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Seasonal variation in the C, N and S stable isotope composition of retail organic and conventional Irish beef

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Abstract

The objective of this study was to investigate seasonal variation in the C, N and S stable isotope composition of retail organic and conventional Irish beef. A total of 242 beef samples (127 organic, 115 conventional) was collected in a one-year survey and analysed by isotope ratio mass spectrometry. The $\delta^{13}C$ time series in conventional beef was significantly non-random, with a pronounced seasonal positive shift of >2‰ between December and June, whilst $\delta^{13}C$ in organic beef was less variable and significantly more negative. In conventional beef, $\delta^{15}N$ was remarkably invariant (remaining close to 7‰) throughout the year, while organic beef was more variable and also significantly lower in $\delta^{15}N$. The S isotope composition ($\delta^{34}S$) exhibited a complex seasonal pattern in both types of beef. These results show that seasonal patterns can occur in the isotopic composition of beef, probably reflecting seasonality in animal feeding practices modulated by tissue turnover rates. Such seasonal variation needs to be considered in the isotopic authentication of beef and other animal-derived products.

Keywords: Authentication; Bovines; Isotope ratio mass spectrometry; Meat; Seasonality; Traceability

1. Introduction

Organic farm products command premium prices and their market share continues to rise. A number of analytical studies have compared the nutritional value, sensory quality and food safety aspects of organically and conventionally produced foods (Bourn & Prescott, 2002; Woese, Lange, Boess, & Bogl, 1997). However, existing analytical approaches cannot provide a reliable designation of the production system of foods (Ulberth, 2004). A robust scientific technique, or combination of techniques, for the authentication of foods labelled organic would be of immense value for consumers, government agencies and the agri-food industry.

Stable isotope ratio analysis (SIRA) provides a promising tool for authenticity tests of organically produced foods (Kelly, 2003; Schmidt, Rossmann, Stöckigt, & Christoph, 2005a). For production system investigations, SIRA exploits variations in the natural stable isotope composition in farm products, which can reflect different crop cultivation and animal husbandry practices. For example, SIRA of C can potentially identify the production origin of beef and milk based on the extent of C_4 photosynthetic plant materials (maize) consumed by cattle (Bahar et al., 2005; Boner & Förstel, 2004; De Smet, Balcaen, Claeys, Boeckx, & van Cleemput, 2004; Knobbe et al., 2006).

SIRA is an authenticity strategy that relies on empirical databases of the chemical composition of genuine

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products, encompassing the full range of variation caused by various factors (Ulberth, 2004). Temperate agriculture is highly seasonal in nature and animal husbandry practices are likely to result in transient seasonal variations in the isotope composition of animal-derived products such as meat and milk. Therefore, information is required on the likely extent of seasonal isotopic variations in animal products from different production systems.

Ireland is a temperate humid country with an annual weather cycle and distinct seasons (Keane & Sheridan, 2004). Husbandry practices, especially the feeding of livestock animals indoors and outdoors at different periods of the year, are governed by seasons (Lynch, 2004). As the difference in isotopic composition between indoor (mostly conserved forages and grain-based diets) and outdoor (mostly grass-based diets) dietary constituents is likely to result in altered isotopic compositions of animal tissues, seasonal variations in the isotopic composition of meat can be expected. The objectives of the present study were to investigate the annual seasonal variation in the stable isotope composition of light elements (C, N and S) of organic and conventional retail Irish beef and to assess its implications for the isotopic authentication of organic beef.

2. Materials and methods

2.1. Sources of samples

Organic beef samples were collected from two large supermarkets (referred to as A and B) and two certified butcher shops dealing exclusively with organic beef (C and D) (Table 1). All sources were approved either by the Irish Organic Farmers' and Growers' Association (IOFGA) or the Organic Trust, Ireland, as certified organic beef retailers. Conventional beef samples were collected from the same supermarkets and three further butcher shops (grouped as E) dealing only with conventional beef produced in Ireland. Of the total organic samples collected ($n = 127$), 96.5% were striploin; in instances where this was unavailable, round steak (2%) and sirloin (1.5%) were sampled. All conventional beef samples ($n = 115$) were striploin.

