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Principles and Limitations of Stable Isotopes in Differentiating Organic and Conventional Foodstuffs: 1. Plant Products

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Among the lighter elements having two or more stable isotopes (H, C, N, O, S), $\delta^{15}N$ appears to be the most promising isotopic marker to differentiate plant products from conventional and organic farms. Organic plant products vary within a range of $\delta^{15}N$ values of +0.3 to +14.6%, while conventional plant products range from negative to positive values, i.e. −4.0 to +8.7%. The main factors affecting $\delta^{15}N$ signatures of plants are N fertilizers, biological N_2 fixation, plant organs and plant age. Correlations between mode of production and $\delta^{13}C$ (except greenhouse tomatoes warmed with natural gas) or $\delta^{34}S$ signatures have not been established, and $\delta^{2}H$ and $\delta^{18}O$ are unsuitable markers due to the overriding effect of climate on the isotopic composition of plant-available water. Because there is potential overlap between the $\delta^{15}N$ signatures of organic and conventionally produced plant products, $\delta^{15}N$ has seldom been used successfully as the sole criterion for differentiation, but when combined with complementary analytical techniques and appropriate statistical tools, the probability of a correct identification increases. The use of organic fertilizers by conventional farmers or the marketing of organic produce as conventional due to market pressures are additional factors confounding correct identification. The robustness of using $\delta^{15}N$ to differentiate mode of production will depend on the establishment of databases that have been verified for individual plant products.

Keywords Stable isotopes, organic fertilizers, manufactured fertilizers, $\delta^{13}C$, $\delta^{15}N$

INTRODUCTION

According to the International Federation of Organic Agriculture Movements (IFOAM, 2011), the organic global market represented 55 billion US dollars in 2009, involving 160 countries, 37.2 million hectares of agricultural land, and 1.8 million farmers. The largest markets are in the United States, Germany, and France, and the highest per capita consumptions are in Denmark, Switzerland, and Austria. Because organically produced foodstuffs command a premium price in the market place compared with conventionally produced products, mechanisms are required to monitor and detect fraud in labeling.

Stable isotope-ratio signatures ($\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$) are playing an increasingly important role in food forensics (Primrose et al., 2010). There are three main areas of application (i) detection of adulteration, (ii) assignment of geographical origin, and (iii) identification of mode of production, i.e. organic vs. conventional farming systems. Although reviews have been written on the use of isotopic markers to detect adulteration (e.g. Förstel, 2007) and pinpoint appellation of origin (e.g. Luykx and van Ruth, 2008), mode of production has not received the same critical analysis.

Organic farming systems rely on the use of organic fertilizers (e.g. animal manures, composts) to maintain productivity because synthetic fertilizers are excluded. Organic fertilizers differ from synthetic fertilizers in physical and biochemical properties. One important chemical distinction is isotopic composition. Synthetic N fertilizers (ammonium salts and urea) are derived from ammonia (NH_3) produced by the Haber–Bosch process, which involves the catalytic reduction of atmospheric N_2 at high temperature and pressure by H_2 derived from methane or natural gas. Therefore, the $\delta^{15}N$ signatures of synthetic fertilizers are expected to be close to that of atmospheric N_2 (0‰ by definition) provided that isotopic fractionation processes are not significant

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during the manufacture of the fertilizer. However, organic fertilizers are generally enriched in the stable isotope ^{15}N compared with synthetic fertilizers due to significant isotopic fractionation that occurs either during storage or processing (Bateman and Kelly, 2007). The main process leading to ^{15}N enrichment of the substrate is NH_3 volatilization (Hristov et al., 2009; Lee et al., 2011). Therefore, it may be possible to differentiate organically and conventionally produced crops by differences in their $\delta^{15}N$ or other stable isotopic signatures.

Until the advent of automated systems, isotope-ratio mass spectrometry (IRMS) was an expensive, labor intensive, and time-consuming analytical procedure. However, with the introduction and continued development of interfaced automated elemental analyzers for sample preparation (e.g. Werner et al., 1999), IRMS has evolved into a cost effective, rapid, and precise analytical technique for measurement of the relative abundance of the stable isotopes of H, C, N, O, and S, which have important applications in the area of food forensics.

The objective of the present review is to synthesize and analyze the published literature to determine whether the mode of production of plant-derived foodstuffs can be differentiated on the basis of stable isotope composition alone or in combination with statistical and/or other analytical techniques. The use of stable isotopes to differentiate organically and conventionally produced animal products will be considered in a subsequent review.

LEGISLATION AND STANDARDS FOR ORGANIC PLANT PRODUCTS

Production, processing, certification, and labeling of organic foods follow specific standards that are governed by legislation in different countries, but all have similarities (e.g. US, 1990; Brasil, 2003; UK, 2004; EU, 2007). They have been based on the IFOAM (2005) basic standards and principles of organic production and accreditation criteria, which are internationally accepted. Frequently, countries use international agreements to trade organic foodstuffs. A brief overview of basic standards (minimum requirements) for organic crop production is presented.

Organic systems are soil based and do not include hydroponic culture. Soil fertility and soil organic matter are maintained or improved through nutrient recycling practices including the use of composts, animal manures, green manures, crop rotations, and legumes. An array of organic amendments is permitted, e.g. urban composts from separated sources which are monitored for contamination, and by-products of food, fodder, oilseed, brewery, distillery, or textile-processing industries. Natural deposits of limestone, gypsum, phosphate rocks, and other pulverized rocks including elemental sulfur are permitted. The use of all synthetic nitrogenous fertilizers, including urea, and other manufactured phosphatic and potassic fertilizers is the first exclusion boundary between organically and conventionally grown crops. The second boundary is exclusion of synthetic pesticides, fungicides, and herbicides. Pests, diseases, and weeds are controlled by a wide range of practices, e.g. biological control techniques, genetic resistance, physical barriers, biodiversity promotion, and crop rotations (IFOAM, 2005).

STABLE ISOTOPIC SIGNATURES OF PLANTS AND SOILS

Stable isotopic values close to the natural abundance of the designated isotope are expressed by the notation (δ) in units of parts per thousand (per mil or ‰) relative to the international standard for that element (Chalk, 1995).

e.g. $\delta^{15}N\ (‰) = \{[(^{15}N/^{14}N)_{sample} / (^{15}N/^{14}N)_{standard}] - 1]\} \times 1000$ where the international standard is atmospheric N_2 ($\delta^{15}N = 0‰$, by definition). The absolute ^{15}N abundance of atmospheric N_2 is 0.3663 ± 0.0004 atom% (Junk and Svec, 1958).

$\delta^{13}C$

The relative isotopic composition of bulk plant tissue ($\delta^{13}C$) is mainly a function of isotopic fractionation of CO_2 during photosynthesis (Dawson et al., 2002). Diffusion of CO_2 through the leaf stomata (a physical process) and enzymatic reduction of CO_2 by RuBisCo during carboxylation (a biochemical process) each contribute to ^{13}C discrimination, as both processes favor the lighter ^{12}C isotope.

