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Isotope ratio mass spectrometry (IRMS) methods for distinguishing organic from conventional food products: A review

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A B S T R A C T

The use of isotopic analytical methods for food authentication was established years ago. Changes in food technology and consumer behavior, as well as the increasing number of cases of food fraud, necessitate ongoing research for reliable analytical authentication techniques. This literature review examines recent applications of stable isotope ratio analysis that can be used in cases of organic food mislabeling. Different isotope ratio mass spectrometry (IRMS) techniques are described in this article, including bulk IRMS analysis and the combination of IRMS with novel sample preparation and compound extraction techniques. Compound-specific IRMS analysis comprising mainly hyphenated techniques, such as gas chromatography GC-IRMS, was also considered, and was found to frequently overcome the limitations exhibited by bulk analysis. A wide range of food product categories were covered, including cereals, vegetables, fruit, animal products, and seafood, while the importance of statistical analysis was underlined in determining which stable isotopic compositions ($\delta(^{15}N)$, $\delta(^{34}S)$, $\delta(^{18}O)$, $\delta(^{13}C)$, or $\delta(^{2}H)$) could be used as reliable organic authenticity markers.

1. Introduction

1.1. Organic foods

As consumers become increasingly concerned about climate change, social inequities, and animal welfare, demand for fair-trade and organic products is on the rise [1]. Consumer preference for organic products is also associated with increased health concerns regarding conventional productions: first and foremost, the concern regarding antibiotics in conventional animal production and their role in societal antibiotic resistance, as well as the fact that pesticide residues in conventional fruits and vegetables are the primary source of human pesticide exposure [2]. On a regulatory level, the European Commission has implemented the "Farm to Fork" strategy, which includes a 50 % reduction in pesticide use and promotes organic production to reach 25 % of agricultural land use in the EU by 2030 [3]. Moreover, despite the current energy and food crises, the organic food and beverage industry is expected to grow from $66 billion in 2019 [4] to $564.22 billion by 2030 [5].

The regulations surrounding organic labeling are extremely stringent to ensure compliance and shield consumers from fraudulent food products. On the other hand, products that claim to be pesticide-free are unregulated and their label is significantly less expensive to acquire than the organic label. However, research indicates that consumers are more willing to pay for organic products than for products labeled pesticide-free [6–8].

The EU organic production rules prohibit the use of GMOs, ionizing radiation, synthetic fertilizers, herbicides, and pesticides in organic farming, as well as the use of hormones and antibiotics [9]. Similarly, according to the United States Department of Agriculture (USDA), a product can be labeled organic if it is certified to have been cultivated on soil that has not been treated with synthetic fertilizers or pesticides in the 3 years preceding harvest [10]. Regulations stipulate that animals used for meat, milk, eggs, and other animal products must be fed 100 % organic feed and not be administered antibiotics or hormones [9,11]. The EU guidelines for organic carnivorous species of fish (such as salmon and trout) specify that their feed must contain at least 40 % organic animal content, whereas feed for conventional carnivorous fish may contain more than 60 % vegetable ingredients [9]. The USDA [10] stipulates that packaged products claiming to be made with a specific organic ingredient or food group must contain at least 70 % organically produced ingredients.

In spite of the regulations in place, cases of food mislabeling and adulteration continue to rise. Such instances are financially damaging

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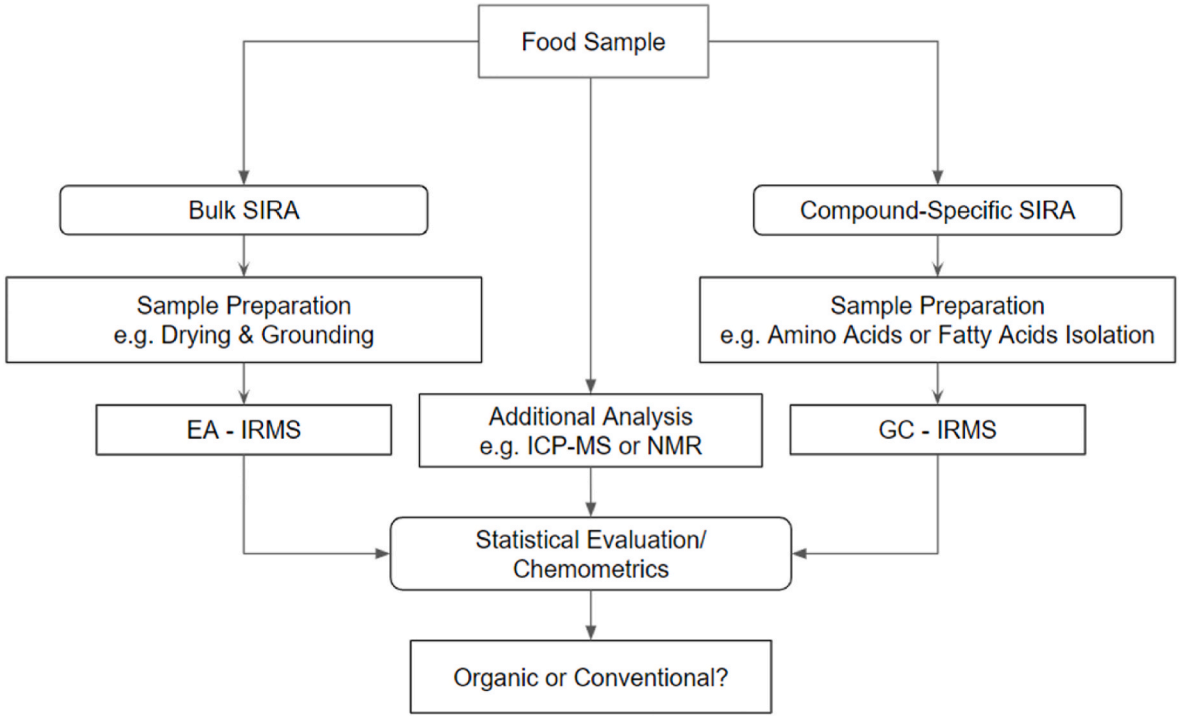

Fig. 1. Schematic representation of the organic authentication process according to the stable isotope ratio analysis (SIRA) methodology.

and potentially harmful to human health, but they are the result of globalization and the complexity of the food trade [12]. Moreover, Brooks et al. [13] conducted an extensive review of the impact of COVID-19 on all types of food fraud across the supply chain, concluding that mislabeling and counterfeiting are the most prevalent categories of food fraud, with organic food fraud falling under these categories. Therefore, it is clear that the development of powerful tools and effective analytical methodologies capable of identifying such incidents is necessary.

1.2. Isotope ratio mass spectrometry (IRMS)

Isotope ratio mass spectrometry (IRMS) is a well-established technique with applications in numerous fields apart from food science, including archaeology [14–16], paleontology [17], forensic science [18,19], environmental sciences [20,21], and medicine [22]. In the context of food science, IRMS analysis is used for the isotopic profiling of products, the investigation of food adulteration, the tracing of geographic origin, and the authentication of organic status (see Fig. 1).

The majority of studies utilizing stable isotopes for the organic authentication of food products have relied on IRMS analysis of the light elements carbon ($^{13}C/^{12}C$), hydrogen ($^{2}H/^{1}H$), oxygen ($^{18}O/^{16}O$), sulfur ($^{34}S/^{32}S$), and nitrogen ($^{15}N/^{14}N$). This technique is effective because the isotopic profile of materials derived from plants is heavily influenced by the plant sources (such as CO_2, H_2O, and NO_2^-/NO_3^-), its growth environment (climate, altitude, and latitude), cultivation procedures, fertilizer type (e.g., organic or synthetic), or quantity used [23]. Regarding livestock and animal products such as dairy, factors including the animal metabolism and diet (e.g., grain-based vs. grass-based) result in variations in their isotopic composition [24,25]. The analysis of elements unsuitable for conventional IRMS (e.g., B, Mg, Sr, and Pb) has frequently been performed by means of MC-ICP-MS; however, it has been used primarily for geographic authentication, as the relative abundance of these isotopes is largely dependent on the local geological conditions [26]. In a single case, $\delta(^{25}Mg)$ and $\delta(^{26}Mg)$ were considered for the organic authentication of wheat samples; however, the data from different geographic locations were inconsistent [27]. This paper examines the research on the organic authentication of food products via IRMS analysis of light elements (H, C, N, O, and S).

1.3. Compound-specific isotope analysis (CSIA)

IRMS is particularly useful for differentiating between organic and conventional products, as it is mainly based on the principle that the two categories involve distinct farming practices. However, the issue arises when organic products are cultivated using legume-based green manures, which are recommended by both EU and US regulations [9,10]. In such cases, organic authentication based on the $\delta(^{15}N)$ value is extremely difficult because both green manures and synthetic fertilizers have $\delta(^{15}N)$ values close to 0 ‰ [28]. Bulk analysis is also unable to differentiate between the various product components in order to determine how each contributes to the total average isotope value [29]. Compound-specific methods can overcome these issues. Moreover, the IRMS analysis of a specific fraction eliminates possible differences in the bulk isotope values that were not attributable to the parameter of interest (e.g., organic vs. conventional) but rather to irrelevant factors (e.g., lipid concentrations) [30].

In compound-specific analysis, an additional step is applied prior to IRMS in order to separate the sample components. This step might involve a gas chromatograph for the determination of the $\delta(^{15}N)$ and $\delta(^{13}C)$ values of amino acids in wheat and rice [28,31] or a liquid chromatograph to obtain the $\delta(^{13}C)$ values of non-extractable proteins in honey [32].

A number of studies have reviewed the application of isotope ratio analysis for the authentication of the agricultural origin of food products. Their aims have been diversified, often focusing on a specific food product category, such as animal products [33], milk [34], or fish [35,36], or examining several authentication techniques [26,37] and various food authenticity cases [38,39]. The application of LC-IRMS in numerous fields was recently reviewed by Perini & Bontempo [29]. LC-IRMS methods have been developed for the detection of food adulteration and geographic characterisation, such as in the case of Italian grape musts [40] or Chinese honey and food [41,42]. In particular this technique has been widely used for the verification of authenticity of

honey based on the carbon stable isotope ratio analysis of the different sugars. As far as our knowledge, the technique has not yet been used for organic authentication cases. In this paper, we discuss the application of bulk IRMS and compound-specific (GC-IRMS) analysis in recent organic food authentication studies. We cover a series of product categories, including fruit, vegetables, meat, cereals, spices, and drinks, among others. In the final section of the paper, we provide a summary of complementary analytical techniques to IRMS, such as ICP-MS and NMR, along with the chemometrics and statistical methods frequently used in each article for data analysis.

2. IRMS methodology

2.1. Sample preparation

2.1.1. Bulk IRMS analysis

The methods used in the reviewed articles to prepare the samples for IRMS analysis can be categorized according to the type of product and analytical instrument used. In the cases of bulk IRMS analysis of cereal grains, the samples were air-dried [43] or freeze-dried [44,45] for 24–72 h and ground to a fine powder, while in other instances the samples were air-dried, powdered, and then oven-dried prior to IRMS analysis [46]. In two cases, sample preparation for the IRMS analysis of coffee was carried out using different techniques: coffee beans were either roasted and milled [47] or ground and then extracted by hexane or water in a Soxhlet apparatus for 5 h in order to reduce the complexity of the analyte [48]. Fresh produce, such as fruit and vegetables, were freeze-dried [49,50] or oven-dried [51] before being ground into a homogenous powder. The same procedure was applied to eggs, specifically freeze-drying, homogenizing, and grounding egg whites [52].

For the IRMS analysis of fat content in cereals [53] or meat [54], the fat was predominantly extracted from the dried samples in a Soxhlet apparatus for 6 h using extracting agents such as ether [54] and dichloromethane [53]. Fat extraction from milk, however, was carried out via different methods, including homogenization with a mixture of 2-propanol and cyclohexane [55] or by first lyophilizing the milk samples and subsequently applying accelerated solvent extraction with a mixture of ethyl acetate and cyclohexane [25]. The former method was used to extract fat from fish [56,57], while the latter was used to extract fat from cheese [25]. The remaining fish tissue was freeze-dried to produce the defatted dry matter [57]. In the case of protein isolation, milk protein was collected by first defatting the samples via centrifugation and then adding HCl for protein precipitation [55,56], whereas potato protein was isolated by precipitation with Na_2WO_4 and acidification [53].

2.1.2. Compound-specific IRMS analysis

Sample preparation procedures for compound-specific analysis typically involve multiple stages and are more complex than those employed for bulk IRMS. Paolini et al. [31] developed a multi-step sample preparation process for the GC-C-IRMS analysis of $\delta(^{15}N)$ and $\delta(^{13}C)$ wheat amino acids, beginning with defatting the samples with a mixture of petroleum ether/ethyl ether, followed by protein hydrolysis with HCl, and amino acid purification using an ion-exchange chromatography resin. N-acetyl isopropyl derivatization was the final phase, which required acidified isopropanol for esterification and a mixture of acetic anhydride/trimethylamine/acetone for acetylation. Bontempo et al. [58] also utilized this technique for the GC-C-IRMS analysis of tomato amino acids. For the amino acid analysis of rice [28] and milk [59], acid hydrolysis was followed by two different derivatization methods. The methoxycarbonyl methyl ester (MOC) method, employing methyl chloroformate as the derivatizing reagent of the acid hydrolysates, was used for the $\delta(^{13}C)_{amino\text{-}acid}$ analysis, while the N-acetyl isopropyl ester (NAIP) method was used for $\delta(^{15}N)_{amino\text{-}acid}$ analysis. GC-C-IRMS analysis of amino acids was also used for the authentication of organic salmon, with sample preparation comprising HCl hydrolysis of salmon muscle tissue, removal of lipophilic compounds with n-hexane/chloromethane, and volatilization of amino acids via derivatization [60]. In this study, the derivatization step was carried out by methylation with acidified methanol and subsequent acetylation to form N-acetyl methyl ester derivatives. For the analysis of rice [28] and milk [59] fatty acids, fatty acids were extracted with heptanes and methylated, converting them to methyl esters (FAMEs). Butter fatty acids were also converted to FAMEs prior to GC-C-IRMS analysis; however, in this case, they were further separated by urea complexation, and the fraction containing phytanic acid methyl ester was taken for analysis [25].