Samples were collected once a week between July 2003 and June 2004. An uneven availability of organic beef throughout the year and the selling of beef from the same sources on consecutive weeks, especially by the small butchers, caused slightly uneven numbers of beef samples collected each week. At the time of collection, the animal ear-tag number and the supplier/farmer information were recorded wherever available. This survey was originally designed to relate patterns in isotopic compositions of beef to geographical and husbandry background information; however, due to the lack of disclosure of farm-level information by the suppliers, the interpretation is mainly restricted to the description of the overall seasonality of Irish organic and conventional beef.

Upon collection, samples were labelled according to an internal coding system to facilitate tracing of samples during subsequent storage and handling. Collected samples were vacuum-packaged and stored at −20 °C until preparation for analysis.

Table 1
Sources of retail organic and conventional Irish beef samples

Source	Organic (n)	Conventional (n)
Supermarket (A)	46	54
Supermarket (B)	35	47
Organic butcher (C)	35	–
Organic butcher (D)	11	–
Conventional butchers (E)	–	14
Total	*127*	*115*

2.2. Preparation of samples

Muscle sub-samples (5 g) were sliced into thin pieces, freeze-dried (Edwards Pirani 501 Freeze Dryer, Edwards Ltd., Crawley, UK) for 48 h and pulverised using a vibrating ball mill (Type MM2, Glen Creston Ltd, Stanmore, UK). The milled samples were then stored in plastic bags under desiccation. Lipids were extracted from 100 mg of milled sub-samples using hexane:isopropanol (3:2 v/v) as described by Radin (1981). Defatted muscle residue (0.9–1.1 mg) was loaded into ultra clean tin capsules for dual C and N isotope analysis. For S isotope analysis, defatted muscle residue (5.0–5.5 mg) and vanadium pentoxide (6.5–7.5 mg) were loaded into tin capsules. All samples were analysed for C and N, but only the samples supplied by one large supermarket (A) were analysed for S (organic $n = 46$, conventional $n = 54$).

2.3. Isotopic analysis

Natural abundance stable isotope ratios of C ($^{13}C/^{12}C$), N ($^{15}N/^{14}N$) and S ($^{34}S/^{32}S$) in defatted muscle were measured by elemental analyser continuous-flow isotope ratio mass spectrometry (EA-CF-IRMS), using a Europa Scientific ANCA-NT 20-20 Stable Isotope Analyser with ANCA-NT Solid/Liquid Preparation Module (Scrimgeour & Robinson, 2004). The analytical precision, as estimated by replicate analysis ($n = 24$) of bovine liver standard (NIST Standard Reference Material 1577b, Bovine Liver) analysed along with the samples, was 0.1‰ (SD) for both C and N. Working standard was 1 mg of leucine prepared by freeze-drying 50 μl of a 20 mg ml^{-1} stock solution in tin cups and then calibrated against 'Europa flour' and IAEA standards N1 and N2.

For S isotope ratio analysis, the bovine liver standard (1577b), quality control reference material and beef samples (all previously mixed with vanadium pentoxide catalyst) were analysed (Scrimgeour & Robinson, 2004). During analysis of samples, NBS 127 (barium sulfate, IAEA, $\delta^{34}S_{V\text{-}CDT} = +20.3‰$), IAEA-S-1 (silver sulfide, $\delta^{34}S_{V\text{-}CDT} = -0.3‰$) and IA-R025 (barium sulfate, $\delta^{34}S_{V\text{-}CDT} = +8.53‰$) were used as internal reference materials. The analytical precision (SD, $n = 9$) was 0.2‰.