There are three distinct types of plant photosynthetic metabolism: C3 (Calvin cycle); C4 (Hatch–Slack pathway), and CAM (Crassulacean Acid Metabolism). The first metabolites in the C3 and C4 cycles are 3-carbon and 4-carbon molecules, respectively. CAM plants have a C4 pathway active at night and a C3 pathway during daylight (Larcher, 2003). Most temperate plant species are C3 (vegetables, legumes, cereals, and fruits), but many tropical species are C4 (maize, sugarcane, and forage grasses). Pineapple (*Ananas comosus*), a member of the Bromeliad family, is a CAM species like the cacti (*Opuntia* spp.) found in arid climates.

Plants having different photosynthetic pathways exhibit specific ranges in $\delta^{13}C$ bulk values. C3 plants have a range of -22 to $-30‰$, C4 plants -10 to $-14‰$, and CAM plants -10 to $-35‰$ (Cerling et al., 1997; Coplen et al., 2002; Larcher, 2003). The $\delta^{13}C$ isotopic composition of atmospheric CO_2 is approximately $-8‰$ (Yun and Ro, 2008), but is gradually becoming more negative as atmospheric CO_2 concentration increases (Peck and Tubman, 2010). Therefore, the bulk plant $\delta^{13}C$ value is a useful index of plant metabolism. The $\delta^{13}C$ signature of the soil organic C in the surface horizon of undisturbed (virgin) soils is similar to that of the native vegetation. A change in vegetation cover from a C3 species (e.g. forest) to a C4 monoculture (e.g. sugarcane) will result in a gradual temporal shift in the $\delta^{13}C$ signature of the soil organic C (Vitorello et al., 1989). The $\delta^{13}C$ signature of the soil organic C is not uniform with depth, and

generally shows a marked increase in $\delta^{13}C$ in the top 20 to 30 cm with little change below this depth (Sisti et al., 2004).

$\delta^{15}N$

Soil organic N is generally slightly enriched in ^{15}N compared with atmospheric N_2. Many authors have reported that $\delta^{15}N$ values in the organic matter of a wide cross-section of surface soils generally fall within the range of +6.4 to +11.2‰ (Piccolo et al., 1996; Bateman et al., 2005; Yun et al., 2006), but negative values have also been reported (Martinelli et al., 1999). Long-term applications of synthetic or organic N fertilizers can modify the $\delta^{15}N$ signature of soil organic N. For example, Choi et al. (2003) found that the average $\delta^{15}N$ value of total N in 20 soils amended annually with compost ($\delta^{15}N = +17.4 \pm 1.2$‰) for five years was $+8.8 \pm 2.0$‰, whereas in 20 fields amended with synthetic fertilizer ($\delta^{15}N = -1.6 \pm 1.5$‰) the mean $\delta^{15}N$ value was significantly lower at $+5.9 \pm 0.7$‰.

Nonlegumes derive N from the uptake of NH_4^+ and NO_3^- ions though their roots, whereas nodulated legumes fix atmospheric N_2 as an additional N source. Plants may also take up N through foliage from atmospheric pollutants such as NH_3 or NO_x. The $\delta^{15}N$ signatures of these available N sources are influenced by various ^{15}N fractionation mechanisms in the N cycle in the soil–plant–atmosphere continuum (Högberg, 1997; Robinson, 2001). The bulk $\delta^{15}N$ signature in plants is related to the $\delta^{15}N$ values of available N sources rather than to soil organic N (Dawson et al., 2002; Yun and Ro, 2008). Mineralization of N from large organic N molecules in soil organic matter is not a significant N fractionation mechanism. Fractionation of ^{15}N is large for volatilization of NH_3, nitrification, and denitrification, but is less expressive for plant uptake (enzyme mediated) of inorganic N (Högberg, 1997; Robinson, 2001). Fractionation during nitrification leads to ^{15}N-enrichment of NH_4^+ and ^{15}N-depletion of NO_3^- in soil (Yoneyama et al., 1990; Yun et al., 2006). Fractionation during biological nitrogen fixation (BNF) by the legume–*Rhizobium* symbiosis is generally small, and legume $\delta^{15}N$ values are therefore close to zero when symbiotic dependence is high (Rogers, 2008). Thus plants are integrators of the various $\delta^{15}N$ signatures of available N sources (Robinson, 2001).

Across a broad range of climate and undisturbed ecosystem types, soil and plant $\delta^{15}N$ values systematically decreased with increasing mean annual precipitation (MAP) and decreasing mean annual temperature (MAT) (Amundson et al., 2003). Thus the foliage of tropical forest species has a higher average $\delta^{15}N$ value ($+3.7 \pm 3.5$‰) than temperate forest foliage (-2.8 ± 2.0‰) (Martinelli et al., 1999). Globally, plant $\delta^{15}N$ values are more negative than soils, but the difference decreases with decreasing MAT, and secondarily with increasing MAP (Amundson et al., 2003). The $\delta^{15}N$ values of agricultural crops fall within a wide range of -4.0 ± 2.0‰ (Yun et al., 2006) to $+14.6 \pm 3.3$‰ (Choi et al., 2003) depending on the N fertilizer regime.

$\delta^{2}H$ and $\delta^{18}O$

Meteoric water derived from the evaporation of ocean water is depleted in ^2H and ^{18}O relative to the source, whereas water in evaporative systems such as lakes, plants, and soils is relatively enriched (Gat, 1996). There is a strong positive linear relationship between the δ^2H and the $\delta^{18}O$ composition of meteoric water collected at different global locations, which is known as the meteoric water line (MWL). There is also a strong positive linear relationship between the $\delta^{18}O$ composition of meteoric water and mean annual temperature (Fontes, 1980), leading to marked differences between the isotopic composition of seasonal precipitation and across latitudinal and altitudinal gradients (Gat, 1996). For example, the annual mean $\delta^{18}O$ in precipitation becomes more negative with increasing latitude, varying from +2 to −2‰ in equatorial regions to as low as −22‰ in the north polar region (Gat, 1996).

Terrestrial plants acquire water mainly by uptake through the root system, and there is no isotopic fractionation during plant uptake. Therefore the δ^2H and $\delta^{18}O$ composition of the xylem sap before water is transpired through the leaf stomata, will reflect the integrated isotopic composition of the sources of water taken up by the plant. The plant may in fact access several sources (soil, ground or stream) of water simultaneously, which themselves can differ in isotopic composition. Plant transpiration will lead to enrichment in the δ^2H and $\delta^{18}O$ values of leaf water. Therefore, considering the complexity of the distribution of the stable isotopes of H and O in the soil–plant–atmosphere continuum due to differences in location and climate, it is highly unlikely that plant δ^2H and $\delta^{18}O$ signatures can differentiate the mode of production. However, these isotopic markers have found an important application in verification of geographical origin (Luykx and van Ruth, 2008). Therefore δ^2H and $\delta^{18}O$ signatures of plant products will not be considered in this review.