Laursen et al. [27] developed a novel sample preparation method for the IRMS analysis of plant-derived nitrate ($\delta(^{15}N)_{nitrate}$ and $\delta(^{18}O)_{nitrate}$) from organic and conventional wheat, barley, faba bean, and potato samples by first extracting the nitrate from freeze-dried samples and then converting it to N_2O using denitrifying bacteria. Novak et al. [61] employed the denitrifier method for the organic authentication of potatoes, carrots, and cabbage, in conjunction with a method devised by the authors for the analysis of plant-derived sulfate ($\delta(^{18}O)_{sulfate}$). This method was based on the extraction of dissolved plant sulfate in water and its precipitation as $BaSO_4$ via the addition of a $BaCl_2$ solution. The $\delta(^{18}O)$ value of water used in the sulfate extraction method was also obtained in the study.

Lastly, Wassenaar et al. [62] developed an alternative method for the analysis of nitrate in fruit extracts that did not involve bacterial reduction. This technique involved the one-step reduction of nitrate from strawberry extracts to N_2O headspace gas utilizing Ti(III) chloride in 30 % hydrochloric acid. The samples were left at room temperature for approximately 24 h to allow for the conversion of NO_3^- to NO_2. The authors suggested that this method may be applied to other fruits and vegetables to determine their organic authenticity.

2.2. Instrumental analysis

The following is a brief overview of IRMS techniques. Kelly et al. [39] provide a detailed description of the instrumentation of IRMS methods, including GC- and LC-IRMS.

Isotope-ratio mass spectrometers use electron impact (EI) ion sources, in which molecules are bombarded with electrons to form positively charged ions ($M + e^- \rightarrow M^{+\cdot} + 2e^-$). These are then focused into an ion beam with a specific m/z ratio through the mass analyzer's entrance slit, the only primary exit available. This "closed source design" ensures the high precision levels necessary for measuring the abundance of natural isotopes. The EI sources used in IRMS are optimized for the ionization of simple gases such as CO_2, N_2, CO, H_2, and SO_2 under vacuum (1×10^{-6} to 7×10^{-8} mbar). Isotope ratio linearity is attained by utilizing the continuous flow (CF) mode for ion extraction from the source, which exhibits high extraction potentials and low ion residence times. The isotope-ratio measurements are performed simultaneously for each isotope, with the universal triple collector (UTC) used most frequently for CO_2, N_2, CO, and SO_2 analysis and the addition of 2 F cups for the measurement of H_2.

The required conversion of the sample into simple gases is accomplished by coupling the IRMS to an introduction source such as an elemental analyzer (EA). EA-IRMS provides low-cost and high-throughput analysis and has been the method of choice for bulk sample analysis. For $\delta(^{13}C)$, $\delta(^{15}N)$, and $\delta(^{34}S)$ measurements in bulk IRMS, the sample is carried into a combustion reactor via helium gas and is converted into CO_2, N_2, and SO_2 gases in the presence of oxygen, whereas for $\delta(^{18}O)$ and $\delta(^{2}H)$ analysis, the oxygen and hydrogen in the sample are converted into CO and H_2, respectively, via quantitative high-temperature conversion (HTC) in a reductive environment. The gases are subsequently separated in a packed GC column.

Alternative sample introduction methods in CF mode involve the coupling of a gas or liquid chromatograph to the IRMS (GC- or LC-IRMS). In cases of compound-specific analyses, these are utilized because they provide additional information on the isotope composition of individual

sample compounds (e.g., amino acids or fatty acids). The components of interest are separated in the GC or LC column prior to their online conversion to simple gases for IRMS analysis. In GC-combustion(C)-IRMS, the compounds eluting from the column are oxidized in a capillary reactor to form CO_2, N_2, and SO_2 at 940–1000 °C, while quantitative pyrolysis by HTC (GC-Py-IRMS) occurs at an inert and reductive environment, at temperatures above 1430 °C. GC-IRMS can analyze volatile molecules (e.g. vanillin) or molecules that can be rendered volatile by derivatization (e.g., amino acids or fatty acids) [29]. On the other hand, LC-IRMS systems measure the $\delta(^{13}C)$ values of all water-soluble compounds, such as sugars and alcohols, using the aqueous phase as a carrier and converting them into CO_2. It is worth noting that GC-C-IRMS requires significantly less carbon in the sample than LC-IRMS [29].

2.3. Results

The stable isotope composition of a substance is typically expressed using the delta (δ) notation, with units in either parts per thousand (per mil, ‰) or in the SI unit Urey (mUr is equivalent to ‰) [63]. Specifically, stable isotope compositions are reported as variations of the molar ratio, R, of the heavy (^{i}E) to light (^{j}E) isotope of an element E or of a rare to common stable isotope (such as $^{13}C/^{12}C$ or $^{15}N/^{14}N$) relative to a reference standard [64]:

$$\delta^{i}\left(E_{sample/standard}\right) = \frac{R\left({}^{i}E/{}^{j}E\right)_{sample}}{R\left({}^{i}E/{}^{j}E\right)_{standard}} - 1$$

The standard is an internationally recognized reference material, as is the Vienna Pee Dee Belemnite (VPDB) for carbon, Air-N_2 for nitrogen, the Vienna Standard Mean Ocean Water (VSMOW) for oxygen and hydrogen, and the Vienna-Canyon Diablo Troilite (VCDT) for sulfur.

In food forensics and other fields, it is also useful to determine the differences between the isotopic compositions of various components in a system, such as the $\delta(^{13}C)$ of a plant and the $\delta(^{13}C)$ of its soil. This is expressed using the Δ-notation, for instance: $\Delta(^{13}C)_{plant/soil} = \delta(^{13}C)_{plant} - \delta(^{13}C)_{soil}$ [65].

3. Nitrogen

The nitrogen stable isotope ratio $\delta(^{15}N)$ has been nominated as the most reliable indicator in the majority of organic authentication cases due to the fact that organic and synthetic fertilizers contain different amounts of $\delta(^{15}N)$ and, for most crops, fertilizer is the main nitrogen source necessary for plant growth [66]. Specifically, synthetic fertilizers used in conventional agriculture have $\delta(^{15}N)$ values ranging from −6 to 6 ‰, whereas the same values for organic fertilizers in organic farming vary between 1 and 37 ‰ [66]. This is due to the different manufacturing processes of the two fertilizer types and their nitrogen sources. In the case of organic fertilizers, nitrogen is derived from plant organic matter and animal materials that are typically composted and richer in ^{15}N, thus exhibiting greater $\delta(^{15}N)$ values. This enrichment is caused by the N isotope fractionation that occurs during composting, where there is a preferential loss of the lighter N isotope (^{14}N) via the processes of NH_3 volatilization and denitrification due to reaction kinetics being favored by ^{14}N-containing compounds rather than by ^{15}N-containing compounds [67]. On the other hand, the nitrogen in synthetic fertilizers is produced through the conversion of atmospheric N_2 into NH_4 via chemical fixation through the Haber-Bosch process (Haber & Le Rossignol, 1913; Galloway et al., 2004). This process does not result in significant N isotope fractionation; therefore, synthetic fertilizers exhibit $\delta(^{15}N)$ values that are close to those of atmospheric nitrogen gas ($\delta(^{15}N)_{atm} = 0$ ‰) [67].

Similar to the chemical N_2-fixation of atmospheric N_2, however, biological N_2-fixation by N_2-fixing plants does not result in significant N isotope fractionation [67]. When organic products are cultivated using N_2-fixing plants (legume family) as cover crops or green manures, it is

Table 1
$\delta(^{15}N)$ values reported in recent studies on the bulk IRMS analysis of plant-based foods. Results are reported as mean ± SD (where available) or as ranges.

Sample(s)	$\delta(^{15}N)$ (‰)		Reference
	Conventional	Organic	
Hemp flowers	2.0 ± 0.2	4.6 (n = 1)	[69]
Hemp seeds	2.7 ± 0.0 (n = 2)	4.8 (n = 1)	
Bananas	2.3	5.2	[70] (dependending on country but includes only graphs)
Yams	−1.88 ± 1.29 to −2.20 ± 1.15	−1.13 ± 0.97 to −1.23 ± 0.77	[51] (dependending on year)
Rice	−5.4 to −7.4	1.2 to 6.5	[71]
Potatoes	2.7 to 3.8	8.3 to 11.4	
Apples	−13.5 to −9.7	−12.5 to −6.5	
Bananas	−10.9 to 2.7	5.4 to 8.3	
Wheat	2.7 ± 1.4 to 3.9 ± 2.5	2.4 ± 1.6 to 3.9 ± 2.2	[53] (dependending on region)
Potatoes (bulk)	4.8 ± 2.1 to 6.2 ± 2.6	5.5 ± 2.2 to 5.7 ± 1.4	
Potatoes (proteins)	3.0 ± 1.8 to 4.9 ± 1.6	5.0 ± 2.2 to 5.2 ± 1.3	
Apples	2.5 ± 1.6 to 2.9 ± 4.1	1.8 ± 0.9 to 2.3 ± 1.2	
Bananas (pulp)	−0.9 ± 0.9 to 2.9 ± 0.8	1.5 ± 0.6 to 6.3 ± 1.3	[50] (dependending on country and farm)
Bananas (peel)	−1.1 ± 0.5 to 3.8 ± 0.3	1.5 ± 0.5 to 8.0 ± 0.4	
Spring barley	2.1 ± 0.3	3.4 ± 0.5	[43]
Hops	4.8 to 9.5	5.3 to 10.9	[72]
Beer	2.9 to 4.9	3.3 to 7.4	
Kiwi	0.42 ± 1.23	−0.18 ± 1.51	[73]
Chicory	4.9 ± 0.5 to 5.5 ± 2.6	11.7 ± 0.6 to 13.1 ± 2.6	[74] (dependending on fertilizer type)
Coffee	3.9 ± 1.0	5.5 ± 1.5	[47]
Oranges (flesh)	5.5 to 6.6	6.1 to 7.6	[75]
Oranges (albedo)	4.8 to 5.9	5.8 to 7.2	
Oranges (flavedo)	4.9 to 5.9	5.7 to 7.1	
Walnuts	2.1 ± 1.4 to 2.7 ± 0.9	−0.7 ± 1.8	[76] (depending on country)
Tomatoes (peel)	−1.1 ± 0.7 to 0.3 ± 2.2	8.5 ± 2.1 to 10.1 ± 0.9	[77] (dependent on cluster & year)
Tomatoes (juice)	−0.9 ± 0.8 to 1.9 ± 1.0	2.3 ± 0.0 to 10.2 ± 2.4	
Olive drupes	−7.1 to −1.7	1.3 to 2.8	[78] (depending on town)

(continued on next page)

Table 1 (*continued*)

Sample(s)	$\delta(^{15}N)$ (‰)			Reference
	Conventional	Green (w/ green manure)	Organic	
Rice	3.5 ± 0.8	4.8 ± 0.7	5.1 ± 0.3	[46]
	Conventional	Pesticide-free	Organic	
Rice	3.87 ± 0.89	5.85 ± 1.33	6.07 ± 0.65 ‰	[45]
	Conventional	Organic		
Potatoes	1.5 ± 2.2 to 1.9 ± 1.2	5.7 ± 0.0 to 6.0 ± 3.7		[79] (dependending on country)
	Conventional	Organic		
Durum wheat	1.5 ± 1.1 to 4.7 ± 1.8	1.4 ± 1.0 to 4.9 ± 2.0		[44] (depending on region)
Flour	1.9 ± 1.9 to 5.4 ± 1.5	2.5 ± 1.6 to 5.8 ± 3.4		
Pasta	1.4 ± 0.5 to 5.3 ± 1.4	2.3 ± 1.3 to 5.5 ± 3.4		
Table grapes	3.8 ± 1.4	3.2 ± 1.6		[80]
	Conventional	Organic w/ green manure	Organic w/animal manure	
Lettuce	8.5 ± 2.7 ‰	9.2 ± 1.1	14.3 ± 1.0	[81]

very difficult to distinguish them from conventional products based on their $\delta(^{15}N)$ content. This is a common issue, as the use of N_2-fixing plants in organic farming is recommended by both EU and US regulations [9,10].

Due to the differences in animal diet composition between organic and conventional farming systems, $\delta(^{15}N)$ values can also be used for the organic authentication of animal products. Differences in the stable isotope content of animal feed are reflected not only in meat, but also in fish flesh, eggs, milk, and dairy products, albeit through different mechanisms for each product [33].

The limitations caused by the use of legumes in organic farming extend to the organic authentication of both animal and plant-derived products, and, as a result, several methodologies are being developed to circumvent them. The N isotope ratio is frequently combined with those of other bio-elements (C, O, H, and S), and a number of compound-specific IRMS approaches are being investigated. GC-IRMS analysis of plant amino acids or fatty acids, as well as nitrate and sulfate extraction and analysis, are examples of the latter.

3.1. Fruit, vegetables, and plant-based products

3.1.1. Bulk IRMS analysis

$\delta(^{15}N)$ values were found to be the most reliable organic authenticity indicators for the majority of studies on cereal, fruit, and vegetables (Table 1). Chung et al. [45] found the IRMS method to be more effective in the organic authentication of rice samples than the certified and widely used multi-residue pesticide analysis. After testing 245 residue pesticides by GC-MS/MS and LC-MS/MS, the results showed no detectable pesticides in any of the samples, making it impossible to differentiate between the different rice categories using this method. In the same study, organic (6.07 ± 0.65 ‰) and pesticide-free (5.85 ± 1.33 ‰) rice had higher mean $\delta(^{15}N)$ values than conventional samples (3.87 ± 0.89 ‰). Organic rice was found to exhibit higher $\delta(^{15}N)$ values than green (where green manure cover crops and compost were used) and conventional rice, with Yuan et al. [46] noting a 2–3‰ difference and Liu et al. [68] finding no long-term agricultural effects on rice $\delta(^{15}N)$ over a 4-year period.