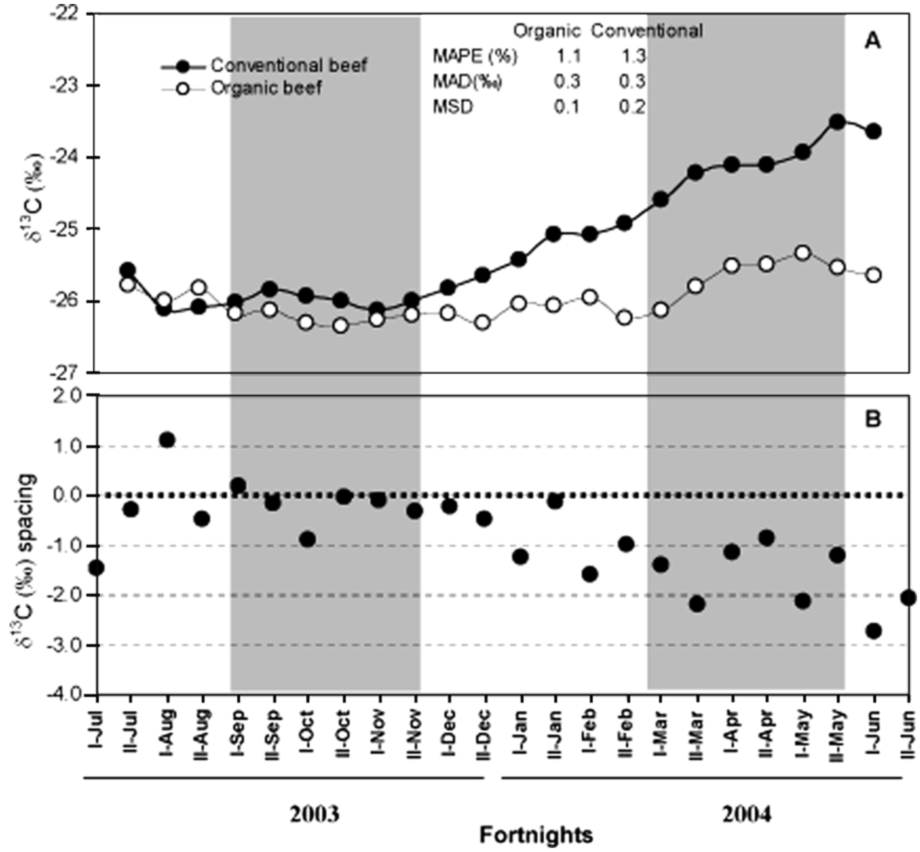

Fig. 1. Time series moving average plots of $\delta^{13}C$ (A), and the $\delta^{13}C$ spacing between fortnightly means of organic and conventional Irish beef (B). MAPE = mean absolute percent error, MAD = mean absolute deviation, MSD = mean square deviation. First (I) and second (II) fortnights of the months and seasons are shown. Seasons are defined as follows – Autumn: September–November; winter: December–February; spring: March–May; summer: June–August (includes data from July to August 2003 and June 2004).

Isotope ratios are expressed in delta notation (δ per mille, ‰) according to the formula:

$$\delta\ (‰) = [(R_{\text{sample}}/R_{\text{reference}}) - 1] \times 10^3$$

where R is the ratio of the heavy to light stable isotope in the sample (R_{sample}) and the standard ($R_{\text{reference}}$). Results are referenced to Vienna Pee Dee Belimnite (V-PDB) for $\delta^{13}C$, air–N_2 for $\delta^{15}N$ and Vienna Canyon Diablo Troilite (V-CDT) for $\delta^{34}S$.

As a quality check, samples with $\delta^{13}C$ and $\delta^{15}N$ values lying outside two standard deviations from the overall organic or conventional mean were prepared again from the frozen muscle and reanalysed ($n = 25$). Since all repeat values were very similar to the original measurements (maximum deviation 0.3‰ for $\delta^{13}C$ and 0.6‰ for $\delta^{15}N$), average values of the two measurements were used in the dataset. One organic beef sample having a $\delta^{13}C$ value of −18.2‰ was considered an outlier and excluded (see Section 3).

2.4. Statistical analysis

Seasonal isotopic patterns in $\delta^{13}C$ and $\delta^{15}N$ data were derived by time series analysis using MINITAB Release 14.13 (Minitab Inc., State College, PA, USA). Randomness of the time series data was tested by autocorrelation analysis of fortnightly means (Box & Jenkins, 1976). Fortnightly mean $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ values were used to calculate the moving average of three adjacent time points; centred moving averages are presented in the time series plots. The accuracy of the fitted time series was expressed in terms of mean absolute percent error, expressed as a % percentage (MAPE), mean absolute deviation, expressed in delta unit, ‰ (MAD) and mean squared deviation (MSD). For all three measures, smaller values indicate a better fitting model. Fortnightly or season-wise mean $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ values of organic and conventional beef were compared by t-tests. Seasons as used here are defined in the legend of Fig. 1.