$\delta^{34}S$

The bulk $\delta^{34}S$ composition (organic-S + sulfate) in surface soils ranges from +1.7 to +18.1‰ (Mizota and Sasaki, 1996) and usually increases with depth (Novák et al., 2003). The $\delta^{34}S$ signature of soil can be influenced by the application of synthetic SO_4^{2-} fertilizers, gypsum, and elemental sulfur (S^o) as well as atmospheric deposition (e.g. rain water and industrial pollution). Coastal regions are influenced by sea-spray having $\delta^{34}S$ values $\sim +20$‰ (Mizota and Sasaki, 1996). Plants acquire S through the uptake of SO_4^{2-} from the soil solution or through foliar absorption of atmospheric pollutants such as SO_2. The reported bulk $\delta^{34}S$ values in crops range from −3.7 to +10.1‰ (Georgi et al., 2005; Rapisarda et al., 2010; Tanz and Schmidt, 2010; Camin et al., 2011). Plant parts and products can differ from bulk $\delta^{34}S$ values by about 3 to 6‰ (Tanz and Schmidt, 2010).

Sulfate fertilizers derive from both sulfuric acid (from metal sulfides, sulfurous gases, and native S°) and marine sources. Sulfate fertilizers derived from H_2SO_4 have a range in $\delta^{34}S$ from

−6.5 to +11.5‰, while marine-derived sulfate fertilizers fall close to +21‰ (Mizota and Sasaki, 1996; Vitòria et al., 2004). Native S^o has values of δ^{34}S ranging from −20 to +15‰ while commercial S^o varies from −5 to +30‰ (Coplen et al., 2002). Commercially available sulfate preservatives were reported by Kelly et al. (2002) to vary in δ^{34}S values from +10.0 to +16.9‰.

FACTORS AFFECTING PLANT ISOTOPIC COMPOSITION

$\delta^{13}C$

As already discussed, the plant's photosynthetic pathway is the major determinant of its bulk δ^{13}C signature. However, some environmental conditions can affect plant δ^{13}C values, such as drought, solar radiation intensity, low temperature, low atmospheric pressure, and ozone stress (Yun and Ro, 2008). These environmental stresses affect the balance of discrimination between stomatal conductance and carboxylation. The supply of N may directly affect δ^{13}C by increasing the rate of photosynthesis, and indirectly by effects on water use efficiency (Högberg et al., 1995). Genotype is also an important source of variation in δ^{13}C values of plants (Serret et al., 2008), and the isotopic composition in (local) atmospheric CO_2 has a strong influence on plant δ^{13}C values (e.g. greenhouse cultivation; Schmidt et al., 2005; Rogers, 2008).

The distribution of ^{13}C within plants is not uniform, and fundamental differences exist between C3 and C4 plants in this respect (Hobbie and Werner, 2004). Thus roots of C3 plants are invariably enriched in ^{13}C by 1 to 4‰ relative to leaves, whereas in C4 plants differences are attenuated. Wheat grain (C3) has a higher δ^{13}C value than leaves or straw (Senbayram et al., 2008; Serret et al., 2008). These differences are related to the nonuniform distribution of ^{13}C within plant biochemical entities. For example, lignin is depleted in ^{13}C relative to cellulosic or hemicellulosic constituents or the bulk material (Benner et al., 1987). The δ^{13}C enrichment of cellulose relative to lignin ranged from 2.5 to 4.6‰ for various organs in C3 plants and from 4.6 to 6.2‰ for C4 plants (Hobbie and Werner, 2004). Thus plant constituents (e.g. straw) high in lignin will have a lower δ^{13}C value than grain which is low in lignin.

$\delta^{15}N$

Fertilizer N

Synthetic N fertilizers have δ^{15}N values in the range of −3.9 to +5.7‰ (Table 1) while organic N fertilizers fall within the range of +2.5 to +45.2‰ (Table 2). As previously noted, δ^{15}N values of plants lie within the range of −4.0 to +14.6‰ (Tables 3 and 4) and are strongly influenced by the type of N fertilizer application. Plant δ^{15}N values well below the value for soil organic N are a general indication that synthetic N fertilizers have been applied, whereas values well above may indicate organic N fertilizer additions (Nakano et al., 2003; Bateman et al., 2005; Rogers, 2008). The extent of these differences will depend on the fertilizer δ^{15}N value, and the rates of application over a given period of time. In the case of some greenhouse crops where soil organic N is low, plant δ^{15}N values will closely resemble the fertilizer N source (Georgi et al., 2004).

Unlike synthetic N fertilizers which are either NH_4^+ salts or urea which rapidly hydrolyses to NH_4^+ in soil, organic fertilizers contain both plant available inorganic N (NH_4^+ and NO_3^-) and potentially available organic N. The relative concentrations and their δ^{15}N signatures can show marked differences. For example, pig manure compost contained 327 ± 14 and 125 ± 8 mg N kg^{-1} of NH_4^+ and NO_3^-, respectively, with δ^{15}N values of +12.5 ± 1.3 and +22.6 ± 0.1‰, respectively (Yun et al., 2011). However, these forms represented, respectively, only 1.5 and 0.5% of the total compost N (23.1 g N kg^{-1}), which had a bulk δ^{15}N signature of +15.3 ± 0.2‰. Nevertheless, even relatively small concentrations of inorganic N relative to organic N can have a significant effect on the plant's δ^{15}N signature (Flores et al., 2011).

Co-application or sequential application of synthetic and organic N fertilizers can influence temporal δ^{15}N signatures in plants. Application of urea reduced the δ^{15}N composition of maize when co-applied with pig manure compost compared

Table 1 δ^{15}N composition of synthetic fertilizers

Type of fertilizer	δ^{15}N (‰)	Reference
Compound (NPK)[a]	−2.2 to +2.5	Choi et al., 2003, 2007; Vitòria et al., 2004; Bateman and Kelly, 2007; Rogers, 2008; Rapisarda et al., 2010
Ammonium nitrate (NH_4NO_3)	−1.7 to +2.6	Nakano et al., 2003; Vitòria et al., 2004; Bateman et al., 2005; Schmidt et al., 2005; Bateman and Kelly, 2007; Rogers, 2008
Potassium nitrate (KNO_3)	−1.5 to +1.6	Schmidt et al., 2005; Bateman and Kelly, 2007; Flores et al., 2007, 2011
Calcium nitrate [$Ca(NO_3)_2$]	−1.7 to +5.7	Vitòria et al., 2004; Bateman and Kelly, 2007; Flores et al., 2007; Šturm et al., 2011; Šturm and Lojen, 2011
Ammonium sulfate [$(NH_4)_2SO_4$]	−3.9 to −1.7	Choi et al., 2003, 2006, 2007; Rogers, 2008; Yun et al., 2011
Urea [$CO(NH_2)_2$]	−2.3 to +0.7	Choi et al., 2002, 2006, 2007; Vitòria et al., 2004; Yun et al., 2006; Serret et al., 2008; Rogers, 2008; Yuan et al., 2012
Mono-ammonium phosphate ($NH_4H_2PO_4$)	−0.3 to −0.9	Bateman and Kelly, 2007

[a]120–200 g N kg^{-1}.