$\delta(^{15}N)$ values were the only useful indicators among N, C, S, and O isotopes for distinguishing organic potato samples, even though, as the authors noted, less nitrogen fertilizer is applied on potatoes compared to wheat and apples because it has little effect on yield [53]. Specifically, organic potatoes exhibited slightly higher $\delta(^{15}N)$ values than conventional potatoes, which was consistent with the study conducted by Magdas et al. [79] on 57 Romanian organic and conventional potatoes and the study by Trapp et al. [71]. In the latter study, potato tubers had positive values of 9.84 ‰ (organic) and 3.25 ‰ (conventional), while apples exhibited negative $\delta(^{15}N)$ values that did not differ significantly between the two systems [71].

Studies have shown that examining the non-edible parts of the fruit can be important. Cuevas et al. [75] established a threshold value for the authentication of organic sweet oranges (*Citrus Sinensis* L. *cv Osbeck*) by analyzing the flavedo (outer/orange) and albedo (inner/white) parts of their flesh. Based on the albedo analysis, values higher than $\delta(^{15}N) = 5.9$ ‰ indicated organic fruit. In a study on tomato leaves, peel, and juice, Trandel et al. [77] applied five different synthetic and two organic fertilizers, and although the $\delta(^{15}N)$ values of the fertilizers differed significantly (varying from 3.7 to 18.6 ‰), this was not reflected in the $\delta(^{15}N)$ of the sampled soil. Wang et al. [50] found that the peel's isotope data was consistent with the pulp of organic and conventional bananas collected from farms in different countries (Colombia, Costa Rica, Dominican Republic, Ecuador, Panama, and Peru). In this study, the highest $\delta(^{15}N)$ values were found in organic pulp and peel at 6.3 ‰ and 8.0 ‰, respectively, while conventional samples typically had values below 1.0 ‰. These results are consistent with those of Trapp et al. [71], who found that organic Brazilian bananas had a mean $\delta(^{15}N)$ value of 6.81 ‰ and their conventional counterparts had negative $\delta(^{15}N)$ values. In contrast, West African and Caribbean bananas exhibited a mean $\delta(^{15}N)$ value of 5.2 ‰ for organic and 2.3 ‰ for conventional bananas [70]. Chung et al. [82] noted that the $\delta(^{15}N)$ values of organic 6-year-old ginseng roots (*Jagyeongjong variety*) rose as the application rates of all fertilizers used in their study (cattle manure, food waste, and rice straw compost) increased. Lastly, Benincasa et al. [78] successfully differentiated between organic and conventional olive drupe and leaf samples, with organic samples exhibiting positive values and conventional samples exhibiting negative values.

A factor to consider when examining different farming systems, as underlined by Buša et al. [43], is the time when these systems were put in place. In their research, they found a significant difference between the mean $\delta(^{15}N)$ values of organic and conventional spring barley (*Hordeum vulgare* L.) grain samples (3.4 ± 0.5 ‰ and 2.1 ± 0.3 ‰, respectively), using an NPK fertilizer in the conventional systems and green manure-peas in the organic system. However, the authors noted that the organic cultivation system was only implemented two years prior to the harvest of the samples; therefore, the preceding land use could still have influenced the results.

Krauβ et al. [76] obtained an unexpected result when they found that the $\delta(^{15}N)$ values of organic walnuts were negative (−0.7 ± 1.8 ‰), while conventional walnuts had positive values (2.1 ± 1.4 ‰ and 2.7 ± 0.9 ‰ in Germany and France, respectively). As previously explained, organic samples typically exhibit greater $\delta(^{15}N)$ enrichment. In this case, however, the authors explained that there were alfalfa plants containing nitrogen-fixing bacteria in between the walnut trees. As they went on to explain, these enhance the homogeneity of the soil nitrogen supply and reduce the fertilizer influence on the isotopic composition, with geographic characteristics being the main influence.

As highlighted in the work of Díaz-Galiano et al. [83], it is important to examine cases where mixtures of organic and synthetic fertilizers are applied. The authors found very small differences between the $\delta(^{15}N)$ values of tomatoes grown with animal manure (10 ‰) and those where amounts of synthetic fertilizer were used (9.2–9.7 ‰). However, it was

Table 2
$\delta(^{15}N)$ values reported in recent studies on the compound-specific IRMS analysis of plant-based foods. Results are reported as mean (± SD where available).

Sample(s)	Isotope Marker(s)	Results (‰)			Reference
Strawberries		Conventional	Organic		[62]
	$\delta(^{15}N)_{bulk}$	4.0 ± 1.4	3.0 ± 1.4		
	$\delta(^{15}N)_{NO3}$	14.9 ± 3.0	17.6 ± 1.2		
Tomatoes		Conventional	Organic		[58]
	$\delta(^{15}N)_{bulk}$	4.8 ± 2.5	9.0 ± 3.8		
	$\delta(^{15}N)_{Alanine}$	1.9 ± 2.5	6.9 ± 3.3		
	$\delta(^{15}N)_{Valine}$	2.8 ± 2.1	8.5 ± 3.5		
	$\delta(^{15}N)_{Isoleucine}$	−0.2 ± 2.0	5.6 ± 3.0		
	$\delta(^{15}N)_{Leucine}$	−2.5 ± 2.3	2.9 ± 3.3		
	$\delta(^{15}N)_{Glycine}$	3.7 ± 3.5	8.3 ± 3.7		
	$\delta(^{15}N)_{Proline}$	10.9 ± 2.4	15.6 ± 3.4		
	$\delta(^{15}N)_{Threonine}$	1.0 ± 2.0	6.3 ± 3.3		
	$\delta(^{15}N)_{Glutamic\ acid}$	4.4 ± 2.2	10.1 ± 2.6		
	$\delta(^{15}N)_{Phenylalanine}$	7.8 ± 1.6	12.9 ± 2.8		
Rice		Conventional	Pesticide-free	Organic	
	$\delta(^{15}N)_{bulk}$	4.11	6.08	6.02	
	$\delta(^{15}N)_{Alanine}$	6.78	6.68	6.96	[28]
	$\delta(^{15}N)_{Aspartic\ acid}$	6.53	8.11	8.25	
	$\delta(^{15}N)_{Glutamic\ acid}$	2.94	4.94	5.20	
	$\delta(^{15}N)_{Glycine}$	0.56	3.83	4.08	
	$\delta(^{15}N)_{Isoleucine}$	3.62	6.13	6.22	
	$\delta(^{15}N)_{Leucine}$	1.50	3.28	3.25	
	$\delta(^{15}N)_{Methionine}$	0.70	3.72	2.82	
	$\delta(^{15}N)_{Phenylalanine}$	7.63	8.83	9.20	
	$\delta(^{15}N)_{Proline}$	5.45	8.00	8.27	
	$\delta(^{15}N)_{Serine}$	−1.37	1.47	1.98	
	$\delta(^{15}N)_{Threonine}$	5.71	8.41	7.74	
	$\delta(^{15}N)_{Valine}$	6.51	8.18	8.63	
		Conventional	Organic w/animal manure	Organic w/green manure	[61]
Potatoes	$\delta(^{15}N)_{bulk}$	1.3 ± 0.3	4.5 ± 0.4	1.7 ± 0.4	
	$\delta(^{15}N)_{NO3}$	20.7 ± 0.8	23.4 ± 0.7	21.2 ± 0.7	
		Conventional	Organic w/animal manure	Organic w/green manure	
Cabbage	$\delta(^{15}N)_{bulk}$	2.9 ± 0.6	7.5 ± 0.4	4.2 ± 0.3	
	$\delta(^{15}N)_{NO3}$	23.7 ± 1.3	26.9 ± 1.5	24.0 ± 1.6	
		Conventional	Organic w/animal manure	Organic w/green manure	
Carrots	$\delta(^{15}N)_{bulk}$	2.7 ± 0.4	5.2 ± 0.7	3.9 ± 0.8	
	$\delta(^{15}N)_{NO3}$	27.9 ± 0.4	36.3 ± 1.9	32.1 ± 1.5	
Winter Wheat		Conventional	Organic w/animal manure	Organic w/green manure	[31]
	$\delta(^{15}N)_{bulk}$				
	$\delta(^{15}N)_{Alanine}$	1.1 ± 1.0	6.2 ± 1.7	1.7 ± 1.3	
	$\delta(^{15}N)_{Aspartic\ acid}$	0.8 ± 1.1	6.0 ± 1.0	1.1 ± 1.8	
	$\delta(^{15}N)_{Glutamic\ acid}$	5.3 ± 1.1	9.3 ± 0.9	5.3 ± 2.3	
	$\delta(^{15}N)_{Glycine}$	−1.2 ± 1.9	3.2 ± 1.3	−1.5 ± 2.5	
	$\delta(^{15}N_{Isoleucine}$	0.1 ± 0.9	5.1 ± 1.4	0.3 ± 1.7	
	$\delta(^{15}N)_{Leucine}$	−1.2 ± 1.2	3.6 ± 1.5	−1.0 ± 1.7	
	$\delta(^{15}N)_{Phenylalanine}$	8.6 ± 0.7	14.5 ± 0.8	9.4 ± 1.7	
	$\delta(^{15}N)_{Proline}$	5.9 ± 0.7	10.4 ± 0.8	6.1 ± 2.1	
	$\delta(^{15}N)_{Threonine}$	−6.4 ± 1.8	−0.2 ± 2.7	−5.4 ± 1.3	
	$\delta(^{15}N)_{Valine}$	2.7 ± 0.9	8.4 ± 1.3	3.3 ± 1.6	
Durum Wheat		Conventional	Organic w/animal manure	Organic w/green manure	
	$\delta(^{15}N)_{Alanine}$	1.2	4.1	1.2	
	$\delta(^{15}N)_{Valine}$	3.1	4.9	3.6	
	$\delta(^{15}N)_{Isoleucine}$	0.4	2.9	1.4	
	$\delta(^{15}N)_{Leucine}$	−1.4	1.0	−1.7	
	$\delta(^{15}N)_{Glycine}$	0.8	2.0	1.1	
	$\delta(^{15}N)_{Proline}$	5.2	7.6	5.2	
	$\delta(^{15}N)_{Threonine}$	−4.5	−3.2	−3.4	
	$\delta(^{15}N)_{Aspartic\ acid}$	2.4	4.4	2.7	
	$\delta(^{15}N)_{Glutamic\ acid}$	4.1	6.2	3.9	
	$\delta(^{15}N)_{Phenylalanine}$	8.4	10.5	9.8	

still possible to distinguish the tomatoes grown with synthetic manure and mineral fertilizer (3.7 ‰) from the rest. In an earlier study, Wang et al. [84] considered systems with different organic/chemical fertilizer ratios and obtained the $\delta(^{15}N)$ values of cauliflower roots, stems, leaves, and flowers. Among the different plant parts, the results showed that the $\delta(^{15}N)$ values of roots and flowers could effectively differentiate between the different fertilization methods. In addition, cauliflower tissues were found to be positively correlated with one another, exhibiting the same responses to the different fertilization treatments. Lastly, different fertility management systems (no added fertilizer/control, two different

Table 3
$\delta(^{15}N)$ values reported in recent studies on the bulk IRMS analysis of meat, fish, and animal products. Results are reported as mean (± SD where available).

Sample (s)	$\delta(^{15}N)$ (‰)			Reference
	Conventional	Organic		
Chicken	−19.51 ± 0.31	−18.03 ± 0.27 to −15.36 ± 0.28 (dependent on city)		[54]
Pork	2.3 to 2.7	2.6 to 3.4		[88] (4 regions examined)
Milk	5.70 ± 0.61	5.00 ± 0.49		[89]
Milk	5.08	4.85		[90]
	Conventional	Wild	Organic	
Salmon	−24.7 to −23.2	−22.2 to −19.3	−24.7 to −23.2	[60]
	Conventional (barn and/or cage)	Free range	Organic	
Egg whites	4.3 ± 1.5 to 6.1 ± 0.8	4.5 ± 0.4 to 5.8 ± 0.9	5.3 ± 0.3 to 7.1 ± 1.0	[52] (dependent on country and year)
	Conventional	Wild	Organic	
Salmon (DDM)	8.92 ± 0.57	11.04 ± 0.48	11.61 ± 0.83	[57]
Brown trout (DDM)	9.29 ± 0.50	NA	11.59 ± 0.87	
	Conventional	Wild	Organic	
Shrimp (DDM)	6.57 ± 1.33	9.44 ± 1.70	5.48 ± 0.74	[56] (dependent on shrimp species)

organic fertilizers, two different mineral fertilizers, and a combination of an organic and mineral fertilizer) were investigated by Sinkovič et al. [74]. In this case, the $\delta(^{15}N)$ values of the chicory plants grown with the mixture of fertilizers (7.1 ‰) were found to be in between those of organic (11.7–13.1 ‰) and those of synthetic fertilizers (4.9–5.5 ‰).

It should be noted that in a few cases, no significant differences were found between the $\delta(^{15}N)$ values of conventional and organic products, specifically in common and durum wheat [44,53] and apples [53]. These studies included organic and conventional samples from more than one geographic region and found that differences between fertilization strategies applied in the different regions significantly affected their $\delta(^{15}N)$ results (for instance, the use of farmyard manure in a conventional system in one case or the use of N_2 fixing plants in others). In the study by Longobardi et al. [80], $\delta(^{15}N)$ values were unable to distinguish between organic and conventional table grapes. The authors attributed this to the plant's low nitrogen requirements and the intentionally reduced nitrogen supplies to the grapevines for the improvement of berry quality.

Even though there was a significant difference between the $\delta(^{15}N)$ values of organic and conventional tomatoes, there was a range of 2–4‰ overlap between the two [85]. The latter was attributed to the use of green manures in some organic cultivations. Similarly, no distinction could be made on the basis of the $\delta(^{15}N)$ means of organic tomatoes and those of soilless hydroponic systems, even though they were distinct from conventional tomatoes [86]. Lastly, Liu et al. [49] obtained the $\delta(^{15}N)$ values of 424 organic, green (with limited quantities of synthetic additives permitted), and conventional vegetable samples, noting that only 3 (roquette, tomato, and water spinach) out of 26 different vegetables could be categorized according to their individual isotope values. The distinction was unclear for the remaining vegetables, including cauliflower, lettuce, celery, cucumber, spinach, and eggplant, among others.