3. Results and discussion

3.1. Seasonal variation in C isotope composition

Of all samples analysed, 66% of conventional beef and 90% of organic beef had a $\delta^{13}C$ value of −25.0‰ or more negative, which supports the view that both types of beef in Ireland are produced predominantly in (C_3) grass-based production systems (Minson, Ludlow, & Troughton, 1975). This is in agreement with the common perception that most conventional beef produced in Ireland is 'traditionally reared' in grass-based production systems (Lynch, 2004; Schmidt et al., 2005b). However, one $\delta^{13}C$ value less negative than −20.0‰ observed for one organic beef sample was probably not in accordance with organic farming rules (Anon, 2002; Boner & Förstel, 2004), because this animal was fed with >50% maize-derived (C_4) feed for an extended period of time (Bahar et al., 2005). Since maize is not (yet) grown as a fodder crop on organic farms in Ireland, this sample was excluded from subsequent analysis.

Moving averages revealed a marked seasonality in $\delta^{13}C$ values for conventional beef which gradually became less negative from early December 2003 until early June 2004; the $\delta^{13}C$ of organic beef was only slightly less negative from early March to early May 2004 (Fig. 1A). The time series of fortnightly mean $\delta^{13}C$ values of conventional beef had a significant autocorrelation ($P < 0.05$), indicating that the observed time series was non-random (Box & Jenkins, 1976); this pattern was non-significant (and thus random) for $\delta^{13}C$ of organic beef.

The observed elevated $\delta^{13}C$ values probably reflect indoor winter-feeding (November–March), when animals receive concentrates and conserved forages, e.g. hay and silages (Lynch, 2004). Concentrate feeds mostly contain grains, which relatively less negative $\delta^{13}C$ values than vegetative tissues, including leaves and stems (O'Leary, 1988; Schwertl, Auerswald, Schaufele, & Schnyder, 2005). Feeding of a high proportion of concentrates during winter resulted in delayed, less negative $\delta^{13}C$ values of meat in spring and early summer because of the slow C turnover in bovine skeletal muscle (Bahar et al., unpublished data). A similar $\delta^{13}C$ seasonality has been reported in cow's milk in Germany where more positive $\delta^{13}C$ values of whole milk were observed in winter due to a high percentage of corn silage in the winter diet (Kornexl, Werner, Rossmann, & Schmidt, 1997). On the other hand, the more negative and consistent $\delta^{13}C$ values in both types of beef in the present study from July to November likely reflect feeding of grass or grass-clover pasture diets throughout the spring and summer.

The pronounced $\delta^{13}C$ seasonality in conventional beef probably reflects starker seasonal changes in the feeding regime used in conventional than in organic farms (Anon., 2002). Unlike organic farms, there is no restriction for conventional farms on the dietary inclusion of the amount or type of concentrate feedstuffs produced both on-farm and off-farm. Specifically, 11% of the conventional animals (i.e. those with $\delta^{13}C$ less negative than −23‰) had possibly received considerable amounts of C_4 feedstuffs, most likely maize grain and/or maize silage during over-wintering (Bahar et al., 2005).

Because of this seasonality, individual fortnightly mean $\delta^{13}C$ values of Irish conventional and organic beef differed most during January–June (mean difference MD = 2.7‰, SED = 0.61, $P < 0.01$), but did not differ from August to December (Fig. 1B). In a previous, preliminary study, a $\delta^{13}C$ difference of 1.5‰ between conventional and organic Irish beef sampled during mid-February to mid-April in 2002 was reported (Schmidt et al., 2005b). This agrees well with the post-winter and spring patterns observed in the present study.

Grouping the data by season (Table 2), revealed that $\delta^{13}C$ values of conventional and organic beef differed significantly during winter (MD = 0.7‰, $P < 0.01$), spring (MD = 1.4‰, $P < 0.001$) and summer (MD = 0.9‰, $P < 0.05$) but not during autumn (MD = 0.2‰); the overall means were also significantly different (MD = 0.8‰, SED = 0.16, $P < 0.001$).

In conclusion, a strong seasonality in $\delta^{13}C$ in conventional beef was observed.

3.2. Seasonal variation in N isotope composition

Autocorrelation functions were non-significant for fortnightly individual $\delta^{15}N$ value plots for either production system. In conventional beef, $\delta^{15}N$ was remarkably invariant, with an overall mean $\delta^{15}N$ value of 7.0‰ (95% CI = 0.10) throughout the year. Organic $\delta^{15}N$ was more variable (reflected by higher error estimates) and had lower values in almost all fortnights (Fig. 2A). Lower $\delta^{15}N$ values could be due to feeding of grass-clover during summer and legume concentrates during winter (Rossmann, Kornexl, Versini, Pichlmayer, & Lamprecht, 1998; Shearer & Kohl, 1986).