Table 2 δ^{15}N composition of organic fertilizers

Type of fertilizer	Source[a]	Total N (g kg^{-1})	δ^{15}N (‰)[b]	Reference
Manure	Cattle		+3.5 to +16.2	Choi et al., 2006, 2007; Bateman and Kelly, 2007; Rogers, 2008
	Poultry	35	+2.7 to +8.6	Rogers, 2008; Rapisarda et al., 2010;
	Horse		+7.2 (0.07)	Flores et al., 2007
	Pig		+6.5 to +11.3	Choi et al., 2006, 2007; Rogers, 2008
	Sheep		+2.0 (0.11)	Flores et al., 2011
	M		+9.6 to +45.2	Choi et al., 2007
	C + P	22−25	+16.7	Nakano and Uehara, 2007
	MP	35	+9.9	
	CMP	60	+4.8 to +8.4	Bateman et al., 2005; Bateman and Kelly, 2007
Compost	Citrus	14	+8.2 (0.15)	Rapisarda et al., 2010
	CM	12	+4.9 to +8.7	Bateman and Kelly, 2007; Rapisarda et al., 2010
	SM	23–26	+13.9 to +16.4	Choi et al., 2002; Yun et al., 2006, 2011
	PM	12.2	+13.6	Yuan et al., 2012
Meal	Canola		+4.2	Hayashi et al., 2011
	Fish		+11.7	
	Horn	140	+6.0	Georgi et al., 2004, 2005
Guano			+14.6	Erskine et al., 1998
Corn steep liquor		3.4	+8.5 (0.7)	Nakano et al., 2003
Seaweed-based			+2.5 (1.5)	Bateman and Kelly, 2007
Commercial		63	+14.8	Šturm et al., 2011

[a]C, cattle; P, poultry; CM, cattle manure; SM, swine manure; PM, poultry manure; M, manure (unspecified); MP, manure pellet (unspecified); CMP, chicken manure pellet.
[b]Data in parentheses are standard deviations of the mean.

Table 3 Statistical tests of differences in δ^{15}N composition between organic and conventional plant products grown in experimental fields and greenhouses

	δ^{15}N (‰)[a]				
Product	Organic	Conventional	Statistical tool[b]	p[c]	Reference
Tomato	+5.9 (2.0)	−2.5 (2.0)	ANOVA	*	Bateman et al., 2005
	+7.1 (0.7)	+0.3 (0.6)	LSD	*	Nakano et al., 2003[e]
	+8.7 to +15.4	−1.2 to +3.1		–	Nakano and Uehara, 2007[f]
	+8.0 and +11.2	−1.0 and 0	ANOVA	–	Georgi et al., 2004
Chinese cabbage	+8.0 and +11.2	−1.0 and +1.6			
	+8.8 to +12.5	−4.0 to +5.5	GLM, ANOVA	*	Yun et al., 2006[f]
	+8.7	+5.7	ANOVA, DMRT	*	Yuan et al., 2012
Lettuce	+5.5	+2.2	ANOVA	*	Bateman et al., 2005
	+8.0 to +9.6	+5.2 to +7.2			Šturm et al., 2011
Sweet pepper	+10.8 to +11.3	+6.8 to +7.6	ANOVA, Tukey	*	Flores et al., 2007[e,f]
	+11.2	+8.7	LSD		del Amor et al., 2008[f]
Carrot	+6.7 (1.0)	+3.5 (0.4)	ANOVA	*	Bateman et al., 2005
Lettuce, onion, cabbage	+5.5 to +7.5	+5.0 to + 6.0		ns	Schmidt et al., 2005
Orange fruit	+6.7 (0.7)	+4.6 (0.4)	ANOVA, Tukey	**	Rapisarda et al., 2010[e]
	+9.0 (0.4)			**	
Various[d]	+8.2	+6.6	ANOVA	*	Georgi et al., 2005[e]
Peach[g]	+6.6 to +8.0	−1.1 to +1.5	ANOVA, Tukey	**	Camin et al., 2011[e]
Strawberry[g]	+2.7 to +4.1	+ 2.9 to +4.0			
Canola, barley, wheat	+2.2 to +8.4	+0.30 to 2.5	ANOVA, GLM, LSD	*	Choi et al., 2006[f]
Maize (30-d)	+7.7	+1.1 and 4.5	ANOVA, GLM, LSD	*	Choi et al., 2002[f]
Maize (70-d)	+6.7	+6.0 and 6.1		*	
Paddy rice	+5.2 to +8.2	+5.4	ANOVA, Tukey	*	Yun et al., 2011[f]

[a]Data in parentheses are standard deviations of the mean.
[b]GLM, general linear model; ANOVA, analysis of variance; LSD, least significant difference; DMRT, Duncan multiple range test.
[c]*, $p < 0.05$; **, $p < 0.01$; ns, not significant; –, no test applied.
[d]Cabbage, lettuce, onion, and Chinese cabbage.
[e]No differences were found for δ^{13}C, δ^{34}S, δ^{2}H, and δ^{18}O as related to production system or fertilizer type.
[f]Differences due to fertilizer type, including green manure.
[g]Different cultivars, years of production and site.

Table 4 Statistical tests of differences in $\delta^{15}N$ composition between organic and conventional plant products from commercial farms and retail sampling

Product	$\delta^{15}N$ (‰)[a]		Statistical tool[b]	p[c]	Reference
	Organic	Conventional			
Tomato	+8.1 (3.2)	−0.1 (2.1)	t test	**	Bateman et al., 2007
	+9.3	0.0		–	Schmidt et al., 2005[d]
	+6.9 to +7.8	−0.7 to −0.9			Rogers, 2008[d,e]
	+0.9 to +5.5	+0.2 to +2.1	ANOVA, PCA	*	Pieper and Barret, 2009
Orange fruit	+5.7 to +6.7	+4.4 to +5.5	ANOVA, LDA	**	Rapisarda et al., 2005
	+7.3 to +7.9	+ 5.1 to +6.1	ANOVA, Tukey	***	Camin et al., 2011[i]
Lettuce	+7.6 (4.1)	+2.9 (4.3)		*	Bateman et al., 2007
Carrot	+5.7 (3.5)	+4.1 (2.6)		ns	
Paprika	+7.9	−0.5		–	Schmidt et al., 2005_d
Wheat	+3.6 (1.6)	+2.3 (1.0)		–	
Peas	+0.3	+0.2			Rogers, 2008[d,e]
Various <80-d[f]	+10.6 to +12.3	+2.4 to 2.7			
Various > 80-d[g]	+3.5 to +8.5	0.0 to +5.7			
Various[h]	+14.6 (3.3)	+4.1 (1.7)	ANOVA, GLM, LSD	*	Choi et al., 2003
Potato	+7.2 (3.4)	+3.4 (1.3)	ANOVA, Tukey	**	Camin et al., 2007
Strawberry[i]	+1.2 to +9.8	+2.9 to +4.0	ANOVA, Tukey	***	Camin et al., 2011
Clemintine[i]	+6.6 to +8.0	+6.7 to +7.1		ns	
Various[j]	+3.0 to +13.7	−2.0 to +8.3	LSD	–	Šturm and Lojen, 2011
Various[k]	+2.2 to +8.6	+0.4 to +8.7			

[a]Data in parentheses are standard deviations of the mean.
[b]GLM, general linear model; ANOVA, analysis of variance; LSD, least significant difference; PCA, principal components analysis; LDA, linear discriminant analysis.
[c]*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$; ns, not significant; –, no test applied.
[d]No differences were found for $\delta^{13}C$, $\delta^{34}S$, $\delta^{2}H$, and $\delta^{18}O$ as related to production system.
[e]Only differences in $\delta^{13}C$ of tomatoes grown in a greenhouse warmed with natural gas (methane).
[f]Cucumber, zucchini, and broccoli.
[g]Pumpkin, eggplant, potato, and corn.
[h]Corn, chili, lettuce, cucumber, cabbage, spinach, and eggplant.
[i]Different cultivars, years of production, and site.
[j]Chicory, tomato, potato, cauliflower, leek, rocket, and endive.
[k]Carrot, sweet pepper, parsley, kohlrabi, onion, and garlic.

with the single compost application (Choi et al., 2002). Plant $\delta^{15}N$ decreased from +10.7‰ at 40 days after transplanting (DAT) to +3.4‰ at 60 DAT when urea was applied to Chinese cabbage fertilized with compost as a basal N input, whereas plant $\delta^{15}N$ increased from −0.1‰ at 40 DAT to +2.7‰ at 60 DAT with compost application to urea basal N input (Yun et al., 2006). The higher availability of urea N caused a greater shift in plant $\delta^{15}N$ than application of compost (Yun et al., 2006).