The $\delta(^{15}N)$ data of complex matrices such as coffee and beer have shown promise as organic authentication markers. In the former case, the authenticity of commercially available coffee is problematic due to the alteration of its chemical composition throughout the necessary production processes from the moment of harvest [87]. Moreover, these coffees are typically packaged with a blend of species (such as Robusta and Arabica), and the beans are frequently sourced from multiple farms [87]. In the study by Carter et al. [48], the aim was to authenticate commercially available roasted coffee beans according to their origin (Africa, Australia, Central America, Indonesia, India, Papua New Guinea, and South America); however, the authors also suggested that the $\delta(^{15}N)$ values could also be used for the authentication of organic coffee beans. Specifically, three conventional Australian coffees were found to have $\delta(^{15}N)$ values close to 0 ‰ (atmospheric nitrogen), while the most enriched sample (+6.4 ‰) claimed to be organic and was also from Australia. This finding was confirmed in a later study focusing on the organic authentication of Brazilian coffee samples, which determined that the $\delta(^{15}N)$ value of organic samples was 5.5 ‰ compared to 3.9 ‰ for conventional samples [47].

Lastly, beer and hop pellets, which are used in beer production in order to give it its distinct bitterness and aromas, were tested for organic authenticity [72]. The $\delta(^{15}N)$ values of organic hops were statistically higher than those of conventional hops, while the distinction for beer was more difficult due to overlapping $\delta(^{15}N)$ values of 3.4–7.4 ‰ for organic and 2.9–4.9 ‰ for conventional [72].

3.1.2. *Compound-specific IRMS analysis*

The $\delta(^{15}N)$ values of amino acids extracted from plant-based samples are a very promising marker of organic authenticity. Chung et al. [28] demonstrated that the $\delta(^{15}N)_{amino\text{-}acid}$ values of glutamic acid, glycine, isoleucine, methionine, proline, serine, and threonine could effectively differentiate organic and pesticide-free rice samples from conventional samples (Table 2). It was also observed that the bulk $\delta(^{15}N)$ values of organic and pesticide-free rice were higher than those of conventional samples. The methodology was incapable of fully differentiating organic from pesticide-free samples; however, some differences could be seen in the values of glutamic acid, methionine, and threonine. In contrast, Paolini et al. [31] found that the $\delta(^{15}N)_{amino\text{-}acid}$ values of conventionally grown winter wheat exhibited significantly lower values than those of organic wheat grown with animal manure, with differences over +5 ‰ for alanine, aspartic acid, isoleucine, phenylalanine, threonine, and valine (Table 2). The $\delta(^{15}N)$ variations observed in amino acids were attributed to the isotopic fractionation processes that occur during the N metabolism within the plant. For example, the $\delta(^{15}N)$ value of glutamic acid (Glx), the first amino acid produced by ammonia assimilation, was found to be lower than that of phenylalanine (Phe) and proline (Pro), which are generally more enriched in cereal grains due to kinetic isotope effects in the associated enzymatic reactions.

It can be seen that the potential $\delta(^{15}N)_{amino\text{-}acid}$ markers are different for rice and wheat, which can be attributed to differences in their physiological metabolism and growth conditions [28]. Furthermore, Paolini et al. [31] found that conventional winter wheat samples were not distinguishable from organic ones grown with green manure, while no statistically significant differences were found between organic and conventional durum wheat samples. Lastly, Bontempo et al. [58] found that $\delta(^{15}N)_{Isoleucine}$, $\delta(^{15}N)_{Glutamic\ acid}$, and $\delta(^{15}N)_{Phenylalanine}$ could be used as organic authentication markers for tomatoes, with differences of approximately +5 ‰ between organic and conventional samples. A comparison of soil samples, tomatoes, and passata in this study also revealed that $\delta(^{15}N)$ values remained unchanged during the production of organic and conventional tomato passata.

Another method that has shown great potential for the organic authentication of vegetables is the analysis of plant-derived nitrate. In a pot experiment on organic and conventional lettuce samples, Mihailova

et al. [91] found that plants grown with organic fertilizer (chicken manure) had significantly higher $\delta(^{15}N)_{bulk}$ and $\delta(^{15}N)_{nitrate}$ values than plants grown with synthetic fertilizer (potassium nitrate). Additionally, two different fertilizer concentrations were compared (50 mg N/kg substrate and 150 mg N/kg substrate), and it was observed that $\delta(^{15}N)_{nitrate}$ values were greater at lower fertilizer concentrations than at higher fertilizer concentrations. Another observation was an increase in the $\delta(^{15}N)_{bulk}$ and $\delta(^{15}N)_{nitrate}$ values of lettuce leaves compared to the same values of lettuce roots and substrates.

Novak et al. [61] used the same methodology and were able to differentiate between conventional and organic (grown with animal manure fertilizers) carrots and potatoes (Table 2). However, no distinction could be made between organic and conventional cabbage samples based on their $\delta(^{15}N)_{nitrate}$ values, while the values of organic vegetables grown with legume-based green manures were found to overlap with those of conventional and organic vegetables grown with animal manures.

Wassenaar et al. [62] also clearly differentiated between organic and conventional samples using Ti(III)-based analyses of nitrate in strawberry extracts. Specifically, organic samples exhibited $\delta(^{15}N)_{nitrate}$ values within the range of +15.1 to +19.3 ‰ and conventional $\delta(^{15}N)_{nitrate}$ values within the range of +10.3 to +22.3 ‰.

3.2. Fish, meat, and animal products

3.2.1. Bulk IRMS analysis

Lv & Zhao [54] and Zhao et al. [88] successfully differentiated between organic and conventional chicken and pork samples based on their $\delta(^{15}N)$ values (Table 3). Four Chinese regions were included in the latter study, and pork samples from all conventional systems had the lowest $\delta(^{15}N)$ values compared to organic systems from the same location. This was mainly attributed to the pigs being fed conventional concentrate feed, which, due to the application of synthetic fertilizer, exhibits lower $\delta(^{15}N)$ values than organic feed.

Several studies have been conducted for the organic authentication of milk samples via IRMS analysis, with each study following a slightly different approach. Chung et al. [89] differentiated between organic and conventional milk samples, finding that conventional $\delta(^{15}N)$ values were higher than organic. This was attributed to the likely presence of nitrogen-fixing plants in the cow feed, such as clover or legumes. The same group of researchers examined the monthly and seasonal fluctuations in the isotope ratios of organic and conventional milk samples, concluding that, across all seasons, the mean $\delta(^{15}N)$ values for conventional samples were again higher than those for organic samples [90].

Organic Dutch and New Zealand eggs were differentiated from conventional (barn/cage) and free-range eggs, with organic samples exhibiting higher $\delta(^{15}N)$ values than the other categories [52]. It was expected that free-range eggs would show $\delta(^{15}N)$ values similar to conventional eggs since the hens' feed composition is generally the same; however, the variation seen in their values was attributed to some hens ranging more freely than others. Since the guidelines for free-range eggs are not as stringent as those for organic products, some variability is generally to be expected.

Few studies on the organic authentication of seafood have been conducted. Molkentin et al. [57] observed higher average $\delta(^{15}N)_{DDM}$ values in organic and wild salmon than in conventional samples. Higher $\delta(^{15}N)_{DDM}$ values were also found, on average, in organic brown trout samples compared to conventional samples. The authors explained that $\delta(^{15}N)$ values in this study were measured in defatted dry matter from fish, but they correspond to those of the whole tissue as the lipid fraction is almost nitrogen-free. Slightly higher $\delta(^{15}N)_{DDM}$ values were noted for organic fish because their feed probably consisted of fish meal from a higher level of the food chain than that of wild salmon, while $\delta(^{15}N)_{DDM}$ was the lowest in conventional fish since the feed in this case consists of a higher quantity of vegetables. No significant differences were found between graved and smoked salmon samples, nor between raw and smoked trout; therefore, the type of processing had no impact on $\delta(^{15}N)_{DDM}$ values. It is worth noting that complete differentiation between organic and conventional fish was only attained by combining $\delta(^{15}N)_{DDM}$ and $\delta(^{13}C)_{DDM}$ data.

Lastly, Ostermeyer et al. [56] differentiated between wild and organic shrimp samples by combining their $\delta(^{15}N)_{DDM}$ and $\Delta(\delta(^{13}C)$ values. On the basis of the same markers, *Litopenaeus vannamei* shrimp were also authenticated as organic; however, it was not possible to differentiate between organic and conventional *Penaeus monodon* shrimp. The combined data of all shrimp species exhibited a high degree of variability, probably reflecting the variation in their nutritional conditions, with the authors emphasizing the influence of factors such as the presence of vegetable fats or animal prey present in the feeds.

Table 4
$\delta(^{15}N)$ values reported in recent studies on the compound-specific IRMS analysis of animal products. Results are reported as mean ± SD.

Sample	Isotope Marker(s) (‰)	Cultivation Types		Reference
Milk		Organic	Conventional	
	$\delta(^{15}N)_{Bulk}$	4.94 ± 0.37	5.15 ± 0.21	
	Amino acids:			
	$\delta(^{15}N)_{Alanine}$	5.15 ± 1.61	6.72 ± 2.50	[59]
	$\delta(^{15}N)_{Aspartic\ acid}$	6.18 ± 0.71	5.97 ± 0.47	
	$\delta(^{15}N)_{Glutamic\ acid}$	8.14 ± 0.50	8.11 ± 0.26	
	$\delta(^{15}N)_{Glycine}$	5.91 ± 1.32	6.94 ± 2.37	
	$\delta(^{15}N)_{Isoleucine}$	8.72 ± 2.36	8.49 ± 2.92	
	$\delta(^{15}N)_{Leucine}$	4.26 ± 0.78	4.65 ± 0.71	
	$\delta(^{15}N)_{Lysine}$	3.08 ± 1.52	2.55 ± 1.08	
	$\delta(^{15}N)_{Methionine}$	0.34 ± 0.89	0.87 ± 0.87	
	$\delta(^{15}N)_{Phenylalanine}$	6.12 ± 0.71	5.42 ± 0.61	
	$\delta(^{15}N)_{Proline}$	6.57 ± 0.30	6.86 ± 0.45	
	$\delta(^{15}N)_{Serine}$	3.44 ± 0.42	4.26 ± 1.01	
	$\delta(^{15}N)_{Threonine}$	−0.66 ± 0.48	0.08 ± 1.01	
	$\delta(^{15}N)_{Valine}$	8.15 ± 1.19	7.72 ± 1.05	

3.2.2. Compound-specific IRMS analysis

Comparatively fewer works have been published recently on compound-specific IRMS methods for organic animal product authentication than on plants, fruits, and vegetables. Moreover, the $\delta(^{13}C)$ values were investigated more frequently than $\delta(^{15}N)$ values. However, Chung et al. [59] identified the $\delta(^{15}N)$ amino acid values of Phe, Ser, and Thr as promising markers of organic milk authenticity (Table 4), while cultivation type and season had an effect on Lys. In winter, $\delta(^{15}N)$ values for aspartic acid (Asp), glutamic acid (Glx), glycine (Gly), leucine (Leu), proline (Pro), and valine (Val) were found to be greater than in summer. The authors also highlighted the effect of amino acid-protein assimilation/metabolism on $\delta(^{15}N)$ values in addition to that of $\delta(^{15}N)$ in animal feed.

4. Carbon

The $\delta(^{13}C)$ content of plants is influenced by plant species, nitrogen fertilizer levels, crop type, and production system, with the main factor, however, being the plant photosynthetic pathway [92]. Specifically, C4 plants (−9‰ to −20 ‰) have higher values than C3 plants (−21 ‰ to −35 ‰), whereas CAM plant values range between those of C4 and C3 plants [93]. An additional $\delta(^{13}C)$ influencing factor that can assist in differentiating between organic and conventional products of the same species is their difference in soil respiration. Higher soil respiration rates can be found in organic fields due to organic fertilizers that enhance the growth and activity of methanotrophic bacteria, which respire CO_2 [92]. During photosynthesis, plants discriminate against the heavier isotope (^{13}C) but respire ^{13}C-enriched CO_2. These higher respiration rates result in lower $\delta(^{13}C)$ values for organic crops, thus allowing them to be distinguished from conventional crops [94,95].

When it comes to authenticating meat and animal products, their $\delta(^{13}C)$ values depend on the animal's diet, which can help distinguish

Table 5
$\delta(^{13}C)$ values reported in recent studies on the bulk IRMS analysis of plant-based foods. Results are reported as mean ± SD (where available) or in ranges.