The $\delta^{15}N$ spacing between individual fortnightly means of organic and conventional beef revealed a maximum dif-

Table 2
Season-wise mean $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ of retail organic and conventional Irish beef

	$\delta^{13}C$			$\delta^{15}N$			$\delta^{34}S$[a]		
	Organic	Conventional	SED[b]	Organic	Conventional	SED	Organic	Conventional	SED
December–February (winter)	−26.1 (24)[c]	−25.4 (23)	0.21**	6.9 (24)	7.2 (23)	0.30	7.4 (6)	7.7 (9)	0.62
Mar–May (spring)	−25.5 (31)	−24.2 (30)	0.32***	6.2 (31)	6.9 (30)	0.25**	7.7 (13)	7.2 (18)	0.31
June–August (summer)[d]	−26.0 (33)	−25.2 (28)	0.37*	6.4 (33)	6.9 (28)	0.22*	7.6 (14)	8.0 (14)	0.47
September–November (autumn)	−26.2 (38)	−26.0 (34)	0.21	6.2 (38)	7.0 (34)	0.22***	8.4 (13)	8.3 (13)	0.64
Overall	−26.0 (126)	−25.2 (115)	0.16***	6.4 (126)	7.0 (115)	0.12***	7.8 (46)	7.8 (54)	0.26

[a] Only samples from Supermarket A were analysed for $\delta^{34}S$.
[b] Significance of difference: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.
[c] Number of samples (*n*) in parentheses.
[d] Summer includes data from July to August 2003 and June 2004.

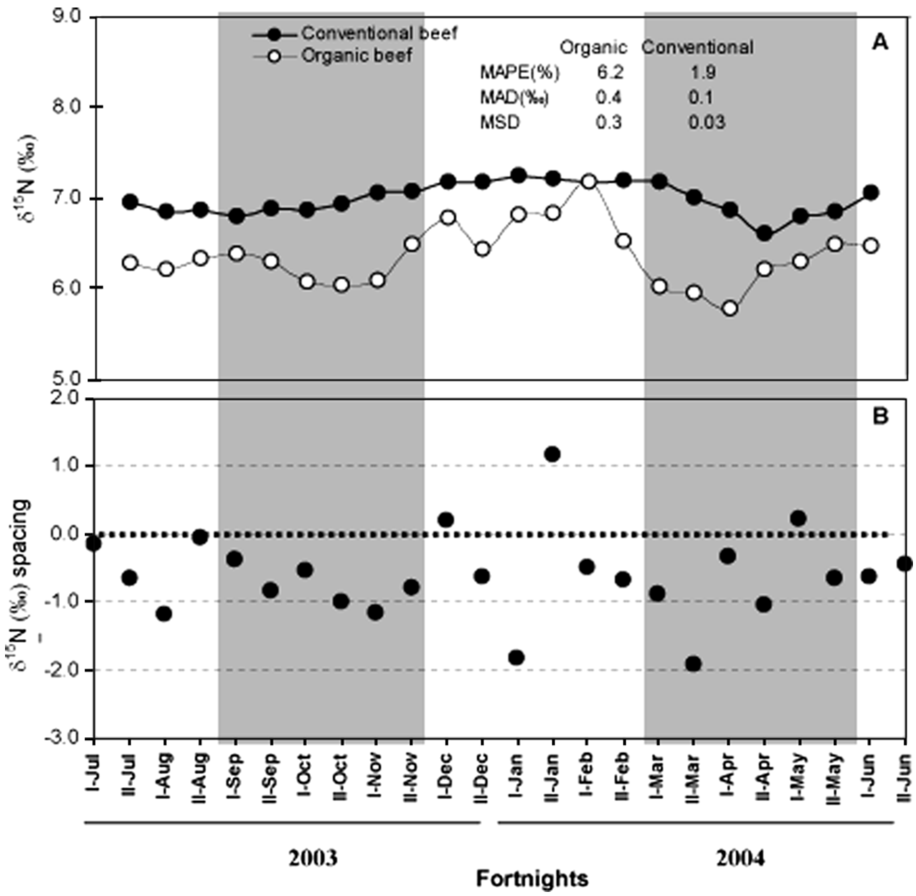

Fig. 2. Time series moving average plots of $\delta^{15}N$ (A), and the $\delta^{15}N$ spacing between fortnightly means of organic and conventional Irish beef (B). See Fig. 1 for other details.

