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Nitrogen Isotopes as a Screening Tool To Determine the Growing Regimen of Some Organic and Nonorganic Supermarket Produce from New Zealand

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An isotopic study was performed on nine varieties of organically and conventionally grown vegetables from an organic food market and a chain supermarket in New Zealand. The main aim of the study was to assess the applicability of stable nitrogen isotopes as a screening tool to differentiate between organic and conventional growing conditions of various vegetable types sampled directly off supermarket shelves. This could be further used as the basis of a simple authentication tool to detect noncompliant organic farming practices and false labeling of organic produce. In this study, nitrogen isotopes are found to be an excellent way of identifying faster growing organic vegetables (maturity time to harvest of <80 days), as these vegetables tend to be significantly more enriched in ^{15}N than conventionally grown vegetables and natural soil N. For slower growing organic produce (maturity time to harvest of >80 days), more information would be required to understand isotopic variations and fractionation effects between vegetables and soil over time as the technique does not discriminate organic from conventional regimens for these vegetables with as much certainty.

KEYWORDS: Nitrogen; isotope; organic; manure; fertilizer; vegetable; carbon; δ^{15}N; δ^{13}C

INTRODUCTION

The use of stable isotopes as tracers for food authentication has been well established (*1–3*); however, little research has been conducted on using stable isotopes to authenticate the growing regimen of organic produce, with most studies focused on experimental studies under laboratory conditions (*4–6*) rather than assessing the method as a direct screening tool for off-the-shelf organic produce (*7*). Adding value to food is one way by which producers can command higher prices for the same produce. The most popular and recent explosion has been in the organic produce market, which is regulated and controlled in New Zealand by three authorities, Biogrow, Demeter, and Agriquality. Foods grown under an organic regimen in New Zealand must meet strict criteria outlined by these regulatory authorities (*8–10*) excluding the use of synthetic fertilizers, chemicals (such as pesticides), and genetically modified organisms while promoting the use of natural fertilizers (such as manure or compost) in a sustainable manner.

In New Zealand specifically, much of the produce farming is performed by either market gardeners, working with heavily used soils requiring significant inputs of organic matter to sustain frequent crop growth, or larger farms with crops often grown on organic-rich soils tilled for one-time cropping, or else using “green” fertilizers such as cover crops (i.e., alfalfa, clover, rye, or peas) or silage (*11*). Where organic-rich soils are utilized, there is often no further (or minimal) requirement for additional fertilizer to sustain crops. For market gardeners, with limited organic-poor land, fertilizers are a primary consideration to ensure sustainability and profitability for the grower. However, in some cases growers are overfertilizing, leading to nitrogen (N) excesses that are not completely taken up by the plants (*12*). There also exists a possibility for any organic grower or manufacturer to fraudulently shortcut the system by boosting production with synthetic fertilizers during growth or by using noncompliant soils that have had recent synthetic fertilizer application.

Growers must therefore undergo testing and follow rigorous guidelines to obtain a certificate to produce and sell authentic organic produce. However, current chemical analytical controls performed on organic vegetables consist of searching for pesticide residues (*13*) rather than confirmation of growing regimen.

Stable nitrogen isotopes can be used to discriminate between synthetic and natural (organic) fertilizers by exploiting the isotopic differences between nitrates derived synthetically by oxidation of atmospheric nitrogen N (usually around -2 to $+2$‰) (*14, 15, 29*), N compounds released by the ammonification and transformation of organic manure to N compounds ($+2$ to $+10$‰) (*16, 17*), and those derived naturally from soil N, which lies in the region of $+2$ to $+5$‰ (*14*). Plants preferentially take up ammonium (*18*); however, most N found in the natural environment is not readily available to plants, as there are only limited ammonium pools due to nitrification processes (*14*). Most N-bearing compounds derived from organic manure are in the form of urea, which is hydrolyzed to

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ammonia. These biological conversion processes have potential for fractionation (e.g., nitrification: organic N → urea → NH_4^+ → NO_2^+ → NO_3^+) (*14*); in particular, the volatilization of ammonia gas from organic animal manure results in isotopic enrichment (^{15}N) of the remaining organic N pool (*16*).