Addition of N poor sources such as rice straw or bark composts had virtually no effect on plant $\delta^{15}N$ compared with N-rich sources such as pig manure or cattle feces (e.g. Yoneyama et al., 1990). The availability of N from an organic source plays a greater role in determining crop $\delta^{15}N$ values than the $\delta^{15}N$ value of the N source itself (Choi et al., 2006). Thus higher values of $\delta^{15}N$ were found in the grain of crops (canola, barley, and wheat) fertilized with liquid hog manure ($\delta^{15}N = +5.1$‰) with high N availability (up to 70% as NH_4^+) than for cattle manure ($\delta^{15}N = +7.9$‰).

In contrast, Šturm et al. (2011) reported that the $\delta^{15}N$ values of lettuce given a basal application of commercial organic fertilizer ($\delta^{15}N = +14.8$‰) and a secondary application of either organic fertilizer or Ca $(NO_3)_2$ ($\delta^{15}N = +5.7$‰) did not differ significantly ($\delta^{15}N = +8.0$ and +7.2‰, respectively). This result was attributed to the small difference ($\delta^{15}N = +9.1$‰) between the organic and synthetic fertilizer, in contrast to the large difference ($\delta^{15}N = +17.7$‰) reported by Yun et al. (2006). Šturm et al. (2011) maintained that it is difficult to detect low or moderate rates of synthetic N fertilizer applied to organic lettuce when the difference in $\delta^{15}N$ between organic and synthetic N fertilizer is <9.1‰.

Absorption of ^{15}N-depleted nitrate from irrigation water may also influences the $\delta^{15}N$ composition of plants, but the effect depends on the concentration of NO_3^- (Bateman et al., 2005; Šturm et al., 2011).

Biological N_2 Fixation

A legume which is actively fixing N_2 through its symbiosis with *Rhizobium* will have a $\delta^{15}N$ signature close to zero as little uptake of soil-derived N will occur. Legumes which are poorly nodulated due to biotic or abiotic stress factors will have a greater reliance on soil N, and the $\delta^{15}N$ signature will mirror that in the soil available N pool. Legume BNF is suppressed by high concentration of soil inorganic N brought about by bare fallowing or application of organic or synthetic N fertilizers. The use of N_2 fixing cover crops is common in organic farming rotation systems including annual (Bateman et al., 2005;

Oberson et al., 2007) and perennial crops (Rapisarda et al., 2005), and might result in relatively low δ^{15}N values in plants even though organic N fertilizers are applied (Camin et al., 2011). Yun et al. (2011) observed that when rice was preceded by a legume (hairy vetch) green manure ($\delta^{15}N = -0.5 \pm 0.1‰$) or was fertilized with ammonium sulfate ($\delta^{15}N = -0.5 \pm 0.1‰$), the shoots had similar but significantly lower δ^{15}N values than the control treatment at 110 DAT.

Plant Organs

Different patterns of N assimilation and reallocation within the plant as well as senescence can cause intraplant variation in δ^{15}N. Leaves, fruits, and roots of plants frequently show differences in δ^{15}N values, as well as interactions with plant age and climate. Leaves can be 3–7‰ enriched in ^{15}N relative to roots and the difference can be greater in dry climates (Evans, 2001). Statistically significant differences in δ^{15}N values among plant organs were found in 70-day maize (Choi et al., 2002) with stems >leaves >grains >roots. Similarly, Flores et al. (2007) and del Amor et al. (2008) found significantly lower values of δ^{15}N in roots and fruits than leaves and stems of sweet pepper. In contrast, higher δ^{15}N values have been reported in grains than in straw of wheat (Senbayram et al., 2008; Serret et al., 2008). Serret et al. (2008) reported that differences in the δ^{15}N values of grain and straw of wheat were consistent among 24 genotypes at five rates of urea application. Intraplant fractionation can be affected by the inorganic N source. For example, Flores et al. (2011) found that shoots of capsicum grown in sterilized peat were enriched in δ^{15}N by $3.7 \pm 0.4‰$ compared with roots when NO_3^- was the sole N source, whereas the difference was only $2.0 \pm 0.2‰$ when NH_4^+ was the sole N source.

Plant Age

Several authors have reported that δ^{15}N signatures vary with the age of the plant or time to maturity (e.g. Choi et al., 2002; Yun et al., 2006; Flores et al., 2007; Rogers, 2008). The main factor driving age-dependent plant δ^{15}N signatures is fertilizer N, with type (organic vs. conventional), timing (basal vs. side dressing), and relative rates of application being the most important variables (Yun et al., 2006). Yun et al. (2006) and Yun and Ro (2009) found differences of δ^{15}N values between the outer, middle, and inner leaves of Chinese cabbage that were related to the source and timing of N fertilization. For example, a side-dress application of urea (−0.7‰) resulted in lower δ^{15}N values of inner (newer) leaves (+0.2‰) than outer (older) leaves (+5.5‰), which reflected the isotopic signatures of the basal compost amendment (+16.4‰) (Yun and Ro, 2009). Convergence of the δ^{15}N signatures of rice was observed between 15 and 110 days after application of compost ($\delta^{15}N = 15.3‰$) or ammonium sulfate ($\delta^{15}N = -0.4‰$) (Yun et al., 2011).

Physiological factors related to initial seed N reserves, growth habit (annual or perennial; deciduous or evergreen), senescence, or reallocation of N within the plant could also play a role. Growth habit may interact with N fertilizer regime, with heavy applications for short-term annual crops, especially vegetables, and more measured seasonal applications tailored to growth habit for long-term perennial fruit crops.

$\delta^{34}S$

Plant bulk δ^{34}S signatures vary with the plant species (Schmidt et al., 2005; Tanz and Schmidt, 2010). There is a small fractionation of δ^{34}S in the assimilatory sulfate reduction process (Trust and Fry, 1992), while plant organs and biochemical components often show distinct δ^{34}S values from the bulk plant (Tanz and Schmidt, 2010). Plant ^{34}S composition reflects local geological conditions which influence the δ^{34}S signature of available sulfate in the soil solution (Mizota and Sasaki, 1996). Application of sulfate fertilizers may also affect soil and plant δ^{34}S values (Mizota and Sasaki, 1996). Other local conditions such as atmospheric deposition and proximity to oceans may affect the bulk δ^{34}S signature of plants (Mizota and Sasaki, 1996; Camin et al., 2011).