ference of 1.9‰ (SED = 0.73, $P < 0.05$) in the second fortnight of March (Fig. 2B). In all but three fortnights, organic beef had a lower $\delta^{15}N$ value than the conventional beef. Evidence from a number of studies suggests that elevated $\delta^{15}N$ values of the conventional beef reflect a system-wide enrichment of ^{15}N in conventional farms where the use of mineral fertilizers results in highly positive N input–output balances (Schmidt et al., 2005b; Schwertl et al., 2005; Watzka, Buchgraber, & Wanek, 2006).

Grouping the $\delta^{15}N$ data by season (Table 2) showed that the $\delta^{15}N$ value of organic and conventional beef differed during spring (MD = 0.7‰, $P < 0.01$), summer (MD = 0.5‰, $P < 0.05$) and autumn (MD = 0.8‰, $P < 0.001$) but not during winter (MD = 0.3‰). Previously, the $\delta^{15}N$ values of organic and conventional Irish beef differed by 1.2‰ in samples collected from mid-February to mid-April, 2002 (Schmidt et al., 2005b).

3.3. Seasonal variation in S isotope composition

Only a subset of samples (those supplied by Supermarket A) were analysed for $\delta^{34}S$. The seasonal patterns in $\delta^{34}S$ were more complex and error estimates were higher (Fig. 3A and B) than those observed in the full $\delta^{13}C$ or $\delta^{15}N$ datasets. Between October and December, 2003 and April–June 2004, the $\delta^{34}S$ of organic beef ($n = 46$) was higher than that of conventional beef ($n = 54$) whereas, during rest of the year, it was lower. Grouping the data by season (Table 2) failed to show any difference between mean $\delta^{34}S$ values of organic and conventional beef in any of the four seasons. However, in agreement with a previous study (Schmidt et al., 2005b), during spring, the organic beef was somewhat enriched in ^{34}S compared to conventional beef.

The causes of this complex seasonality pattern of $\delta^{34}S$ in beef are unclear and explanatory background information (such as geographical origin of the samples) is lacking. Since there is little fractionation of ^{34}S in normal animal metabolism (Peterson & Fry, 1987), the seasonal patterns in muscle $\delta^{34}S$ values likely reflect (with a delay due to tissue turnover) seasonality of $\delta^{34}S$ in feedstuffs. The latter can be diverse, depending on, *inter alia*, the location (proximity to sea) and season of production (atmospheric deposition) (Krouse, Stewart, & Grinenko, 1991; Novak, Jackova, & Prechova, 2001). Coastal effects are likely in an island the size of Ireland (Richards, Fuller, Sponheimer, Robinson, & Ayliffe, 2003). Further, Schmidt et al. (2005b) speculated that elevated $\delta^{34}S$ values of organic beef could be due to feeding of seaweed having much higher $\delta^{34}S$ values than those of terrestrial feedstuffs. On the other hand,