Sample(s)	$\delta(^{13}C)$ (‰)			Reference
	Conventional	Organic		
Hemp flowers	−28.5 ± 0.3	−28.2 (n = 1)		[69]
Hemp seeds	−27.9 ± 1.4	−29.3 (n = 1)		
Bananas	2.34	5.24		[70] (dependending on country)
Spring barley	−28.75 ± 0.04 to −28.24 ± 0.03	−28.499 ± 0.017 to −27.464 ± 0.026		[43]
Hops	−27.5 to −25.1	−27.6 to −25.5		[72]
Beer	−28.4 to −22.6	−28.4 to −25.9		
Wheat (bulk)	−27.1 ± 0.3 to −26.7 ± 0.7	−26.7 ± 0.5 to −26.2 ± 0.7		[53] (dependending on region)
Wheat (lipids)	−33.5 ± 0.8 to −33.1 ± 0.8	−33.1 ± 0.4 to −32.5 ± 0.7		
Potatoes (bulk)	−26.2 ± 0.8 to −26.0 ± 0.4	−26.2 ± 1.0 to −25.8 ± 1.1		
Potatoes (proteins)	−28.4 ± 0.6 to −28.2 ± 0.4	−28.3 ± 0.8 to −27.8 ± 1.0		
Apples (bulk)	−27.1 ± 0.9 to −26.2 ± 0.8	−26.4 ± 0.8 to −26.2 ± 0.8		
Yams	−26.97 to −26.62	−26.91 to −26.46		[51]
Bananas (pulp)	−23.8 ± 0.6 to −23.0 ± 0.8	−23.3 ± 0.5 to −22.6 ± 0.3		[50] (dependending on country and farm)
Bananas (peel)	−25.3 ± 0.3 to −24.7 ± 0.5	−25.6 ± 0.5 to −23.6 ± 0.5		
Kiwi	−26.33 ± 0.77	−26.10 ± 0.70		[73]
Chicory	−31.0 ± 0.7 to −29.2 ± 0.9	−29.3 ± 0.7 to −28.9 ± 0.6		[74] (dependending on fertilizer type)
Oranges (flesh)	−26.52	−26.16		[75]
Oranges (albedo)	−27.11	−26.81		
Oranges (flavedo)	−27.51	−27.44		
	Conventional	Organic w/ animal manure	Organic w/green manure	[61]
Potato	−27.2 ± 0.3	−26.5 ± 0.2	−26.6 ± 0.3	
Cabbage	−24.0 ± 0.1	−23.9 ± 0.1	−23.8 ± 0.1	
Carrot	−27.8 ± 0.1	−27.8 ± 0.2	−27.8 ± 0.2	
Coffee	−27.4 ± 0.6	−27.3 ± 0.7		[47]
	Conventional	Green	Organic	
Rice	−27.5 ± 0.4	−27.4 ± 0.4	−27.7 ± 0.5	[46]
	Conventional	Pesticide-free	Organic	
Rice	−26.79 ± 0.3	−26.66 ± 0.4	−26.70 ± 0.2	[45]
Potatoes	−25.8 ± 1.2 to 1.5 ± 1.7	−26.7 ± 0.9 to −26.3 ± 0.8		[79] (dependending on country)
	Conventional	Organic		
Onions	−27.8 to −23.8	−29.2 to −28.2		[96]
Durum wheat	−27.2 ± 0.1 to −23.3 ± 0.4	−27.2 ± 0.1 to −23.9 ± 0.5		[44] (dependending on region)
Flour	−27.2 ± 0.2 to −23.3 ± 0.5	−27.2 ± 0.1 to −23.8 ± 0.3		
Pasta	−27.2 ± 0.1 to −23.4 ± 0.4	−26.9 ± 0.8 to −24.0 ± 0.3		
Table grapes	−28.3 ± 0.6	−28.0 ± 0.6		[80]
Tomatoes	only boxplots			[85]

between organic and conventional farming due to the different feed supplied in these systems. For instance, pasture and hay (C3 plants) are mainly used in organic agriculture, while concentrate and maize silage (C4 plants) are mostly used in conventional agriculture [25]. The differences between the $\delta(^{13}C)$ content of the two plant categories used in the feed can influence the $\delta(^{13}C)$ content of meat [88] and animal products such as milk [25]. Variations seen between the $\delta(^{13}C)$ values of bulk products, proteins, and lipids are a result of differences in the fractionation taking place in the metabolic pathways from which proteins and lipids are produced.

4.1. Plant species

4.1.1. Bulk IRMS analysis

In contrast to $\delta(^{15}N)$ and $\delta(^{34}S)$, the bulk $\delta(^{13}C)$ values of common wheat produced significant differences between organic and conventional crop management systems in the study by Gatzert et al. [53] (Table 5). However, it was not possible to distinguish between organic and conventional potatoes in the same study, with the authors stating that potato $\delta(^{13}C)$ values varied between regions and were associated with local growing conditions. Similar conclusions were reached by Bontempo et al. [44], who found highly significant differences between the $\delta(^{13}C)$ of organic and conventional wheat, flour, and pasta samples when examining only one of the four Italian regions analyzed in their study, as opposed to all four regions collectively. Specifically, ^{13}C levels in organic products were depleted when compared to conventional products due to the previously discussed bacterial fermentation phenomenon. The same trend was seen in kiwi samples [73]; however, the opposite was observed by Chung et al. [45], who noted that organic and

Table 6
$\delta(^{13}C)$ values reported in recent studies on the compound-specific IRMS analysis of plant-based foods. Results are reported as mean (± SD where available).

Sample(s)	Marker	δ13C (‰)			Reference
		Conventional	Organic		
Tomato passata	$\delta(^{13}C)_{bulk}$	−25.1 ± 0.7	−23.7 ± 0.4		[58]
Tomatoes	$\delta(^{13}C)_{bulk}$	−28.0 ± 1.2	−27.4 ± 0.8		
	Amino acids:				
	$\delta(^{13}C)_{Ala}$	−27.8 ± 1.2	−27.3 ± 0.8		
	$\delta(^{13}C)_{Val}$	−34.0 ± 0.7	−33.8 ± 0.8		
	$\delta(^{13}C)_{Ileu}$	−25.6 ± 1.3	−25.5 ± 1.2		
	$\delta(^{13}C)_{Leu}$	−36.9 ± 0.9	−36.5 ± 0.9		
	$\delta(^{13}C)_{Gly}$	−38.8 ± 2.3	−38.9 ± 1.7		
	$\delta(^{13}C)_{Pro}$	−26.2 ± 2.5	−25.8 ± 2.2		
	$\delta(^{13}C)_{Thr}$	−23.7 ± 2.6	−22.7 ± 2.0		
	$\delta(^{13}C)_{Glx}$	−28.4 ± 0.5	−26.9 ± 0.6		
	$\delta(^{13}C)_{Phe}$	−29.4 ± 0.9	−29.2 ± 0.7		
Rice		Conventional	Pesticide-free	Organic	
	$\delta(^{13}C)_{bulk}$	−26.79	−26.78	−26.69	
	Amino acids:				
	$\delta(^{13}C)_{Ala}$	−27.11	−27.25	−26.57	[28]
	$\delta(^{13}C)_{Asx}$	−27.08	−26.66	−26.68	
	$\delta(^{13}C)_{Glx}$	−30.13	−30.32	−30.10	
	$\delta(^{13}C)_{Gly}$	−17.70	−17.48	−17.02	
	$\delta(^{13}C)_{Ileu}$	−29.19	−30.00	−29.30	
	$\delta(^{13}C)_{Leu}$	−37.72	−37.99	−37.64	
	$\delta(^{13}C)_{Met}$	−24.77	−26.78	−26.28	
	$\delta(^{13}C)_{Phe}$	−29.21	−29.74	−29.62	
	$\delta(^{13}C)_{Pro}$	−32.02	−32.02	−31.73	
	$\delta(^{13}C)_{Ser}$	−27.14	−27.47	−26.92	
	$\delta(^{13}C)_{Thr}$	−28.09	−30.36	−29.20	
	$\delta(^{13}C)_{Tyr}$	−32.64	−33.07	−30.88	
	$\delta(^{13}C)_{Val}$	−33.18	−33.66	−33.41	
	Fatty acids:				
	$\delta(^{13}C)_{Tridecylic\ acid}$	−27.31	−26.90	−27.97	
	$\delta(^{13}C)_{Myristic\ acid}$	−38.38	−37.87	−37.67	
	$\delta(^{13}C)_{Palmitic\ acid}$	−35.88	−35.23	−35.41	
	$\delta(^{13}C)_{Stearic\ acid}$	−33.01	−32.99	−32.61	
	$\delta(^{13}C)_{Oleic\ acid}$	−34.23	−34.06	−33.73	
	$\delta(^{13}C)_{Linoleic\ acid}$	−35.34	−34.52	−35.40	
Winter Wheat		Conventional	Organic w/green manure	Organic w/animal manure	[31]
	Amino acids:				
	$\delta(^{13}C)_{Ala}$	−24.9 ± 1.0	−23.7 ± 0.5	−24.1 ± 1.0	
	$\delta(^{13}C)_{Asx}$	−25.2 ± 1.0	−24.1 ± 0.9	−24.4 ± 2.0	
	$\delta(^{13}C)_{Glx}$	−26.1 ± 0.3	−24.6 ± 0.6	−24.0 ± 1.0	
	$\delta(^{13}C)_{Gly}$	−14.7 ± 1.4	−13.4 ± 1.0	−13.4 ± 0.8	
	$\delta(^{13}C)_{Ileu}$	−26.9 ± 0.9	−26.1 ± 0.7	−26.1 ± 1.6	
	$\delta(^{13}C)_{Leu}$	−34.0 ± 0.8	−33.7 ± 0.5	−33.8 ± 0.7	
	$\delta(^{13}C)_{Phe}$	−26.5 ± 1.4	−26.4 ± 1.6	−27.2 ± 1.7	
	$\delta(^{13}C)_{Pro}$	−28.1 ± 0.8	−26.8 ± 0.7	−27.3 ± 1.4	
	$\delta(^{13}C)_{Thr}$	−14.6 ± 0.5	−12.5 ± 1.1	−12.8 ± 3.1	
	$\delta(^{13}C)_{Val}$	−30.8 ± 0.7	−30.3 ± 0.9	−30.2 ± 1.4	
Durum Wheat		Conventional	Organic w/green manure	Organic w/animal manure	
	Amino acids:				
	$\delta(^{13}C)_{Ala}$	−25.5 ± 1.9	−27.0 ± 0.1	−22.8 ± 1.9	
	$\delta(^{13}C)_{Asx}$	−24.3 ± 3.0	−25.8 ± 0.8	−24.5 ± 1.5	
	$\delta(^{13}C)_{Glx}$	−27.0 ± 0.9	−22.8 ± 0.6	−23.8 ± 1.4	
	$\delta(^{13}C)_{Gly}$	−15.8 ± 2.1	−21.1 ± 2.5	−15.0 ± 3.5	
	$\delta(^{13}C)_{Ileu}$	−27.0 ± 1.3	−28.7 ± 0.2	−26.6 ± 1.7	
	$\delta(^{13}C)_{Leu}$	−34.9 ± 1.0	−37.1 ± 1.1	−34.5 ± 0.6	
	$\delta(^{13}C)_{Phe}$	−26.2 ± 1.2	−33.4 ± 3.5	−27.1 ± 2.9	
	$\delta(^{13}C)_{Pro}$	−26.2 ± 1.5	−29.4 ± 0.8	−25.3 ± 1.0	
	$\delta(^{13}C)_{Thr}$	−13.1 ± 1.9	−17.0 ± 2.5	−11.5 ± 2.0	
	$\delta(^{13}C)_{Val}$	−30.9 ± 1.5	−32.7 ± 0.3	−31.5 ± 1.2	

pesticide-free rice exhibited slightly higher mean values than their conventional counterparts. As explained by Paolini et al. [31], lower $\delta(^{13}C)$ in conventional samples can be the result of higher stomatal conductance caused by higher nitrogen content. In addition, Chung et al. [45] noted that $\delta(^{13}C)$ depended significantly on the type of rice and producer, while Sinkovič et al. [74] found that $\delta(^{13}C)$ values were dependent on the specific fertilizer used rather than on the type, i.e., mineral or organic. In two more recent studies on organic rice authentication, Yuan et al. [46] found lower $\delta(^{13}C)$ values in organic rice samples than in conventional samples, whereas in the study by Liu et al. [68], rice samples initially followed the same trend, but this reversed over the course of 3 years, with organic $\delta(^{13}C)$ values becoming more positive than conventional values. Therefore, rice $\delta(^{13}C)$ values can be substantially affected by annual climatic changes; however, in the case

Table 7
$\delta(^{13}C)$ values reported in recent studies on the bulk IRMS analysis of meat, fish, and animal products. Results are reported as mean (± SD where available).

Sample (s)	$\delta(^{13}C)$ (‰)			Reference
	Conventional	Organic		
Chicken	−19.43 ± 0.37	−18.06 ± 0.34 to −15.37 ± 0.33 (dependent on area)		[54]
Pork	−18.4 to −15.1	−17.2 to −14.7		[88] (4 regions considered)
Milk	−23.60 ± 0.24	−22.39 ± 0.63		[89]
Milk	−22.06	−22.44		[90]
Milk fat Milk protein	−26.0 ± 2.53 −23.2 ± 1.89	−30.0 ± 1.07 −26.2 ± 0.83		[55]
Milk fat Cheese	−24.74 ± 0.15 −26.1 ± 2.45	−31.07 ± 0.18 −30.0 ± 1.12		[25]
	Conventional (barn and/or cage)	Free range	Organic	
Egg whites	−22.6 ± 0.8 to −19.2 ± 1.1	−22.2 ± 2.3 to −20.1 ± 2.5	−21.3 ± 3 to −19.5 ± 0.9	[52] (dependent on country and year)
	Conventional	Wild	Organic	
Salmon (DDM)	−21.98 ± 0.55	−20.37 ± 0.37	−19.68 ± 0.62	[57]
Salmon (LIP)	−27.66 ± 0.26	−27.85 ± 0.59	−25.96 ± 0.45	
Brown trout (DDM)	−22.03 ± 0.62	NA	−20.46 ± 0.72	
Brown trout (LIP)	−27.11 ± 0.54	NA	−27.19 ± 0.37	
	Conventional	Wild	Organic	
Shrimp (DDM)	−20.56 ± 2.31	−18.45 ± 1.96	−16.89 ± 2.21	[56]
Shrimp (LIP)	−26.48 ± 2.11	−24.86 ± 1.51	−23.45 ± 2.44	

of banana $\delta(^{13}C)$ values, Wang et al. [50] found that these are negatively correlated with rainfall.

4.1.2. Compound-specific IRMS analysis

By adding a step to the stable isotope ratio analysis methodology, amino acid analysis could circumvent several of the aforementioned issues. Chung et al. [28] were able to identify pesticide-free rice samples by their $\delta(^{13}C)_{isoleucine}$ values, organic rice samples by their $\delta(^{13}C)_{tyrosine}$ values, and conventional samples by their $\delta(^{13}C)_{lysine}$ values (Table 6). In the same study, neither bulk analysis nor $\delta(^{13}C)_{fatty\text{-}acid}$ analysis attained this result. However, the majority of $\delta(^{13}C)_{fatty\text{-}acid}$ and $\delta(^{13}C)_{amino\text{-}acid}$ values were found to be lower than the mean bulk values, a trend that was not observed in the $\delta(^{15}N)$ values, indicating isotopic fractionation in the synthesis of fatty acids and amino acids during rice production. On the other hand, organic winter and durum wheat were differentiated from conventional samples on the basis of the $\delta(^{13}C)$ values of glutamine, which were greater than those of conventional samples [31]. Overall, the authors concluded that the combination of the $\delta(^{15}N)$ and $\delta(^{13}C)$ values of 10 amino acids, i.e., alanine (Ala), valine (Val), isoleucine (Ile), leucine (Leu), glycine (Gly), proline (Pro), threonine (Thr), aspartic acid (Asx), glutamic acid (Glx), and phenylalanine (Phe), could improve the ability to differentiate between conventional and organic wheat samples when compared with the results obtained by bulk analysis. The differences between the results for rice and wheat were attributed to their different metabolic and growth mechanisms [28]. Lastly, the $\delta(^{13}C)$ values of glutamine were again found to be effective organic markers for tomatoes when differentiation was not possible through bulk analysis [58].