DIFFERENTIATION OF ORGANIC AND CONVENTIONAL PLANT PRODUCTS

$\delta^{13}C$

As discussed previously, isotopic discrimination during photosynthesis is the main determinant of δ^{13}C values in plants. However, the effects of types and rates of N fertilizers have been investigated in relation to photosynthesis and the potential differentiation of organically and conventionally grown plants (Nakano et al., 2003; Georgi et al., 2005; Rapisarda et al., 2010; Camin et al., 2011).

Nakano et al. (2003) found no differences among δ^{13}C values of leaves, stems, or fruits of tomatoes in either organic fertigation (corn steep liquor) or inorganic fertigation treatments. Similarly, Georgi et al. (2005) found that δ^{13}C values of organic vegetables fertilized with horn meal were not significantly different than those fertilized with synthetic fertilizers, e.g. the values for cabbage were −26.4 and −25.3‰, respectively. Values of δ^{13}C were in a narrow range for orange fruit (−25.9 to −27.5‰) under different fertilizer regimes, showing that ^{13}C composition was independent of fertilizer source (Rapisarda et al., 2010).

However, Camin et al. (2011) found significantly different ($p < 0.01$) δ^{13}C values between organic (−26.7‰) and conventional (−25.7‰) peaches from experimental fields, and between organic (−25.4‰) and conventional (−25.0‰) strawberries ($p < 0.05$) from experimental and commercial fields. These results were attributed to the influence of biological respiration (organic matter decomposition) on the isotopic composition of CO_2 at the micro-environmental level. However, cultivar or site of production resulted in more statistically significant differences than the agricultural regime. Although differences in production

regime for peaches and strawberries were statistically significant, the absolute differences were so small as to be of little value as a routine diagnostic tool. In addition, while differences in δ^{13}C values of potato (−29.0 to −25.0‰) and orange juice (−27.1 to −24.3‰) were much larger for mode of production, they were not significantly different (Camin et al., 2007, 2011).

Increasing rates of compound (NPK) fertilizer together with a fixed rate of horse manure did not significantly affect the δ^{13}C values (−28.1 to −27.7‰) of sweet pepper (Flores et al., 2007). Although supply of N or other nutrients may greatly influence the rate of photosynthesis, there is no evidence that the δ^{13}C values of plants are affected to the same degree. Jenkinson et al. (1995) found that δ^{13}C values in wheat without N fertilizer were depleted (−26.4 ± 0.3‰) in relation to wheat fertilized with 190 kg N ha^{-1} (−25.6 ± 0.4‰). However, this difference varied from year-to-year and it was less expressive in wet years (0.2‰) than in dry years (1.7‰). More recently, it was found that δ^{13}C values of well-irrigated wheat increased moderately as a result of increasing N supply (Serret et al., 2008).

Rogers (2008) analyzed the ^{13}C isotopic composition of various vegetables from organic and conventional regimes and found differences only in δ^{13}C values for tomatoes growing in hothouses (warmed by natural gas). Conventional hothouse tomatoes had δ^{13}C values more depleted (−44.9 to −36.3‰) than field-grown organic tomatoes (−27.7 to −26.5‰). Schmidt et al. (2005) reported similar results which are related to the influence of depleted δ^{13}C values of the natural gas heating source on the micro-environment CO_2.

The results of investigations into the potential use of δ^{13}C as a marker for organic vs. conventional production have shown that insufficient variation exists to establish mode of production. However, results have been confined to C3 species, particularly vegetables, and thus it is not possible to extrapolate with respect to C4 species. δ^{13}C values are mainly used to detect adulteration of foodstuffs, e.g. wine, juices, honey, maize oil, and palm sugar (Rossmann, 2001; Primrose et al., 2010). Stable isotope ratios allow otherwise chemically identical materials to be differentiated, e.g. adulteration of fruit beverages with sucrose from C4 plants, which cannot be detected by conventional chemical methods (Rossmann, 2001).

δ15N

The ^{15}N isotopic composition of plant products is strongly related to the signature of the predominant source of plant-available N. Because organic and synthetic fertilizer sources differ markedly in δ^{15}N composition, it would appear to be a promising marker to distinguish organically and conventionally fertilized plant products. A synthesis of published data on δ^{15}N values of plant products grown organically or conventionally is given in Tables 3 (experimental fields and greenhouses) and 4 (commercial farms and retail samples). It should be noted, however, that the use of an organic N fertilizer source does not denote that the product derives from a completely organic system, whereas use of a synthetic fertilizer implies a nonorganic system. As discussed in the previous Section, factors other than N source can influence the plant's δ^{15}N signature, and so differentiation must be supported by appropriate statistical analyses.

Published data show that organic plant products vary within a range of positive δ^{15}N values, i.e. +0.3 to +14.6‰, while conventional plant products vary from negative (−4.0‰) to positive (+8.7‰) values (Tables 3 and 4). Larger differences in δ^{15}N values between organically and conventionally grown vegetables have been reported for tomatoes and Chinese cabbage, whereas smaller differences appear for lettuce, carrots, and peas (Georgi et al., 2004; Bateman et al., 2005, 2007; Yun et al., 2006; Rogers, 2008; Šturm and Lojen, 2011). Therefore, it may only be practical to approach differentiation on a product-specific basis. In general, differences in δ^{15}N values are large and statistically significant for most vegetables and annual crops (Tables 3 and 4). However, it will almost certainly not be possible to differentiate legume products on the basis of δ^{15}N composition due to BNF. For example, the difference between organically and conventionally grown peas was around 0.1‰ (Rogers, 2008), and no significant difference was found for soybean under the different production systems (Oberson et al., 2007). Perennial or semiperennial crops such as orange, peach, and strawberry tend to show smaller differences in δ^{15}N values between organic and conventional production, but nevertheless were statistically significant (Rapisarda et al., 2005, 2010; Camin et al., 2011; Tables 3 and 4). Differentiation of mode of production was significant ($p < 0.01$) for δ^{15}N values of pulp protein and juice amino acids from two orange cultivars (Rapisarda et al., 2005, 2010).

Bateman et al. (2005) studied the influence of pelleted chicken manure (+5.4‰) and NH_4NO_3 (−1.3‰) on the ^{15}N composition of tomatoes, carrots, and lettuce in experimental plots. Synthetic N fertilizer application resulted in plants with significantly lower δ^{15}N values ($p < 0.05$) compared with the manure treatment. Different plant species differ in their N requirements and this may explain differences observed between species in their δ^{15}N response to N fertilizer source. Larger differences in δ^{15}N values were found between organically and conventionally fertilized tomatoes (∼8.6‰) compared with lettuce (∼3.3‰) and carrot (∼3.2‰).

