delta^{15}N$ (−3.866), and $\delta^{34}S$ (−6.956), and it meant that the independent variable ($\delta^{18}O$) emerged as the most important variable for predicting OR, PFR, and CR authentication in milled rice, as indicated by SVM analysis. In general, multivariate statistical tests prove highly effective in discerning production modes by minimizing or eliminating sources of variability such as geographical origin, genotype, and year of production for the measured variables. Various (un)supervised-multivariate statistical approaches, such as principal component, canonical correlation, discrimination, and/or cluster analysis, have been employed to differentiate crop production modes [31].

A recent study [12] employed a SVM model based on variables such as %C, %N, $\delta^{13}C$, and $\delta^{15}N$ in milled rice, resulting in an overall predictability of ~65% by SVM, with a notable misclassification rate of ~85% for PFR, inaccurately classified as CR or OR. Additionally, a PLS-DA model using stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) and multielement data from a four-year field trial study displayed an overall discrimination accuracy of ~82% for organic, green, and conventional rice. However, this model also showed a poor

Table 3
Area under the curve, sensitivity, specificity, and cutting score determined by the receiver operating characteristic (ROC) curves for ecofriendly authentication (ecofriendly *vs* conventional) according to the rice milling state.

Classification	Referenced figure	Area Under the Curve					Calculated by ROC curve		
		Test Result Variable(s):							
		Area	Std. Error[a]	Asymptotic Sig.[b]	Asymptotic 95% Confidence Interval		Sensitivity	Specificity	Cutting score
					Lower Bound	Upper Bound			
Brown rice	Fig. 2a	0.868	0.044	0.000	0.781	0.954	75.6%	76.2%	−0.247
Milled rice	Fig. 2b	0.904	0.046	0.000	0.814	0.993	85.7%	85.7%	−0.477
Rice bran	Fig. 2c	0.907	0.041	0.000	0.827	0.988	86.5%	85.7%	−0.227

[a] Under the nonparametric assumption.
[b] Null hypothesis: true area = 0.5.

Table 4
Confusion matrix of rice type classification using the supporting vector machine (SVM) manner.

Predicted	CR[a], $n = 21$	OR, $n = 21$	PFR, $n = 21$	Total, $n = 63$
Actual	% predictability			
Milled rice	100.0	85.7	100.0	95.2
Brown rice	90.5	85.0	81.0	85.5
Rice bran	100.0	90.5	87.5	93.1

[a] Conventional rice (CR), organic rice (OR), pesticide-free rice (PFR).

differentiation accuracy of 58.3% for green rice, indicating that ~42% was misclassified as organic or conventional rice. Binary classification models substantially improved accuracy, achieving rates of 85.33–100% for each pair of classes [2].

Here, a SVM model was developed utilizing bulk $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ in milled rice and demonstrated a notably higher predictability of ~95% for OR, PFR, and CR groups. Intriguingly, unlike the aforementioned models, the SVM model based on these four bulk isotope variables significantly ameliorated the misclassification rate between CR and PFR, leading to an accurate predictability of 100% per each group. However, among the four variables employed here, the correlation between production mode and $\delta^{18}O$ or $\delta^{34}S$ remains unclear. Consequently, further investigation, involving controlled long-term field studies or extensive sample analyses, is imperative to establish robust and reliable methods for organic authentication.

4. Conclusion

In summary, as per the growing global demand for organic products, the importance of accurate organic authentication cannot be overstated for maintaining consumer trust and ensuring a fair marketplace. This study describes the potential of multiple bulk SIR analyses to enhance the authenticity determination of OR, PFR, and CR across milling states. Pesticide residue screening was able to discriminate ecofriendly rice from conventional counterparts; however, it does not differentiate between OR and PFR. Furthermore, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ standalone use was insufficient for accurate organic authentication. Nevertheless, in the case of milled rice, a combination of these isotopes led to enhanced distinguishability, with the SVM model achieving 95 % predictability for differentiating between OR, PFR, and CR. Despite some challenges like interannual fluctuations and overlapping isotopic values between production modes, our findings contribute to the ongoing efforts to establish reliable methods to combat organic fraud within the global food supply chain.

CRediT authorship contribution statement

Hee-Youn Chi: Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **Won-Ryeol Kim:** Writing – original draft, Formal analysis, Data curation. **Ji-Ye Kim:** Writing – original draft, Formal analysis, Data curation. **Seung-Hyun Kim:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

conventional rice   CR
European Union   EU
limit of quantification   LOQ
linear discriminant analysis   LDA
organic rice   OR
pesticide-free rice   PFR
quality assurance   QA
quality control   QC
receiver operating characteristic   ROC
stable isotope ratio   SIR
standard deviation   SD
support vector machine   SVM

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e26725.

References

[1] J.M. Muñoz-Redondo, J.C. Montenegro, J.M. Moreno-Rojas, Using nitrogen stable isotopes to authenticate organically and conventionally grown vegetables: a new tracking framework, Agronomy 13 (2023) 131. https://www.mdpi.com/2073-4395/13/1/131.