Nitrogen isotopes are also dependent on plant type, as N-fixing plants (i.e., legumes and some grasses) assimilate atmospheric N directly, whereas non-N-fixing plants assimilate ammonium or nitrate from the soil. It has previously been noted (*16*) that assimilation and N-fixing do not alter the original isotopic signature significantly, resulting in $\delta^{15}N$ of plants which are a few per mil lower than the source of nitrogen. However, non-N-fixing plants are dependent on nitrogen sources that are easily volatilized, nitrified, and denitrified, resulting in often large differences between the $\delta^{15}N$ value of a plant and its original source.

Terrestrial plants use atmospheric CO_2 as their carbon source, which has shifted from −7 to −8.5‰ during the past century due to human activities (*19*). Most terrestrial plants fall into three main groups, which have different photosynthetic pathways. C_4 plants consist of corn, sugar cane, and warm-season grasses and convert atmospheric CO_2 into a chemical compound with four carbon atoms, and they absorb ^{13}C more quickly than they do ^{12}C, so the total biomass of C_4 plants ranges between −9 and −16‰ (*21, 22*). C_3 plants are far more abundant than C_4 plants and consist of most other plants, trees, and other woody vegetation, as well as cool-season grasses. They convert atmospheric CO_2 into a chemical compound with three carbon atoms and are slower to absorb ^{13}C than ^{12}C, so their total biomass ranges between −22 and −35‰ (*23*). The third plant group is called CAM, for Crassulacean acid metabolism, which can use either pathway for photosynthesis and have values that look like C_3 or C_4 plants (*21, 23*). These plants are usually succulents or cacti found in arid regions.

With increasing demand for organic produce in our diet, there is a need to find suitable authentication tools to rapidly distinguish if organically certified supermarket produce is indeed organically grown, and not simply labeled incorrectly (*13, 24*) or produced using inorganic fertilizers. This research investigates the use of stable isotopes as a screening tool to understand and determine the growing regimen of nine commonly obtained vegetables from an organic market and a chain supermarket in New Zealand.

MATERIALS AND METHODS

Nine different types of organic vegetables were selected from an organic grocery store and their conventionally grown counterparts from a chain supermarket selling mass-produced vegetables in Lower Hutt, New Zealand. In the selection of organic produce, labeled and certified foods were preferentially chosen. Conventionally grown (nonorganic) vegetables were sampled from bulk produce display areas in the chain supermarket. Four different types of animal manure (organic) and four different types of synthetic fertilizers (inorganic) were analyzed for their nitrogen isotope composition.

Vegetables (rinsed in distilled water and chopped into small pieces) and organic fertilizers (sampled as liquid effluent from four different farms) were frozen and freeze-dried. Subsamples of granular inorganic fertilizers were taken from commercial suppliers. Vegetables and fertilizers were ground into a fine, homogeneous powder using a mortar and pestle, and 0.5−2.0 mg of each sample was transferred into tin capsules. Carbon and nitrogen contents and isotopic composition from two composite samples of each organic and nonorganic vegetable were analyzed in triplicate at the Stable Isotope Laboratory, GNS Science, New Zealand, using a Europa Geo 20/20 (PDZ Europa Ltd. U.K.) isotope ratio mass spectrometer, interfaced to an ANCA-SL elemental analyzer (PDZ Europa Ltd. U.K.) in continuous flow mode (EA-IRMS).

Table 1. $\delta^{15}N$ Values of Some Synthetic Fertilizers and Animal Manure

fertilizer	type	mean ($n = 3$) $\delta^{15}N$ (‰) ± 0.3‰
ammonia sulfate	synthetic	−1.6
urea	synthetic	−1.7
ammonium nitrate	synthetic	−1.7
14−12−24 (P−N−K)	synthetic	−1.2
poultry	manure	+2.7
dairy	manure	+4.5
pork	manure	+11.3
pork	manure	+6.5

The carbon dioxide gas was resolved from nitrogen gas using gas chromatographic separation on a column at 65 °C and analyzed simultaneously for isotopic abundance as well as total organic carbon and nitrogen. International and working reference standards (NIST-N1, IAEA-CH_6, wheat flour, and beet sugar) and blanks were included during each run for calibration.