Retail samples from supermarkets have shown differences in δ^{15}N signatures between products labeled as organic or nonorganic (Bateman et al., 2007; Rogers, 2008). However, comparison of retail samples is confounded by potential differences in δ^{15}N due to geographic origin caused by differences in MAP and/or MAT, as well as fraud in labeling. Rogers (2008) found larger differences between organic and conventional retail samples for faster growing vegetables (maturity <80 days) such as tomatoes, broccoli, cucumber, and zucchini, than vegetables with a maturity >80-days, such as pumpkin, eggplant, potatoes, and corn. Zucchini and cucumber had the largest δ^{15}N difference of 10.2 and 9.6‰, respectively. Eggplants (90–100 days), corn, and pumpkin (100–120 days) had the smallest differences in

δ^{15}N values of 2.2, 3.0, and 4.0‰, respectively (Rogers, 2008). Bateman et al. (2007) also found significant differences in δ^{15}N values of retail samples of organically and conventionally grown lettuce and tomatoes from farms across the EU. However, plant δ^{15}N values showed significant overlap. Overlapping was large for lettuce and almost complete for carrots, and it confers considerable uncertainty when attempting to differentiate samples where precise geographical origin is unknown. Organic tomato samples with a mean δ^{15}N value of +8.2‰ were overlapping between 0 and +6‰. Ninety-five percent ($p < 0.05$) of the modeled organic population would be expected to have δ^{15}N values between +1.7 and +14.4‰, and <50% of conventional tomatoes would be expected to have δ^{15}N values <-0.5‰ (Bateman et al., 2007). Other examples of overlapping of δ^{15}N values have been reported for fruits (e.g. Camin et al., 2011), tomatoes (e.g. Pieper and Barret, 2009) carrot, garlic, onion, and other vegetables (e.g. Šturm and Lojen, 2011; Table 4).

Bateman et al. (2007) point to two factors that may contribute to δ^{15}N overlapping between organic and conventional products: (i) conventional growers may legitimately choose not to use synthetic fertilizer and instead use organic N sources with high δ^{15}N values, or perhaps a combination of both sources; and (ii) organic products may be sold as conventional when market supply exceeds demand. Application of compost or manure on conventional farms may result in very close δ^{15}N values between organic and conventional plant products, as seen for orange (Camin et al., 2011). This practice is not unusual among vegetable growers in many countries, and it may even be recommended by the local agricultural service, being referred to as the "integrated system" (e.g. Georgi et al., 2005). A third factor may be that organic farms are often established on land that was formerly under a conventional production regime. During such a transition, it may take some time for the new system to adjust to the changed fertilizer practices. For example, differences between δ^{15}N values of organic and conventional tea were reported to be significant only in the third year after the beginning of organic production that was preceded by long-term conventional cultivation (Hayashi et al., 2011).

Schmidt et al. (2005) reported no significant differences between organically and conventionally grown wheat in different regions of Germany. Differentiation of fertilizer regime was unsuccessful due to the confounding effects of different vegetables with two levels of N (full supply and 65% less) and two types of N fertilizers (horn meal + green manure; ammonium nitrate). However, Georgi et al. (2005) reanalyzed the results of the same experiments, and found significant differences for fertilizer types (Table 4). Overlapping δ^{15}N values can be attributed to the use of legumes in farm rotations which attenuates the variation in δ^{15}N of the synthetic and organic N sources (Yun et al., 2011). In contrast, over application of synthetic N fertilizer can lead to significant N losses via NH_3 volatilization and/or denitrification which enrich ^{15}N in the soil solution (Schmidt et al., 2005).

In summary, differentiation of organically and conventionally grown plant products using δ^{15}N composition will be possible when compost or manure with high positive δ^{15}N values are applied as the N fertilizer sources in organic production, and N fertilizer with negative or small positive δ^{15}N values are used in conventional production. The greater the difference between organic and synthetic fertilizer the more robust will be the differentiation. Nevertheless, many production or external factors may confound product designation, e.g. (i) legume products or the use of legume cover crops on organic farms (ii) crop species with a low N requirement (iii) annual vs. perennial growth habit (iv) use of organic fertilizers by conventional farmers (v) marketing of organic products as conventional products (vi) transition from conventional to organic production.

δ^{34}S

While the application of manufactured sulfate fertilizers is prohibited in organic farming, S° from both native and commercial sources is allowed for insect and disease control and as a soil amendment (USDA, 2002). Therefore, in order for δ^{34}S to be able to discriminate mode of production, conventional farms would have to use sulfate fertilizers and/or S° that differed significantly in δ^{34}S composition compared with organic S sources and/or S° used on organic farms. Because of the partial overlap in the forms of S permitted on organic and conventional farms as well as the overlap in δ^{34}S signatures of various sources of SO_4^{2-} and S°, together with the confounding factors of proximity to oceans or industrial areas, it is highly unlikely that the δ^{34}S composition of plant products can differentiate mode of production. Thus plant δ^{34}S values could not distinguish between mode of production or fertilizer type, but showed correlation with geographical origin because of different geological and soil conditions (Georgi et al., 2005; Schmidt et al., 2005; Tanz and Schmidt, 2010; Camin et al., 2011). Also, special attention has to be given to the possibility of addition of sulfite preservatives in foods and drinks, which can vary from +2.5 to +13.7‰ (Kelly et al., 2002) and can further confound the interpretation of δ^{34}S signatures of foodstuffs.

COMPLEMENTARY MARKERS AND STATISTICAL TOOLS

A combination of ^{15}N isotopic composition and simple complementary markers (e.g. quality parameters, ascorbic acid, total soluble solids, specific N compounds) may improve the power of discrimination between organically and conventionally grown foodstuffs (Table 5), particularly when isotopic composition alone is known to be inadequate, e.g. in the case of legumes such as peas and soybean. However, the use of quality parameters has generally been unsuccessful due to high sample variability, and no statistically significant differences were found among organic versus conventional plant products (Rapisarda et al., 2005, 2010; Camin et al., 2007, 2011; Pieper and Barret, 2009).

Table 5 Complementary markers for mode of production of plant products

Product	Marker	Technique[a]	Statistical tool[b]	p[c]	Reference
Potato	Ascorbic acid, protein, synephrine	HPLC, KJ	Tukey's test	ns	Camin et al., 2007
Wine	Ochratoxin A (mycotoxin)	HPLC, LC-MS	Shapiro-Wilk test, Mann-Whitney test	ns	Chiodini et al., 2006
Various[f]	Multi-elemental	ICP-MS; ICP-OES,	PCA, t-test; modelling; CDA	* / ns	Gundersen et al., 2000; Kelly and Bateman, 2010; Laursen et al., 2011
Wheat	Radionuclides	HPGe	Parametric and nonparametric tests	ns	Lindahl et al., 2011
Tomato	Quality parameters[d]	COL, Bradford assay, SM	ANOVA, PCA	ns	Pieper and Barrett, 2009
Fruits[g]	Physico-chemical parameters[e]	COL, HPLC, IEC, SM, AAS, AES, KJ	ANOVA, Tukey	*, ns	Camin et al., 2011
Orange			ANOVA, Tukey, CDA, LDA	** ns	Rapisarda et al., 2005, 2010
Red grape juice and vinegars	Polyphenol content	Folin-Ciocalteu, HPLC	SD, ANOVA, Tukey's test	ns	Machado et al., 2011