[2] Z. Liu, Y. Yuan, T. Xie, Y. Zhang, S. Shao, J. Nie, W. Xia, K.M. Rogers, W. Zhang, Long-term agricultural effects on the authentication accuracy of organic, green, and conventional rice using isotopic and elemental chemometric analyses, J. Agric. Food Chem. 68 (2020) 1213–1225, https://doi.org/10.1021/acs.jafc.9b06847.

[3] H.-l. Schmidt, A. Roßmann, S. Voerkelius, W.H. Schnitzler, M. Georgi, J. Graßmann, G. Zimmermann, R. Winkler, Isotope characteristics of vegetables and wheat from conventional and organic production, Isot. Environ. Health Stud. 41 (2005) 223–228, https://doi.org/10.1080/10256010500230072.

[4] IFOAM, The World of Organic Agriculture Statistics and Emerging Trends 2022, Research Institute of Organic Agriculture FiBL, Frick, and IFOAM – Organics International, Bonn, 2022. https://www.fibl.org/fileadmin/documents/shop/1344-organic-world-2022.pdf.

[5] G. Ferreira, J. Tucker, E. Rakola, S.R. Skorbiansky, Fraud in organic foods, in: R.S. Hellberg, K. Everstine, S.A. Sklare (Eds.), Food Fraud: A Global Threat with Public Health and Economic Consequences, Academic Press, London, 2021, pp. 335–350, https://doi.org/10.1016/B978-0-12-817242-1.00001-4.

[6] Agdaily Reportes, Minn. Farmer Pleads Guilty in $19M Organic Grain Fraud Scheme, accessed on February 03 2024, AGDAILY, 2023, https://www.agdaily.com/crops/minn-farmer-pleads-guilty-in-19m-organic-grain-fraud-scheme/.

[7] M. Georgi, S. Voerkelius, A. Rossmann, J. Graßmann, W.H. Schnitzler, Multielement isotope ratios of vegetables from integrated and organic production, Plant Soil 275 (2005) 93–100, https://doi.org/10.1007/s11104-005-0258-3.

[8] K. Giannakas, Information asymmetries and consumption decisions in organic food product markets, Can. J. Agric. Econ. 50 (2002) 35–50, https://doi.org/10.1111/j.1744-7976.2002.tb00380.x.

[9] H.J. Oh, Y.J. Kim, Discriminant analysis of organice vegetables and non-organic vegetables using stable isotope ratios, J. Kor. Soc. Food Sci. Nutr. 51 (2022) 942–949, https://doi.org/10.3746/jkfn.2022.51.9.942.

[10] Z. Giannioti, N. Ogrinc, M. Suman, F. Camin, L. Bontempo, Isotope ratio mass spectrometry (IRMS) methods for distinguishing organic from conventional food products: a review, TrAC, Trends Anal. Chem. 170 (2024) 117476, https://doi.org/10.1016/j.trac.2023.117476.

[11] P. Tixier, D. Loeillet, M. Coulis, T. Lescot, L. de Lapeyre de Bellaire, Isotopes Don't Lie, differentiating organic from conventional banana (Musa AAA, Cavendish subgroup) fruits using C and N stable isotopes, Food Chem. 394 (2022) 133491, https://doi.org/10.1016/j.foodchem.2022.133491.

[12] I.M. Chung, Y.J. Kim, H.S. Moon, H.Y. Chi, S.H. Kim, Long-term isotopic model study for ecofriendly rice (Oryza sativa L.) authentication: updating a case study in South Korea, Food Chem. 362 (2021) 130215, https://doi.org/10.1016/j.foodchem.2021.130215.

[13] X. Gatzert, K.P. Chun, M. Boner, R. Hermanowski, R. Mäder, L. Breuer, A. Gattinger, N. Orlowski, Assessment of multiple stable isotopes for tracking regional and organic authenticity of plant products in Hesse, Germany, Isot. Environ. Health Stud. 57 (2021) 281–300, https://doi.org/10.1080/10256016.2021.1905635.

[14] M. Nishida, Y. Sato, Characteristics of the relationship between natural 15N abundances in organic rice and soil, Plant Prod. Sci. 18 (2015) 180–186, https://doi.org/10.1626/pps.18.180.

[15] Y. Yuan, W. Zhang, Y. Zhang, Z. Liu, S. Shao, L. Zhou, K.M. Rogers, Differentiating organically farmed rice from conventional and green rice harvested from an experimental field trial using stable isotopes and multi-element chemometrics, J. Agric. Food Chem. 66 (2018) 2607–2615, https://doi.org/10.1021/acs.jafc.7b05422.

[16] I.M. Chung, J.-K. Kim, Y.-J. An, C. Kwon, S.-Y. Kim, Y.-J. Yang, C.T. Yarnes, H.-Y. Chi, S.-H. Kim, Compound-specific δ13C and δ15N analyses of fatty acids and amino acids for discrimination of organic, pesticide-free, and conventional rice (Oryza sativa L.), Food Chem. 283 (2019) 305–314, https://doi.org/10.1016/j.foodchem.2018.12.129.