Isotopic ratios ($^{15}N/^{14}N$ and $^{13}C/^{12}C$) are expressed as isotopic deviations δ defined as

$$\delta\ (‰) = \frac{R_s - R_{Ref}}{R_{Ref}} \times 1000$$

where R_s is the isotopic ratio measured for the sample and R_{Ref} that of the international standards. The $\delta^{13}C$ value is relative to the international Vienna Pee Dee Belemnite (VPDB) standard, and the $\delta^{15}N$ value is relative to atmospheric air. Results are expressed in δ (‰) versus the specific reference. The analytical precision of the measurements is ±0.2‰, and reproducibility of the results is within ±0.2‰ for carbon and ±0.3‰ for nitrogen ($1\sigma n$).

Isotopic differences between corresponding organic and conventional vegetable types were determined by

$$\Delta^{15}N_{[org-nonorg]}‰ = \delta^{15}N_{organic} - \delta^{15}N_{nonorganic}$$

RESULTS AND DISCUSSION

Nitrogen isotopes of several commonly used inorganic fertilizers and animal manures are listed in **Table 1**. The synthetic fertilizers all had $\delta^{15}N$ values between −1 and −2‰, whereas animal manure had a wider range of $\delta^{15}N$ values and ranged between 2.7 and 11.3‰. Isotope results for a range of commercially available organic and conventionally (nonorganic) grown vegetables are listed in **Table 2**.

In general, produce purchased in this study from an organic market, assumed to be grown under an organic regimen, had more positive $\delta^{15}N$ values (+4.3 to +12.3‰) than the median literature values for total soil N [∼+5‰ (*25, 26*)]. Conventionally grown produce purchased from a supermarket had less positive $\delta^{15}N$ values (−1.2 to +4.5‰) than the median literature values for total soil N. The exception was peas grown under nonorganic and organic regimens, which had $\delta^{15}N$ values of 0.2 and 0.3‰, respectively. The ^{15}N differences ($\Delta^{15}N_{[org-nonorg]}$) between various organic and nonorganic vegetable types from this study are listed in **Table 2**. Faster growing vegetables (maturity time to harvest <80 days, i.e., tomatoes, peas, broccoli, cucumber, and zucchini) were compared to slower growing vegetables (maturity time to harvest >80 days, i.e., pumpkin, eggplant, potatoes, and corn). Zucchini and cucumber show the biggest isotopic difference, with $\Delta^{15}N_{[org-nonorg]}$ values of 10.2 and 9.6‰ between organic and nonorganic produce, respectively. Both of these crops are harvested at around 50 days from planting, and fast uptake of the available nitrogen compounds is assume, although plant fractionation can be variable (*31*). Tomatoes and broccoli also have slightly smaller $\Delta^{15}N_{[org-nonorg]}$ values of 8.5 and 7.9‰, respectively, between organic and

Table 2. Isotopic Values of Some Vegetables Grown under Conventional (Nonorganic) and Organic Regimens[a]

produce ($n = 3$)	days to maturity	regimen	mean δ^{15}N (‰) ± 0.3‰	mean δ^{13}C (‰) ± 0.2‰	$\Delta^{15}N_{[org-nonorg]}$ (‰)
		Faster Growing			
tomatoes	70−80	nonorganic hothouse 1[a]	−1.2	−36.3	
	70−80	nonorganic hothouse 2	−0.7	−44.9	
	70−80	organic [a]	7.3	−27.7	8.5
	70−80	low acid (organic)	6.9	−26.5	
	70−80	mini toms (nonorganic)	7.8	−28.0	
peas	55−65	nonorganic	0.2	−25.7	
	55−65	organic	0.3	−28.1	0.1
cucumber	50−60	nonorganic	2.7	−24.3	
	50−60	organic	12.3	−26.0	9.6
zucchini	50	nonorganic	2.4	−22.7	
	50	organic	10.6	−25.4	10.2
broccoli	60−80	nonorganic	4.3	−28.6	
	60−80	organic	12.2	−27.3	7.9
Slower Growing					
pumpkin	100−120	nonorganic	3.5	−24.7	
	100−120	organic	5.7	−23.8	2.2
eggplant	90−100	nonorganic	4.5	−28.0	
	90−100	organic	8.5	−26.8	4.0
potatoes	90−120	nonorganic	0.9	−24.5	
	90−120	organic	4.3	−27.0	3.4
corn	100−120	nonorganic	0.8	−10.4	
	100−120	organic	4.8	−10.9	3.0

[a] Tomatoes used to calculate $\Delta^{15}N_{[org-nonorg]}$.