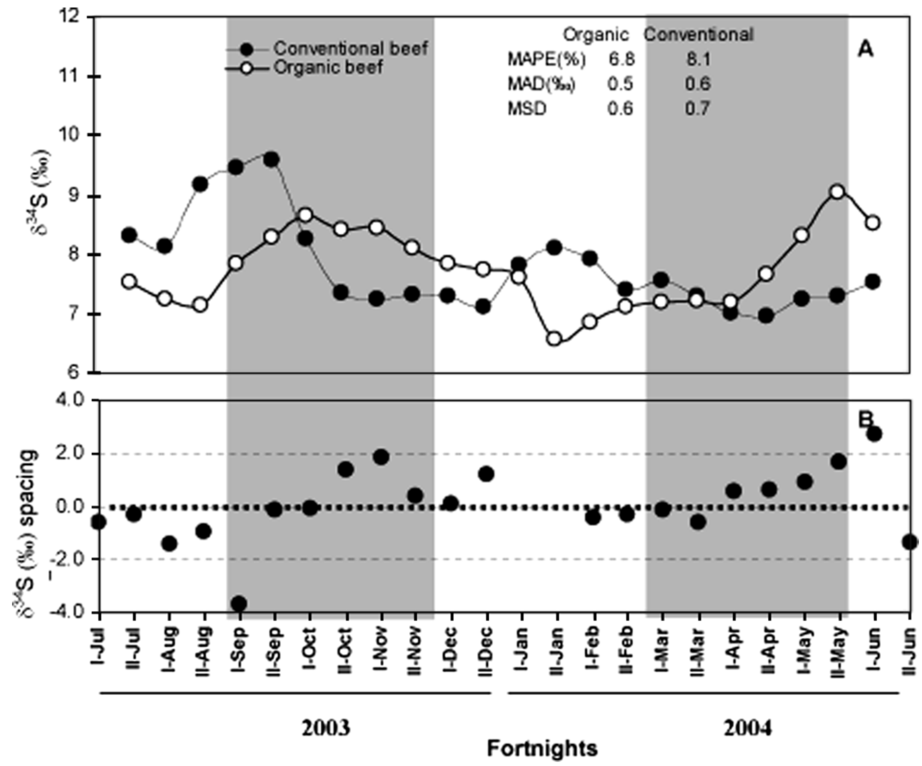

Fig. 3. Time series moving average plots of $\delta^{34}S$ (A), and the $\delta^{34}S$ spacing between fortnightly means of organic and conventional Irish beef (B). Note that only samples from supermarket A were analysed for $\delta^{34}S$ and no samples were available for January. See Fig. 1 for other details.

dietary supplements in conventional cattle rearing may include various sources of sulfates or elemental sulfur (Subcommittee on Beef Cattle Nutrition, 1996), which could influence muscle $\delta^{34}S$. Clearly, the dynamics of $\delta^{34}S$ is understood least and requires more research.

4. Implications for authentication applications

These results show that seasonal patterns in the isotopic composition of beef exist, probably reflecting seasonality in animal feeding practices modulated by tissue turnover rates. Comparing isotopic compositions without reference to this temporal dynamic may confound or fail authentication applications. For instance, while preliminary research suggested that SIRA can distinguish between organically and conventionally produced Irish beef (Schmidt et al., 2005b), the power of this method varies between seasons.

The occurrence of seasonal variation in the isotopic composition of light elements, reported here, suggests strongly that there is a need to consider possible seasonal variation (and ultimately to understand its underlying causes, including tissue turnover) when applying multi-elemental SIRA to the authentication of beef in particular and to livestock-derived products in general.

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References

Anon. (2002). *The Standards for Organic Food and Farming in Ireland*. Dublin: Demeter Ltd., IOFGA Ltd., Organic Trust Ltd., pp. 66–84.

Bahar, B., Monahan, F. J., Moloney, A. P., O'Kiely, P., Scrimgeour, C. M., & Schmidt, O. (2005). Alteration of the carbon and nitrogen stable isotope composition of beef by substitution of grass silage with maize silage. *Rapid Communications in Mass Spectrometry, 19*, 1937–1942.

Boner, M., & Förstel, H. (2004). Stable isotope variation as a tool to trace the authenticity of beef. *Analytical and Bioanalytical Chemistry, 378*, 301–310.

Bourn, D., & Prescott, J. (2002). A comparison of the nutritional value, sensory qualities, and food safety of organically and conventionally produced foods. *Critical Reviews in Food Science and Nutrition, 41*, 1–34.

Box, G. E. P., & Jenkins, G. M. (1976). The autocorrelation function and spectrum. In E. Robinson (Ed.), *Time series analysis forecasting and control* (pp. 23–44). San Francisco: Holden-Day Publications.

De Smet, S., Balcaen, A., Claeys, E., Boeckx, P., & van Cleemput, O. (2004). Stable carbon isotope analysis of different tissues of beef animals in relation to their diet. *Rapid Communication in Mass Spectrometry, 18*, 1227–1232.

Keane, T., & Sheridan, T. (2004). Climate of Ireland. In T. Keane & J. F. Collins (Eds.), *Climate, weather and Irish agriculture* (pp. 27–62). Dublin: AGMET.

Kelly, S. D. (2003). Using stable isotope ratio mass spectrometry (IRMS) in food authentication and traceability. In M. Lees (Ed.), *Food authenticity and traceability* (pp. 156–183). Cambridge: Woodhead Publishing.

Knobbe, N., Vogl, J., Pritzkow, W., Panne, U., Fry, H., Lochotzke, H. M., et al. (2006). C and N stable isotope variation in urine and milk of cattle depending on the diet. *Analytical and Bioanalytical Chemistry, 386*, 104–108.