[17] M. Paolini, L. Ziller, K.H. Laursen, S. Husted, F. Camin, Compound-specific δ15N and δ13C analyses of amino acids for potential discrimination between organically and conventionally grown wheat, J. Agric. Food Chem. 63 (2015) 5841–5850, https://doi.org/10.1021/acs.jafc.5b00662.

[18] A. Mihailova, N. Pedentchouk, S.D. Kelly, Stable isotope analysis of plant-derived nitrate – novel method for discrimination between organically and conventionally grown vegetables, Food Chem. 154 (2014) 238–245, https://doi.org/10.1016/j.foodchem.2014.01.020.

[19] I.M. Chung, S.-K. Park, K.-J. Lee, M.-J. An, J.-H. Lee, Y.-T. Oh, S.-H. Kim, Authenticity testing of environment-friendly Korean rice (Oryza sativa L.) using carbon and nitrogen stable isotope ratio analysis, Food Chem. 234 (2017) 425–430, https://doi.org/10.1016/j.foodchem.2017.05.014.

[20] I.-M. Chung, J.-T. Kim, H.-S. Moon, Y.-J. Kim, S.-H. Kim, Geographical origin discrimination of Agaricus bisporus produced by the complete medium: a pilot study in South Korea, Food Chem. 386 (2022) 132820, https://doi.org/10.1016/j.foodchem.2022.132820.

[21] S.-H. Kim, J.-K. Moon, H.-W. Jo, J.-T. Kim, Ecofriendly shiitake authentication using bulk and amino acid-specific stable isotope models, Food Chem. 397 (2022) 133819, https://doi.org/10.1016/j.foodchem.2022.133819.

[22] Z. Sharp, Principles of Stable Isotope Geochemistry, Pearson/Prentice Hall, 2017, https://doi.org/10.25844/h9q1-0p82.

[23] I.M. Chung, Y.J. Kim, C. Kwon, H.S. Moon, J.G. Han, W.S. Kong, S.H. Kim, An origin identification model for labeling of shiitake (Lentinula edodes), npj Sci. Food 5 (2021) 2, https://doi.org/10.1038/s41538-021-00085-4.

[24] MFDS, MFDS Residue Information, Ministry of Food and Drug Safety (MFDS), Cheongju-Si, accessed on 03 February 2024, Chungcheongbuk-do, Korea, 2023, https://residue.foodsafetykorea.go.kr/.

[25] T.E. Dawson, S. Mambelli, A.H. Plamboeck, P.H. Templer, K.P. Tu, Stable isotopes in plant ecology, Annu. Rev. Ecol. Systemat. 33 (2002) 507–559, https://doi.org/10.1146/annurev.ecolsys.33.020602.095451.

[26] S.I. Yun, H.M. Ro, A tool to interpret interacting environmental stresses on soil and plant, J. Appl. Biol. Chem. 51 (2008) 262–271, https://doi.org/10.3839/jabc.2008.041.

[27] L. Buša, M. Bērtiņš, A. Vīksna, L. Legzdiņa, D. Kobzarevs, Evaluation of carbon, nitrogen, and oxygen isotope ratio measurement data for characterization of organically and conventionally cultivated spring barley (*Hordeum vulgare* L.) grain, Agron. Res. 19 (2021) 1364–1372. http://hdl.handle.net/10492/6933.

[28] A. Nakano, Y. Uehara, A. Yamauchi, Effect of organic and inorganic fertigation on yields, δ15N values, and δ13C values of tomato (Lycopersicon esculentum Mill. cv. Saturn), Plant Soil 255 (2003) 343–349, https://doi.org/10.1023/A:1026180700963.

[29] P. Rapisarda, F. Camin, S. Fabroni, M. Perini, B. Torrisi, F. Intrigliolo, Influence of different organic fertilizers on quality parameters and the δ15N, δ13C, δ2H, δ34S, and δ18O values of orange fruit (citrus sinensis L. Osbeck), J. Agric. Food Chem. 58 (2010) 3502–3506, https://doi.org/10.1021/jf903952v.

[30] S.I. Yun, S.-S. Lim, G.-S. Lee, S.-M. Lee, H.-Y. Kim, H.-M. Ro, W.-J. Choi, Natural 15N abundance of paddy rice (Oryza sativa L.) grown with synthetic fertilizer, livestock manure compost, and hairy vetch, Biol. Fertil. Soils 47 (2011) 607–617, https://doi.org/10.1007/s00374-011-0571-3.

[31] C.T. Inácio, P.M. Chalk, A.M. Magalhães, Principles and limitations of stable isotopes in differentiating organic and conventional foodstuffs: 1. Plant products, Crit. Rev. Food Sci. Nutr. 55 (2015) 1206–1218, https://doi.org/10.1080/10408398.2012.689380.

[32] USDA, United States department of agriculture. National organic program board, national list of allowed and prohibited substances. http://www.ams.usda.gov/AMSv1.0/nop, 2002.

[33] P. Tsakanikas, A. Karnavas, E.Z. Panagou, G.-J. Nychas, A machine learning workflow for raw food spectroscopic classification in a future industry, Sci. Rep. 10 (2020) 11212, https://doi.org/10.1038/s41598-020-68156-2.