4.2. Meat and animal products

4.2.1. Bulk IRMS analysis

As mentioned at the beginning of this section, the differentiation between organic and conventional meat and animal products is based on the assumption that the former will exhibit lower $\delta(^{13}C)$ values, as free-grazing animal feeds consist of fresh grass and pasture (mainly C3 plants), whereas conventionally raised animals are fed maize-containing feeds (C4). This was confirmed in the $\delta(^{13}C)$ values of milk fat and protein [55], while Kaffarnik et al. [25] noted that in the case of a gradual transition from conventional to organic feed, the $\delta(^{13}C)$ values of milk fat decreased linearly by about 0.3 ‰ daily until the transition was complete. The $\delta(^{13}C)$ values of organic cheeses, including Edam, Gouda, and Emmental, were generally found to be depleted (Table 7) [25], while the values of their conventional counterparts varied. The latter was attributed to mountain cheeses being traditionally made from grass- and hay-fed cows, while semi-hard and butter cheeses are made from grass- and maize-fed cows.

Higher $\delta(^{13}C)$ values have often been found in organic meat and animal products in cases where C4 plants are present in areas where animals are allowed to graze freely, thus increasing their $\delta(^{13}C)$ values. For instance, Lv & Zhao [54] found higher $\delta(^{13}C)$ values in organic chicken than in conventional chicken (Table 7), with the highest being in an area where maize is one of the primary crops. Similarly, Zhao et al. [88] found more positive values in organic pork from four areas in China, and Rogers et al. [52] noticed that Dutch barn and free-range egg whites had a narrower range of $\delta(^{13}C)$ values compared to organic, with the latter having more positive values than the other two.

Interestingly, Chung et al. [89] found more positive $\delta(^{13}C)$ values in bulk organic milk; however, in their later study, the trend was reversed, with organic samples exhibiting lower $\delta(^{13}C)$ values than conventional samples. In the second case, the researchers conducted a 1-year case study and concluded that the $\delta(^{13}C)$ values of the organic samples showed significant seasonal variability, with lower values in the summer and higher values in the winter. This was attributed to seasonal variations in organic animal feed, as sufficient pasture or fresh grass is typically available during the warmer months.

In marine samples, organic $\delta(^{13}C)$ values were found to be, on average, higher than conventional values. Specifically, this was the case for Molkentin et al. [57] in the $\delta(^{13}C)$ values of salmon defatted dry matter (DDM) and lipids (LIP) and for Ostermeyer et al. [56] in the $\delta(^{13}C)$ of shrimp DDM and LIP, even though a clear distinction between farming types was not possible. In both studies, the authors attributed the enriched $\delta(^{13}C)$ values in organic and wild samples to higher ingestion of animal-derived feed or prey, while conventional farming incorporated mainly vegetable feeds. Moreover, the isolation of the lipid fraction allowed for the clear differentiation of wild salmon samples, which exhibited lower $\delta(^{13}C)$ values compared to organic fish since the latter are supplied with high-fat feeds.

4.2.2. Compound-specific IRMS analysis

Unlike the compound-specific IRMS findings in plant-based samples, $\delta(^{13}C)_{fatty\text{-}acid}$ values (all except for palmitic acid) in milk samples were able to successfully distinguish between organic and conventional samples [59]. Specifically, the majority of $\delta(^{13}C)_{amino\text{-}acid}$ and $\delta(^{13}C)_{fatty\text{-}acid}$ values were lower in organic than conventional samples (Table 8). The authors subsequently proposed maximum thresholds of −33.5 ‰ for $\delta(^{13}C)_{linoleic\text{-}acid}$ and −28 ‰ for $\delta(^{13}C)_{myristic\text{-}acid}$ for organic milk, irrespective of the seasonal differences in animal diets.

Amino acid GC-IRMS analysis again proved useful in the study by

Table 8
$\delta(^{13}C)$ values reported in recent studies on the compound-specific IRMS analysis of meat, fish, and animal products. Results are reported as mean (± SD where available).

Sample(s)	$\delta(^{13}C)$ (‰)	Type			Reference
Milk		Organic	Conventional		
	$\delta(^{13}C)_{bulk}$	−22.43 ± 0.81	−22.03 ± 0.14		[59]
	Amino acids:				
	$\delta(^{13}C)_{Ala}$	−19.40 ± 2.87	−19.16 ± 0.97		
	$\delta(^{13}C)_{Asx}$	−16.44 ± 1.47	−16.48 ± 2.37		
	$\delta(^{13}C)_{Glx}$	−17.55 ± 1.78	−17.35 ± 1.85		
	$\delta(^{13}C)_{Gly}$	−17.27 ± 2.06	−17.23 ± 1.31		
	$\delta(^{13}C)_{Ileu}$	−24.06 ± 1.18	−23.37 ± 0.78		
	$\delta(^{13}C)_{Leu}$	−29.61 ± 0.97	−28.17 ± 0.58		
	$\delta(^{13}C)_{Lys}$	−17.79 ± 1.37	−18.10 ± 1.63		
	$\delta(^{13}C)_{Met}$	−22.07 ± 0.54	−21.08 ± 1.05		
	$\delta(^{13}C)_{Phe}$	−27.31 ± 0.70	−26.65 ± 0.62		
	$\delta(^{13}C)_{Pro}$	−18.93 ± 1.14	−18.02 ± 1.17		
	$\delta(^{13}C)_{Ser}$	−13.09 ± 1.00	−12.20 ± 0.51		
	$\delta(^{13}C)_{Thr}$	−25.67 ± 1.46	−25.36 ± 1.40		
	$\delta(^{13}C)_{Val}$	−26.47 ± 1.42	−25.75 ± 0.97		
	Fatty acids:				
	$\delta(^{13}C)_{Myristic\ acid}$	−28.42 ± 0.22	−27.63 ± 0.21		
	$\delta(^{13}C)_{Palmitic\ acid}$	−30.00 ± 0.28	−29.90 ± 0.21		
	$\delta(^{13}C)_{Stearic\ acid}$	−33.85 ± 0.43	−32.81 ± 0.44		
	$\delta(^{13}C)_{Oleic\ acid\text{-}cis}$	−33.50 ± 0.33	−32.81 ± 0.58		
	$\delta(^{13}C)_{Oleic\ acid\text{-}trans}$	−37.13 ± 1.33	−36.29 ± 0.70		
	$\delta(^{13}C)_{Linoleic\ acid}$	−34.71 ± 0.50	−32.93 ± 0.49		
	$\delta(^{13}C)_{iso\text{-}C15:0}$	−34.62 ± 1.18	−33.92 ± 0.32		
		Organic	Wild	Conventional	
Salmon	$\delta(^{13}C)_{bulk}$ (lipid corrected values)	10.7 to 12.6	10.6 to 12.8	6 to 8.8	[60]
	Amino acids:				
	$\delta(^{13}C)_{Histidine}$	−18.50 to −15.80	−20.30 to −14.50	−24.10 to −22.50	
	$\delta(^{13}C)_{Ileu}$	−20.0 to −17.60	−22.10 to −18.00	−24.70 to −22.50	
	$\delta(^{13}C)_{Leu}$	−27.50 to −25.20	−29.90 to −26.00	−31.20 to −28.40	
	$\delta(^{13}C)_{Lys}$	−18.60 to −15.40	−19.90 to −15.30	−20.70 to −18.20	
	$\delta(^{13}C)_{Met}$	−22.50 to −19.80	−22.60 to −20.00	−27.90 to −22.90	
	$\delta(^{13}C)_{Phe}$	−28.30 to −25.80	−30.20 to −26.60	−30.90 to −27.90	
	$\delta(^{13}C)_{Thr}$	−9.80 to −5.80	−14.00 to −5.40	−14.90 to −10.80	
	$\delta(^{13}C)_{Val}$	−25.00 to −21.60	−27.70 to −21.80	−27.50 to −24.50	
	$\delta(^{13}C)_{Ala}$	−18.30 to −13.80	−17.70 to −12.10	−20.20 to −18.00	
	$\delta(^{13}C)_{Asx}$	−19.60 to −15.70	−18.60 to −15.20	−20.90 to −19.70	
	$\delta(^{13}C)_{Glx}$	−16.80 to −13.50	−17.80 to −13.90	−19.80 to −18.10	
	$\delta(^{13}C)_{Gly}$	−8.90 to −4.30	−13.30 to −4.60	−15.00 to −11.00	
	$\delta(^{13}C)_{Pro}$	−17.10 to −14.70	−19.60 to −14.90	−23.40 to −21.70	
	$\delta(^{13}C)_{Ser}$	−5.80 to −0.60	−8.30 to 0.20	−9.50 to −7.90	
	$\delta(^{13}C)_{Tyr}$	−26.00 to −24.00	−27.70 to −24.50	−28.70 to −26.70	
		Organic	Conventional		
Butter	$\delta(^{13}C)_{phytanic\ acid\ methyl\ ester}$	both approx. −35.9 ‰			[25]

Wang et al. [60], enabling the distinction between wild and organic salmon, which was not possible using only the bulk results. Moreover, it was concluded that the most negative $\delta(^{13}C)_{amino\text{-}acid}$ values in all amino acids were obtained from conventional salmon, while the most positive $\delta(^{13}C)_{amino\text{-}acid}$ values resulted from wild Atlantic salmon samples. This was attributed to the significantly smaller quantities of marine-derived ingredients in conventional fish feeds compared to those of organic fish, which generally increase $\delta(^{13}C)$ values.

Lastly, Kaffarnik et al. [25] attempted a different approach for the organic authentication of butter based on the $\delta(^{13}C)$ values of phytanic acid methyl ester. In spite of their finding that the SRR/RRR diastereomeric ratio of phytanic acid differed between organic and conventional samples due to differences in feed, the $\delta(^{13}C)$ values of phytanic acid methyl ester did not reflect this. Both sample types exhibited high ^{13}C depletion with $\delta(^{13}C)$ values around −35.9 ‰, thus rendering this compound an unsuitable organic marker.

5. Oxygen

Several studies have found bulk $\delta(^{18}O)$ values to be suitable markers of geographic origin rather than cultivation or farming systems. This is due to the fact that plant O isotope composition is primarily affected by the O isotope value of groundwater, the average precipitation in the region, and evapotranspiration, which are in turn influenced by geographical coordinates and climatic conditions [97,98]. Similarly, the $\delta(^{18}O)$ values in meat and animal products are mainly determined by the source water available to the animal (mainly precipitation or deep groundwater) [34]. Georgi et al. [92] suggested that agricultural practices, such as plant density and growth rates, could have an effect on leaf water $\delta(^{18}O)$; however, no clear distinction could be obtained between organic and conventional systems in their study based on this isotope alone. Nevertheless, oxygen isotope analysis has often been used in conjunction with $\delta(^{15}N)$ and $\delta(^{13}C)$ parameters to achieve organic authentication, especially in cases where organic products originate from specific locations, e.g., organic mountain cheese or milk.

Compound-specific IRMS methods, such as nitrate or sulfate $\delta(^{18}O)$ analysis, have frequently distinguished organic from conventional systems [61,91]. Nitrate $\delta(^{18}O)$ analysis is based on the fact that the oxygen contained in the nitrate of organic and synthetic fertilizers derives from different sources and has different isotopic values. Specifically, the 3

Table 9
$\delta(^{18}O)$ values reported in recent studies on the bulk IRMS analysis of plant-based products. Results are reported as mean (± SD where available).

Sample(s)	$\delta(^{18}O)$ (‰)			Reference
	Conventional	Organic		
Spring barley	14.7 ± 1.4	17.3 ± 0.6		[43]
Tomatoes	25.0 ± 1.8	25.9 ± 1.3		[58]
Tomato passata	24.1 ± 0.9	25.3 ± 0.5		
Hemp flowers	23.1 ± 1.0	23.3 (n = 1)		[69]
Hemp seeds	24.0 ± 0.8	23.7 (n = 1)		
Yams	22.50 to 23.13	22.52 to 23.06		[51]
	Conventional	Green	Organic	
Rice	30.9 ± 1.8	29.8 ± 2.3	30.3 ± 2.2	[46]
	Conventional	Organic		
Wheat (organic matter)	28.2 ± 0.6 to 29.6 ± 2.0	29.2 ± 1.0 to 29.5 ± 1.1		[53] (dependending on region)
Wheat (lipids)	24.3 ± 0.8 to 24.9 ± 1.3	25.5 ± 0.7 to 26.4 ± 0.9		
Potatoes (organic matter)	14.4 ± 0.9 to 14.6 ± 1.2	14.4 ± 0.4 to 14.5 ± 0.8		
Potatoes (bulk)	−5.3 ± 0.9 to −4.7 ± 0.7	−5.3 ± 0.8 to −5.0 ± 0.7		
Apples (organic matter)	19.8 ± 1.3 to 20.0 ± 1.2	19.8 ± 1.3 to 20.1 ± 1.1		
Apples (bulk)	−4.1 ± 0.5 to −3.9 ± 0.6	−4.2 ± 0.6 to −3.8 ± 0.4		
Kiwi	12.05 ± 1.32	11.66 ± 1.97		[73]
Potatoes	−5.3 ± 1.2 to 1.8 ± 2.1	−6.4 ± 0.9 to −5.3 ± 1.4		[79] (dependending on country)
Bananas (pulp)	28.4 ± 0.5 to 31.9 ± 0.7	29.1 ± 0.7 to 31.5 ± 0.8		[50] (dependending on country and farm)
Bananas (peel)	25.2 ± 0.5 to 28.4 ± 0.8	26.7 ± 0.7 to 29.8 ± 0.3		
Spring barley	14.7 ± 1.4	17.3 ± 0.6		[43]
Durum wheat	28.1 ± 0.5 to 29.7 ± 0.6	28.2 ± 0.5 to 30.2 ± 1.5		[44] (depending on region)
Flour	27.6 ± 0.5 to 30.1 ± 0.6	28.2 ± 0.1 to 30.3 ± 0.9		
Pasta	28.6 ± 0.1 to 30.6 ± 0.4	29.2 ± 0.7 to 31.4 ± 1.2		
Table grapes	26.9 ± 0.8	26 ± 1.1		[80]
Tomatoes	only boxplots			[85]
Coffee	28.8 ± 1.6	29.0 ± 1.5		[47]

oxygen atoms contained in synthetic nitrate fertilizers are derived from atmospheric oxygen ($\delta(^{18}O)_{atm}$ = +23.5 ‰) [99], while in the case of organic fertilizers, their nitrate is formed through the process of nitrification by soil microorganisms, with two of the nitrate oxygen atoms derived from soil water ($\delta(^{18}O)$ values typically between −25 ‰ and +4 ‰) [100] and one from atmospheric oxygen ($\delta(^{18}O)_{atm}$ = +23.5 ‰) [99]. Due to this difference, synthetic fertilizers exhibit $\delta(^{18}O)$ values that are comparable to those of atmospheric oxygen (typically between +17 ‰ and +25 ‰) [101], whereas organic fertilizers exhibit lower values (in the range of −10 to +10 ‰) [100].