Kornexl, B. E., Werner, T., Rossmann, A., & Schmidt, H. L. (1997). Measurement of stable isotope abundances in milk and milk ingredients – A possible tool for origin assignment and quality control. *Zeitschrift für Lebensmittel-Untersuchung und-Forschung A, 205*, 19–24.

Krouse, H. R., Stewart, J. W. B., & Grinenko, V. A. (1991). Pedosphere and biosphere. In H. R. Krouse & V. A. Grinenko (Eds.), *Stable isotopes: Natural and anthropogenic sulphur in the environment* (pp. 267–306). Chichester: John Wiley & Sons.

Lynch, P. B. (2004). Effect of the climatic environment on farm animals. In T. Keane & J. F. Collins (Eds.), *Climate, weather and Irish agriculture* (pp. 303–338). Dublin: AGMET.

Minson, D. J., Ludlow, M. M., & Troughton, J. H. (1975). Differences in natural carbon isotope ratios of milk and hair from cattle grazing tropical and temperate pastures. *Nature, 256*, 602.

Novak, M., Jackova, I., & Prechova, E. (2001). Temporal trends in the isotope signature of air-borne sulfur in Central Europe. *Environmental Science and Technology, 35*, 255–260.

O'Leary, M. H. (1988). Carbon isotopes in photosynthesis – Fractionation techniques may reveal new aspects of carbon dynamics in plants. *BioScience, 38*, 328–336.

Peterson, B. J., & Fry, B. (1987). Stable isotopes in ecosystem studies. *Annual Review of Ecology Evolution and Systematics, 18*, 293–320.

Radin, N. S. (1981). Extraction of tissue lipids with solvent of low toxicity. *Methods in Enzymology, 72*, 5–7.

Richards, M. P., Fuller, B. T., Sponheimer, M., Robinson, T., & Ayliffe, L. (2003). Sulphur isotopes in palaeodietary studies: A review and results from a controlled feeding experiment. *International Journal of Osteoarchaeology, 13*, 37–45.

Rossmann, A., Kornexl, B., Versini, G., Pichlmayer, F., & Lamprecht, G. (1998). Origin assignment of milk from alpine regions by multielement stable isotope ratio analysis (Sira). *Rivista Scientifica Alimenta, 27*, 9–21.

Schmidt, H. L., Rossmann, A., Stöckigt, D., & Christoph, N. (2005a). Herkunft und Authentizität von Lebensmitteln. *Chemie in unserer Zeit, 39*, 90–99.

Schmidt, O., Quilter, J. M., Bahar, B., Moloney, A. P., Scrimgeour, C. M., Begley, I. S., et al. (2005b). Inferring the origin and dietary history of beef from C, N and S stable isotope ratio analysis. *Food Chemistry, 91*, 545–549.

Schwertl, M., Auerswald, K., Schaufele, R., & Schnyder, H. (2005). Carbon and nitrogen stable isotope composition of cattle hair: Ecological fingerprints of production systems? *Agriculture Ecosystems and Environment, 109*, 153–165.

Scrimgeour, C. M., & Robinson, D. (2004). Stable isotope analysis and applications. In K. A. Smith & M. S. Cresser (Eds.), *Soil and environmental analysis: Modern instrumental techniques* (3rd ed., pp. 381–431). New York: Marcel Dekker.

Shearer, G., & Kohl, D. H. (1986). N_2-fixation in field settings: Estimations based on natural ^{15}N abundance. *Australian Journal of Plant Physiology, 13*, 699–756.

Subcommittee on Beef Cattle Nutrition (1996). *Nutrient requirements of beef cattle* (seventh ed.). Washington DC: National Academy Press.

Ulberth, F. (2004). Analytical approaches for food authentication. *Mitteilungen aus Lebensmitteluntersuchung und Hygiene, 95*, 561–572.

Watzka, M., Buchgraber, K., & Wanek, W. (2006). Natural ^{15}N abundance of plants and soil under different management practices in a montane grassland. *Soil Biology and Biochemistry, 38*, 1564–1576.

Woese, K., Lange, D., Boess, C., & Bogl, K. W. (1997). A comparison of organically and conventionally grown foods – Results of a review of the relevant literature. *Journal of the Science of Food and Agriculture, 74*, 281–293.