[a]HPLC, high-performance liquid chromatography; LC-MS, liquid chromatography-mass spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry; HPGe, high-purity germanium for gamma ray spectrometry; AAS, atomic absorption spectroscopy, AES, atomic emission spectroscopy, KJ, Kjeldahl, COL, colorimetry; IEC, ion exchange chromatography; SM, standard methods for physico-chemical parameters; Folin–Ciocalteu colorimetric method.
[b]ANOVA, analysis of variance; PCA, principal components analysis; LDA, linear discriminant analysis;
CDA; canonical discriminant analysis.
[c]*, $p < 0.05$; **, $p < 0.001$; ns, not significant; –, no test applied.
[d]Visual inspection (color and defects), °Brix, pH, tritatable acidity, bostwick consistency, moisture content, total solids, vitamin C (ascorbic acid and dehydroascorbic acid), lycopene, flavonols, amino acids, and mineral content.
[e]Physicochemical parameters (fruit weight, juice yield, total soluble solids, titratable acidity, and pH), color, ascorbic acid, total N, and synephrine.
[f]Onions, peas, wheat barley, fava bean, potato, tomato, and lettuce.
[g]Orange, peach, strawberry, and clementine.

A variety of advanced analytical techniques has also been employed, including the measurement of natural radioactivity (^{40}K, ^{226}Ra, ^{228}Ra, and ^{228}Th) in winter wheat (Lindahl et al., 2011). Multi-element fingerprinting combined with chemometrics allowed discrimination between organic and conventional wheat, barley, and potato, when the effects of three geographical locations and two cropping seasons were removed by principal component analysis (Laursen et al., 2011). Similarly, conventional and organic onions and peas (Gundersen et al., 2000) and Rio Red grapefruit (Chen and Harnly, 2010) could be identified by mass spectral fingerprinting. Metabolic profiling (metabolomics) is an emerging analytical tool that is being increasingly applied to differentiate conventional and organic products (e.g. Zorb et al., 2006; Röhlig and Engel, 2010; Søltoft et al., 2010; Vallverdú-Queralt et al., 2011). Complementary analyses can also be used to monitor the safety of organic foodstuffs, which is an area of increasing concern. For example, mycotoxin contamination in wine depends on the production regime (Chiodini et al., 2006).

The statistical comparison of organic and conventional δ^{15}N values of plant samples commonly involves a univariate analysis. Analysis of variance (ANOVA) and hypothesis testing can be applied in this case,. e.g. Student t-test, Tukey test, and Fisher Least Significant Difference (LSD). The statistical tools applied in individual studies are given in Tables 3 and 4. However, Bateman et al. (2007) suggested that the modeled normal distribution curves for the organic and conventional plant samples could show the manner in which this type of data might be analyzed, taking into account the probability of overlapping δ^{15}N values (Fig. 1). Depending on the degree of overlap, Bateman et al. (2007) proposed that a sample with a specific δ^{15}N value could be assigned a probability that it had been grown with or without the use of synthetic N fertilizer.

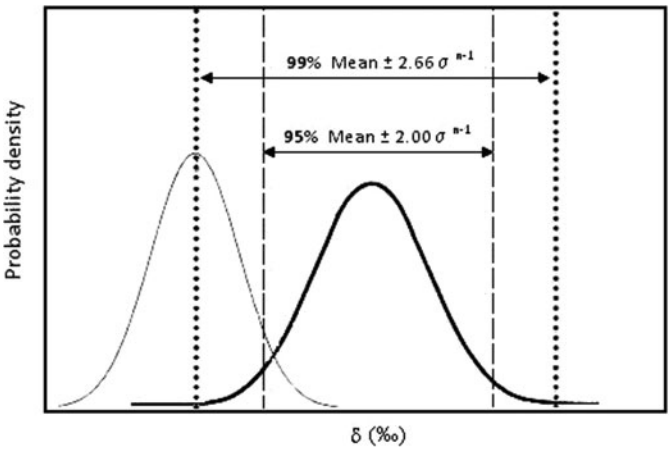

Figure 1 Schematic diagram of the frequency distribution of isotopic signatures (δ, ‰) of organic (bold curve) and conventional (fine curve) products. The limits between which 95 and 99% of the δ values of organic products would be expected to fall and overlap with δ values of conventional products are indicated (Adapted from Bateman et al., 2007).

This type of analysis depends on the establishment of a large product-specific and representative (unbiased) database for conventional and organic samples. Bateman et al. (2007) established databases for tomatoes, lettuce, and carrots originating mainly in the UK but also from several EU countries. The number of organic samples varied from as few as 13 for carrots up to 61 for tomatoes, with roughly equivalent numbers of conventional samples. Care was taken to avoid fraudulent labeling by obtaining organic samples directly from certified farms or shops selling their produce. Conventional products were obtained from retail outlets on the basis that fraudulent labeling is unlikely. The assumption in this type of analysis is that the sample subsets are representative or random samples of the entire population. Bateman et al. (2007) concluded that their relatively small number of samples with a skewed geographical distribution had created the potential for bias in their datasets. The integrity of the database can only be assured if samples are obtained across a wide geographical area with contrasting climates and soils, with proof that the plant products were soil-based and not hydroponic.

Multivariate analyses have been used when multiple isotope analyses were performed or where δ^{15}N data were combined with other parameters, e.g. trace elements, etc. Examples of the use of multivariate data analyses are principal component analysis (PCA) (Gundersen et al., 2000; Pieper and Barret, 2009), canonical correlation analysis (CCA) (Camin et al., 2011), and cluster analysis (Suhaj and Koreňovská, 2005). When multivariate statistical tests were applied, mode of production of plant products was pinpointed following removal of common sources of variability such as site, cultivar, and year of production (Camin et al., 2011). In the same way, production regime affected the concentrations of some trace elements, and concentration profiles were different for organically and conventionally grown onions and peas when data were analyzed by principal component analysis (Gundersen et al., 2000).

CONCLUSIONS

There are at least two prerequisites for the successful application of a stable isotope differentiation technique (i) the physical, chemical, or biochemical processes causing isotope fractionation must be known and (ii) a relevant database for statistical evaluation must be established (Rossmann, 2001). Differentiation of organic and conventional plant products requires an understanding of isotopic fractionation processes occurring in soils and plants and the processes that lead to the specific isotopic signatures seen in synthetic and organic N fertilizers.

At the present time, there is no universal analytical method that can be applied to differentiate organic and conventional plant products. A limited database exists on the stable isotopic composition of specific plant products grown under conventional and organic systems. Of these, δ^{15}N appears to be the most promising isotopic marker. However, only occasionally it has been used successfully as the sole criterion, but when combined with complementary analytical techniques and appropriate statistical tools, the probability of a correct identification greatly increases. Correlations between mode of production and δ^{13}C (except greenhouse tomatoes warmed with natural gas) and δ^{34}S signatures have not been established at present.

Besides routine stable isotope analysis of retail samples marked "organic", sampling in organic farms could be considered as part of the certification process. In some cases, samples of plants at early growth stages and of organic fertilizers in use on the farm could constitute evidence to verify production system compliance to organic standards. In any case, stable isotope analysis is not a substitute for *in locus* verification of organic farming, but may improve the robustness of organic labeling in some cases, especially with respect to the use of N fertilizers in crops.

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