Similarly, the differentiation between organic and conventional vegetables based on their $\delta(^{18}O)_{sulfate}$ values relies on the assumption that the $\delta(^{18}O)_{sulfate}$ value of the fertilizer used will have a significant impact on the plant's $\delta(^{18}O)_{sulfate}$ content [61]. This is specifically true in the case of synthetic fertilizers since they have been reported to exhibit higher $\delta(^{18}O)_{sulfate}$ values (between +7.7 ‰ and +16.5 ‰) [102] than those of soil sulfate (between +4.3 ‰ and 6.3 ‰) [103].

5.1. Plant species

5.1.1. Bulk IRMS analysis

The area dependence of $\delta(^{18}O)$ in plant-based products has been observed in a number of organic food authentication studies. In the study by Bontempo et al. [44], the $\delta(^{18}O)$ values of wheat and pasta samples followed a latitude-dependent trend, with an increase from northern to southern regions of Italy. Peng et al. [47] observed the same trend with elevated $\delta(^{18}O)$ values in coffee samples from high-temperature regions of Brazil. However, no significant differences were observed between the different farming systems in these studies. Authentication was also not possible using $\delta(^{18}O)$ values in cases of sample collection from adjacent organic and conventional fields irrigated with the same water source, as there were no statistically significant differences [43,46,85]. In some studies, it was noted that the highest $\delta(^{18}O)$ values were found in organic samples, such as coffee beans [48] and bananas [50]. Moreover, despite the significant variations in the $\delta(^{18}O)$ values of organic wheat among different German regions, organic $\delta(^{18}O)$ values were generally higher than in conventional wheat [53]. It can be seen, however, that the difference in bulk $\delta(^{18}O)$ concentrations between farming types was not so great (Table 9).

5.1.2. Compound-specific IRMS analysis

In a number of cases, oxygen isotopes of nitrate were found to be promising markers for the organic authentication of vegetables, with organic $\delta(^{18}O)_{nitrate}$ values being lower than conventional values. Most recently, Wassenaar et al. [62] found a difference of circa 10 ‰ between the $\delta(^{18}O)_{nitrate}$ values of organic and conventional strawberries after applying a novel Ti(III)-based analysis of nitrate in fruit extracts (Table 10). In their studies, Mihailova et al. [91] and Novak et al. [61] found that the majority of conventional potato samples had $\delta(^{18}O)_{nitrate}$ values higher than 20 ‰, whereas the majority of organic $\delta(^{18}O)_{nitrate}$ values were lower than 20 ‰. These differences were attributed to the oxygen sources of synthetic and organic fertilizers, namely atmospheric oxygen in the case of synthetic fertilizers and oxygen from both air and water sources in the case of organic fertilizers. The $\delta(^{18}O)_{nitrate}$ values of organic and conventional tomatoes and lettuce also differed significantly [91] (Table 10) (see Table 11).

No significant differences were observed between the $\delta(^{18}O)_{nitrate}$ values of organic and conventional cabbage and carrot samples [61]. However, differentiation was attained through a different approach, i.e., the values of sulfate $\delta(^{18}O)$. The authors managed to establish thresholds for organic vegetables: $\delta(^{18}O)_{sulfate}$ was set at 5.1 ‰ for organic potatoes, 3.6 ‰ for organic cabbage (enabling a 100 % correct classification of cabbage samples), and 3 ‰ for organic carrots [61].

Table 10
$\delta(^{18}O)$ values reported in recent studies on the compound-specific IRMS analysis of plant-based products. Results are reported as mean (± SD where available).

Sample(s)		$\delta(^{18}O)$ (‰)			Reference
		Conventional	Organic		
Strawberries	$\delta(^{18}O)_{NO3}$	28.2 ± 4.5 ‰	18.3 ± 1.2 ‰		[62]
		Conventional	Organic w/animal manure	Organic w/green manure	
Potato	$\delta(^{18}O)_{bulk}$	26.6 ± 0.3	26.7 ± 0.4	26.8 ± 0.4	[61]
	$\delta(^{18}O)_{NO3}$	23.4	18.1	17.9	
	$\delta(^{18}O)_{Sulphate}$				
Cabbage	$\delta(^{18}O)_{bulk}$	25.5 ± 0.0	25.6 ± 0.1	25.4 ± 0.1	
	$\delta(^{18}O)_{NO3}$	20.2			
	$\delta(^{18}O)_{Sulphate}$				
Carrot	$\delta(^{18}O)_{bulk}$	24.2 ± 0.1	24.1 ± 0.2	24.4 ± 0.1	
	$\delta(^{18}O)_{NO3}$				
	$\delta(^{18}O)_{Sulphate}$	4.2 ± 0.8			
		Conventional	Organic		
Potatoes	$\delta(^{18}O)_{NO3}$	22.6	15.1		[91]
Tomatoes	$\delta(^{18}O)_{NO3}$	45.3	27.3		

5.2. Meat and animal products

5.2.1. Bulk IRMS analysis

In three of the four Chinese regions included in the study, Zhao et al. [88] found significantly higher $\delta(^{18}O)$ values in conventional pork samples than in organic pork from the same region. The authors attributed this to differences between the feed and plants consumed by organic and conventional pigs, resulting in their consuming different amounts of water.

6. Hydrogen

Similar to $\delta(^{18}O)$ values, $\delta(^{2}H)$ values are frequently used for geographic authentication as they are latitude-dependent and reflective of the H isotopes of the source water (mainly precipitation water) ingested by the plant or animal [34,104]. The tendency for conventional cereals to have higher $\delta(^{2}H)$ values has been attributed to higher transpiration and evaporative loss of $^{1}H_2O$ [27], which was linked to increased stomatal conductance in the presence of a higher nitrogen content in these plants [105].

Due to the influence of geographic regions on $\delta(^{2}H)$ values, it is important to compare the findings to the regional $\delta(^{2}H)$ values of groundwater and precipitation in organic authentication studies [27].

6.1. Plant species

6.1.1. Bulk IRMS analysis

In the majority of studies, $\delta(^{2}H)$ values alone were insufficient as organic markers, with their potential to distinguish between geographic locations frequently emphasized instead, such as in the cases of apples and potatoes [53], coffee [47], and various vegetables [96]. However, the trend of more depleted $\delta(^{2}H)$ values in organic products was observed by Lyu et al. [51], who attributed this to the synthetic nitrogen fertilizer used in conventional cultivation, which would lead to higher transpiration rates. Specifically, organic yams exhibited $\delta(^{2}H)$ values in the range of −61.40 ± 6.58 ‰ (2019) and −62.79 ± 9.69 ‰ (2018), while conventional yams exhibited $\delta(^{2}H)$ values in the range of −53.37 ± 6.67 ‰ (2019) and −53.81 ± 9.27 ‰ (2018). Similarly, Yuan et al. [46] found lower $\delta(^{2}H)$ values in organic rice samples than in conventional rice samples. In this case, the authors attributed the depletion to the use of milk vetch mulch, which was added as a base fertilizer to the organic samples to reduce evapotranspiration and control the loss of ^{1}H from the rice paddies.

7. Sulfur

The variation of the $\delta(^{34}S)$ content in plants and animals has been less thoroughly investigated than the other isotopes (N, C, H, and O), primarily due to limitations in the IRMS analysis of SO_2 and the requirement for large sample sizes and long sample preparation [39]. The S isotope composition of plants can be used in geographic authenticity studies since it is affected by the geology of the area, the sea spray effect, i.e., the distance from the ocean, and industrial emissions via wet and dry deposition [97]. $\delta(^{34}S)$ values can also be used to distinguish between different agricultural practices, given that the bulk plant sulfur depletes by 1–2‰ relative to its primary sources, which include soil and sea spray sulfate or atmospheric SO_2 [106]. This low depletion is also similar in animal tissues and products, which exhibit almost no shift in S isotope content relative to the primary source, which is mainly plant sulfur [107].

The variable $\delta(^{34}S)$ content in synthetic fertilizers, which often overlaps with that of organic fertilizers, poses a challenge when using the S isotope to identify the fertilizer and thus the farming method used. This is mainly attributed to the two major sources of sulfate used in chemical fertilizer production, which are sulfuric acid and marine evaporites [102]. The latter has $\delta(^{34}S)$ values in the range of +10 to +35 ‰, while the raw materials used for acid production (including metal sulfides such as pyrite, sulfurous gases such as H_2S, and native S) exhibit $\delta(^{34}S)$ values between −5‰ and +12 ‰ [102].

7.1. Plant species

7.1.1. Bulk IRMS analysis

The challenges mentioned above were noted in a number of studies, with Bontempo et al. [44] finding statistically significant differences between the $\delta(^{34}S)$ of organic and conventional wheat, flour, and pasta samples in only one of the four Italian regions examined. The authors mentioned that various naturally-derived products can be used as organic fertilizers (such as $CaSO_4$ chalk, $MgSO_4$, elemental sulfur, and marine weed), and as a result, organic products exhibit a wide range of $\delta(^{34}S)$ values, often overlapping with those of products grown with synthetic fertilizers. Similarly, no differences were found in common wheat [53] or tomatoes [58]. However, in the region where organic wheat could be distinguished (Basilicata), the organic $\delta(^{34}S)$ values were below 0 ‰, while those of conventional products were above 0 ‰ [44] (Table 12). This was attributed to both the differences in agricultural practices as well as the isotopic signatures of the soil in this region. The same trend with lower $\delta(^{34}S)$ values in organic rather than conventional products was observed by Sinkovič et al. [74] on chicory plants. Chung

Table 11
$\delta(^2H)$ values reported in recent studies on the bulk IRMS analysis of plant-based food products. Results are reported as mean ± SD or ranges.

Sample(s)	$\delta(^2H)$ (‰)			Reference
	Conventional	Organic		
Hemp flowers	−89 ± 4	−100 (n = 1)		[69]
Hemp seeds	−117 ± 1.0	−134 (n = 1)		
Yams	−53.81 to −53.37	−62.79 to −61.40		[51]
Wheat (organic matter)	−59.5 ± 7.3 to 57.0 ± 7.4	−63.1 ± 2.9 to −56.9 ± 7.1		[53] (dependent on region)
Wheat (lipids)	−211.1 ± 5.0 to −209.2 ± 7.3	−210.9 ± 6.0 to −210.1 ± 3.1		
Potatoes (organic matter)	−128.1 ± 6.5 to −127.0 ± 9.5	−128.2 ± 8.3 to −125.1 ± 9.5		
Potatoes (bulk)	−52.7 ± 4.3 to −49.4 ± 4.6	−53.3 ± 3.4 to −51.6 ± 5.1		
Apples (organic matter)	−64.4 ± 6.0 to −64.1 ± 3.4	−66.6 ± 6.0 to 63.7 ± 6.8		
Apples (bulk)	−50.8 ± 2.2 to −48.5 ± 4.0	−50.3 ± 3.1 to −48.7 ± 4.7		
Tomatoes	−37 ± 8	−37 ± 8		[58]
Tomato passata	−38 ± 4	−34 ± 7		
Coffee	−59.7 ± 6.3	−58.9 ± 8.1		[47]
	Conventional	Green	Organic	
Rice	−59.9 ± 3.9	−59.6 ± 2.5	−63.2 ± 3.2	[46]
	Conventional	Organic		
Potatoes	−49.5 ± 7.3 to 14.2 ± 18.0	−52.4 ± 13.0 to −49.8 ± 5.4		[79] (dependent on country)
Durum wheat	−58 ± 4.0 to −48 ± 8	−68 ± 6 to −55 ± 8		[44] (depending on region)
Flour	−56 ± 5 to −49 ± 10	−65 ± 4 to −54 ± 5		
Pasta	−61 ± 2 to −49 ± 6	−67 ± 5 to −55 ± 4		
Table grapes	−80 ± 5	−79 ± 7		[80]

Table 12
$\delta(^{34}S)$ values reported in recent studies on the bulk IRMS analysis of plant-based products. Results are reported as mean (± SD where available).

Sample(s)	$\delta(^{34}S)$ (‰)		Reference
	Conventional	Organic	
Hemp flowers	12.1 ± 1.2	11.5 (n = 1)	[69]
Hemp seeds	8.7 ± 0.5	9.5 (n = 1)	
Wheat	4.7 ± 1.4 to 6.2 ± 1.9	4.9 ± 0.7 to 5.5 ± 1.1	[53] (dependent on region)
Potatoes (protein)	2.5 ± 1.1 to 3.6 ± 1.1	2.7 ± 1.2 to 2.9 ± 1.0	
Apples	4.7 ± 1.6 to 5.2 ± 0.6	4.7 ± 1.0 to 5.5 ± 1.3	
Tomatoes	−1.7 ± 2.3	−1.7 ± 3.0	[58]
Tomato passata	−3.7 ± 1.2	−2.0 ± 3.1	
Chicory	7.2 ± 0.7 to 7.8 ± 0.4	4.1 ± 1.1 to 5.0 ± 0.8	[74] (dependent on fertilizer type)
Durum wheat	−22.8 ± 2.0 to 5.2 ± 2.8	−20.4 ± 4.4 to 4.9 ± 3.7	[44] (depending on region)
Flour	−22.3 ± 1.9 to 4.6 ± 3.9	−20.2 ± 3.0 to 3.7 ± 2.0	
Pasta	−22.4 ± 1.6 to 4.2 ± 2.1	−15.8 ± 8.9 to 5.8 ± 4.3	

et al. [82] distinguished between ginseng roots (*Jagyeongjong variety*) grown under different organic fertilizer treatments based on $\delta(^{34}S)$, with no synthetic treatments examined. In particular, the values of the samples grown with rice straw compost (4.4 ± 0.4 ‰) were higher than those cultivated with cattle manure (2.7 ± 0.3 ‰), food waste (3.0 ± 0.3 ‰), and control (3.2 ± 0.7 ‰), while an increase was observed with higher quantities of rice straw compost.

8. Complementary techniques & data analysis

8.1. Bulk IRMS studies

In several cases, bulk IRMS was used in conjunction with other analytical techniques to improve the distinction between organic and conventional products. Hohmann et al. [85] noted that the combined data from three methods, ^1H NMR, MIR, and IRMS, improved the validation results for organic tomatoes compared to those obtained from each method separately. Another example is the study by Lyu et al. [51] on Chinese yams, where chemometric methods applied to multi-elemental (ICP-OES) and isotopic data were able to clearly distinguish between organic and conventional samples. In this case, an RF model yielded the best distinction, with the $\delta(^{15}N)$ isotope being a less significant parameter than elements such as Mn, Cr, and others but still improving the model's results. Similarly, the differentiation potential between organic and conventional carrots increased from 71.4 % when only using elemental analysis results to 83.3 % when incorporating the $\delta(^{15}N)$ values [108].

In many cases, the use of chemometric analysis and statistical evaluation of IRMS data significantly facilitated the understanding of differences between farming systems. However, the results frequently varied depending on the method used.

For instance, in the study of Longobardi et al. [80] on table grapes, a *t*-test of the $\delta(^{13}C)$ and $\delta(^{18}O)$ ratios showed that these were good indicators of organic authenticity. However, a 2D scatter plot failed to satisfactorily distinguish between the organic and conventional categories. The authors found that the combination of principal component analysis (PCA) with the $\delta(^{18}O)$, $\delta(^2H)$, and $\delta(^{13}C)$ values, but not $\delta(^{15}N)$, was satisfactory for classifying the samples. Better separation was achieved using general discriminant analysis (GDA), with a prediction ability of 75 %.

Another example is the work of Liu et al. [68], in which an ANOVA comparison of the $\delta(^{15}N)$ values of organic, conventional, and green rice indicated a distinction for the years 2014, 2015, and 2017, but not 2016. Due to this variation, the authors concluded that N isotope ratio analysis should not be used as the only organic authenticity indicator. Moreover, the usefulness of techniques in addition to IRMS (in this case, ICP-MS/MS) was demonstrated in this study, since a number of elemental variables (K, Ni, Cd, and others) in addition to $\delta(^{15}N)$ significantly contributed to the achievement of 100 % accuracy using partial least squares-discriminant analysis (PLS-DA) modeling for organic rice.

There are also cases in which chemometrics assisted in identifying missing data, such as in the study of Buša et al. [43], where PCA clustering failed to distinguish between conventional and organic spring barley samples; consequently, the authors recommended increasing the sample size and the number of variables to improve future results.

All analytical and statistical methods applied in the bulk IRMS studies that were reviewed in this paper are listed in Table 13 below.

Table 13
Analytical techniques and statistical evaluation in different bulk IRMS studies.

Product(s)	Complementary Techniques	Data Analysis	Reference
Cereals			
Hemp	–	Kruskal–Wallis, Spearman's rank correlation coefficient	[69]
Spring barley	–	PCA, Student's t-test	[43]
Wheat, potatoes and apples	–	Kolmogorov–Smirnov test, Shapiro–Wilk test, Levene's test, Kruskal–Wallis rank sum tests, ANOVAs, Dunnett-T3	[53]
Durum wheat, flour and pasta	–	ANOVA, Tukey's test, paired *t*-test, CDA, segmented cross validation	[44]
Rice	–	General linear model, LSD test	[45]
Rice	ICP-MS	ANOVA, Tukey's test, PCA, LDA	[46]
Rice	ICP-MS/MS	ANOVA, ROC, AUC, PLS-DA, heat maps	[68]
Vegetables & Fruit			
Potatoes	ICP-MS	ANOVA, Pearson correlation, PCA, LDA	[79]
Parsley, celery and parsnip root, cucumber, vegetable marrow, onion, and pepper samples	ICP-MS	LDA	[96]
Tomatoes, strawberries and lettuce	–	Anderson–Darling test, Barnett and Levene tests, Dunnett-test	[86]
Bananas	ICP-MS	PCA, ANOVA, Tukey's test, Pearson correlation	[50]
Carrots	ICP-MS	ANOVA, Tukey's test, Pearson correlation, LDA	[108]
Brassica Chinensis/ Bok choy	ICP-MS	ANOVA, PCA, LDA	[109]
Yams	ICP-MS, Determination of protein, total free amino acids, total starch and amylose content, total soluble polyphenol, total flavonoid, total saponin content and antioxidant activity assays	PCA, OPLS-DA, kNN, SVM, Lasso, CART, RF, ROC (AUC), ANOVA	[51]
Cauliflower, lettuce, brassica oleracea, broccoli, cabbage, cabbage mustard, cucumber, asparagus, amaranth, brassica chinensis, celery, Chinese cabbage, flowering Chinese cabbage, Chinese little greens, garland chrysanthemum, lettuce, roquette, spinach, water spinach, hyacinth bean, radish, taro, eggplant, pepper, wuta-tsai and tomato	Pesticide residue analysis	ANOVA, PLS-DA, SVM, Kennard-Stone	[49]
Tomatoes	^{1}H NMR, MIR	PCA, PLS-DA, LDA, ComDim	[85]
Cauliflower	–	ANOVA, Tukey's test	[84]
Lettuce	–	ANOVA, Anderson–Darling test, Barnett and Levene tests, Tukey's test, Kruskal–Wallis test	[81]
Sweet oranges	Assessment of fruit moisture, firmness, acidity and sugar, Total phenolic content, Antioxidant capacity, Targeted (poly) phenols analysis	Shapiro-Wilk test, Levene's test, ANOVA, k-NN	[75]
Olives	–	ANOVA, Fisher test	[78]
Kiwi	ICP-OES	SIMCA, PLSDA, LS-SVM	[73]
Strawberries, Raspberries, Blueberries, Blackberries and Currants	SNIF-NMR	Tukey HSD test, Student's t- test, ANOVA, Pearson correlation	[110]
Chicory plants	Total phenolics content (TPC), antioxidant potential (AOP), total flavonoid content (TFC), Nitrogen assimilation, multi-elemental profile (XRF)	ANOVA, Duncan's test, Kruskal-Wallis test, DA	[74]
Ginseng	–	General linear model, LSD test	[82]
Table grapes	–	PCA, GDA	[80]
Walnuts	–	ANOVA	[76]
Meat			
Chicken	ICP-MS	ANOVA, PCA	[54]
Pork	ICP-MS	t-tests, PCA, OPLS-DA	[88]
Animal Products			
Milk	–	LSD test	[89]
Milk	GC-FID	General linear model (GLM), ANOVA, LSD tests, PCA, OPLS-DA, PLS-DA, Pearson's correlation	[90]
Milk	GC-FID, ^{1}H NMR, ^{13}C NMR	PCA, LDA, FDA, PLS-DA, ComDim	[55]
Milk and Cheese	GC-MS	ANOVA, Pearson's correlation	[25]
Eggs	–	MANOVA, Fisher's LSD tests	[52]
Fish and Seafood			
Salmon and Trout	Isoelectric focusing (IEF), PCR based DNA analysis, GC-FID, HPLC	Student's t-test, Mann–Whitney's test	[57]
Shrimp	Moisture content, Protein content, Lipid content, PCR-based DNA analysis, GC-FID, HPLC	PLS-DA	[56]
Others			
Coffee	GC-MS, ICP-OES	Two-tailed t-tests, LAD, PCA, DA	[48]
Coffee	–	Brown-Forsythe test, ANOVA, Welch's ANOVA, Fisher's LDA test, Unpaired Student-t	[47]

(*continued on next page*)

Table 13 (*continued*)

Product(s)	Complementary Techniques	Data Analysis	Reference
		test, Mann-Whitney test, PCA, LDA, k-NN, ROC, SVM	
Beer and hops	UHPLC-MS/MS	Student t-test, OPLS-DA	[72]

Table 14
Analytical techniques and statistical evaluation in different compound-specific IRMS studies.

Product(s)	Isotopic Analysis	Complementary Techniques	Data Analysis	Reference
Cereals				
Rice	EA-IRMS, GC-C-IRMS	–	General linear model, LDA, Pearson correlations, HCA, PCA, PLS-DA, OPLS-DA	[28]
Common wheat and Durum wheat	EA-IRMS, GC-C-IRMS	–	HSD Tukey's test, LDA	[31]
Vegetables & Fruit				
Strawberries	EA-IRMS, gas source IRMS	Ion chromatography	DD-SIMCA (PCA), t-tests	[62]
Tomatoes	EA-IRMS, GC-C-IRMS	–	ANOVA, Tukey's test, paired *t*-test, CDA	[58]
Lettuce, Potato and Tomato	EA-IRMS, GC-C-IRMS	–	t-tests, Mann–Whitney *U* test, ANOVA, Tukey test, Games–Howell test, CDA	[91]
Potatoes, Carrots and Cabbage	EA-IRMS	ICP-OES, Ion chromatography	ANOVA, Tukey's test, QDA	[61]
Animal Products				
Milk	EA-IRMS, GC-C-IRMS	–	General linear model, LSD test, Pearson correlations, HCA, PCA, PLS-DA,	[59]
Butter	GC-IRMS	–	–	[25]
Fish				
Salmon	EA-IRMS, GC-C-IRMS	–	Fligner-Killeen tests, ANOVA, Tukey HSD test, PCA, LDA, Pillai's trace MANOVA	[60]

8.2. Compound-specific IRMS studies

The volume of CSIA studies for the organic authentication of food products is significantly less than that of bulk studies, with the majority of the former only employing IRMS methods as opposed to the latter, in which additional techniques were included. A similarity between the two, however, is that chemometric analysis played an important role in improving differentiation between the samples. Particularly notable is the case of Wang et al. [60], who were initially able to clearly distinguish between organic and conventional salmon but not between organic and wild salmon using compound-specific IRMS. Ultimately, compound-specific (amino acid) data were subjected to a linear discriminant analysis (LDA) to obtain the latter distinction.

Correlation studies often proved to be useful for understanding the relationship between the isotope values of different compounds. For example, bulk $\delta(^{13}C)$ values in milk were closely correlated with those of alanine and *trans*-oleic acid, and high correlations were determined between $\delta(^{13}C)_{Valine}$ - $\delta(^{13}C)_{Isoleucine}$ and $\delta(^{15}N)_{Threonine}$ - $\delta(^{15}N)_{Serine}$ [59]. Moreover, $\delta(^{13}C)_{bulk}$ values in rice samples were correlated with most $\delta(^{13}C)_{fatty\text{-}acid}$ values, while in the same samples, $\delta(^{15}N)_{bulk}$ was strongly correlated with most $\delta(^{15}N)_{amino\text{-}acid}$ [28].

All analytical and statistical methods applied in the CSIA studies that were reviewed in this paper are listed in Table 14 below.

9. Conclusion

The bulk IRMS analysis results of the majority of studies indicate that $\delta(^{15}N)$ values are promising markers for differentiating organic from conventional products. However, fluctuations due to seasonal variability or the presence of N_2-fixing plants often led to the conclusion that $\delta(^{15}N)$ alone was not an adequate indicator. $\delta(^{13}C)$ values were the second-most-studied isotope parameter after $\delta(^{15}N)$ and, while in some cases they helped determine the farming method, it was also understood that they are heavily influenced by plant species and sampling site. Compound-specific data were able to overcome some of these limitations and further enhance the discriminatory power of the applied IRMS methods. By analyzing on-line or off-line isolated compounds, it was possible to authenticate an organic sample based on the $\delta(^{15}N)$ or $\delta(^{13}C)$ value of its amino/fatty acids or the $\delta(^{18}O)$ value of its nitrates or sulfates. Nevertheless, in certain more similar food categories, compound-specific analysis exhibited limitations, such as when attempting to distinguish between organic and pesticide-free rice or organic and wild salmon.

The use of additional methods in addition to IRMS, such as multi-element analysis or NMR, yielded promising results, given the large number of elements covered by ICP techniques or the detailed spectral information obtained from NMR. Metabolomic approaches (through LC and high-resolution MS) may also be combined with IRMS in the future, given the potential of both techniques for organic food authentication. Naturally, the use of supervised (such as PCA and HCA) and unsupervised (such as PLS and SVM) chemometrics to extract the relevant information from data significantly aided the classification potential of the different analytical methods.

Further research on compound-specific isotope analysis is expected to provide more insights into the reliability of the different ratios $\delta(^{15}N)$, $\delta(^{34}S)$, $\delta(^{18}O)$, $\delta(^{13}C)$, or $\delta(^{2}H)$ in organic food authentication. Additional information regarding the above-mentioned variability factors can be gleaned from studies conducted over several seasons and incorporating different sampling areas with specific climatic and geographical conditions. Future research for the same purpose should also include different plant species. CSIA should be combined with other analytical techniques in order to obtain comparative results and assess their complementarity.

Disclaimer

The data, results, and conclusions in the paper are the author's work in their personal capacity and have no connection with their employer.

CRediT authorship contribution statement

Zoe Giannioti: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Formal analysis, Data curation. **Nives Ogrinc:** Writing – review & editing, Writing – original draft, Project administration, Funding acquisition, Conceptualization. **Michele Suman:** Writing – review & editing. **Federica Camin:** Writing – review & editing. **Luana Bontempo:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Funding acquisition, 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.

Data availability

No data was used for the research described in the article.

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