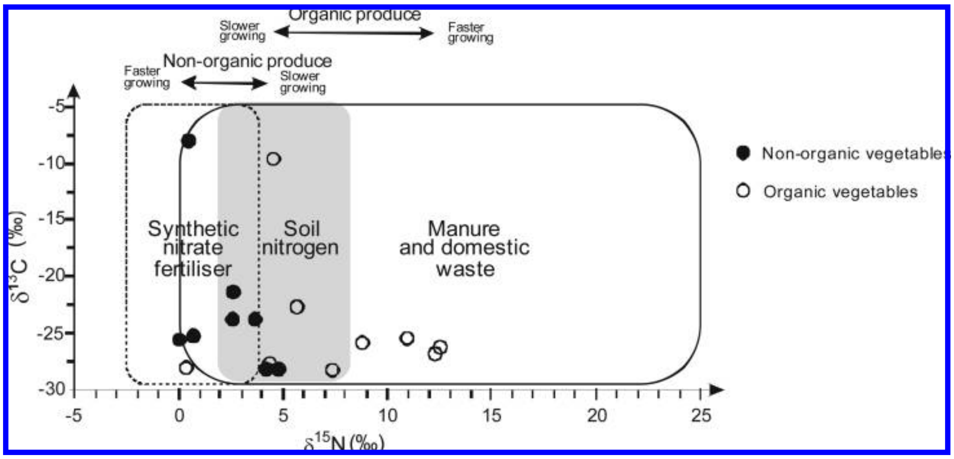

Figure 1. δ^{15}N values of nine types of vegetables grown under conventional (nonorganic) (●) and organic (○) regimens to confirm growing regimen.

nonorganic produce than zucchini and cucumber, but both have longer maturity periods of 70−80 days. Slower growing crops such as eggplant (90−100 days to harvest), corn, and pumpkin (100−120 days to harvest) have the smallest $\Delta^{15}N_{[org-nonorg]}$ values between organic and nonorganic varieties of 2.2, 3.0, and 4.0‰, respectively.

Carbon isotopes were analyzed concurrently (**Table 2**), and all produce analyzed had δ^{13}C values between −22.7 and −28.6‰, which corresponds to the range of C3 plants (literature δ^{13}C values between −22 and −32‰) (*26*) apart from corn, with δ^{13}C values between −10.4 and −10.9‰ (a C4 plant with literature δ^{13}C values between −9 and −16‰) (*26*). However, some tomatoes sourced from a chain supermarket were relatively depleted in ^{13}C, with δ^{13}C values between −36 and −45‰.

A plot of δ^{13}C versus δ^{15}N values of the vegetables (**Figure 1**) shows that apart from peas, vegetables grown under organic conditions lie predominantly in the literature soil nitrate and manure/septic waste region, with δ^{15}N values between 4.3 and 12.3‰, typical of the range of manure fertilizers found in **Table 1**. Conventionally grown vegetables in this study have more positive δ^{15}N values than the typical range of inorganic fertilizers in **Table 1**.

Fertilizers. From the two types of fertilizer analyzed (synthetic and animal manure) it is possible to discriminate between organic and inorganic fertilizers using nitrogen isotopes. Synthetic fertilizers in this study are manufactured by extracting nitrogen from air (which has an isotopic composition of around 0‰) (*27*). Animal manures in this study have more positive ^{15}N signatures than synthetic fertilizers as animals eat plants (with ^{15}N signatures that reflect the soil N), and their body waste undergoes further ^{15}N enrichment after excretion with the onset of fractionation processes such as volatilization of ammonia and denitrification or bacterial reworking of the nitrogen (*4, 14, 28*).

Soil nitrogen usually ranges from 0 to 10‰ depending on plant growth regimen such as N fixers or N assimilators and environmental variables such as climate (*14, 18, 29*). Assuming soil δ^{15}N values near 5‰ (*14*), the use of ^{15}N depleted synthetic fertilizers would lower the overall soil δ^{15}N values due to mixing of both inorganic fertilizer N and soil derived N, whereas the use of ^{15}N-enriched organic fertilizers would increase the overall soil δ^{15}N values (**Figure 2**).

Vegetables. Organic and conventionally grown vegetables in this study had δ^{15}N values that were generally more positive than δ^{15}N values to their corresponding range of fertilizers

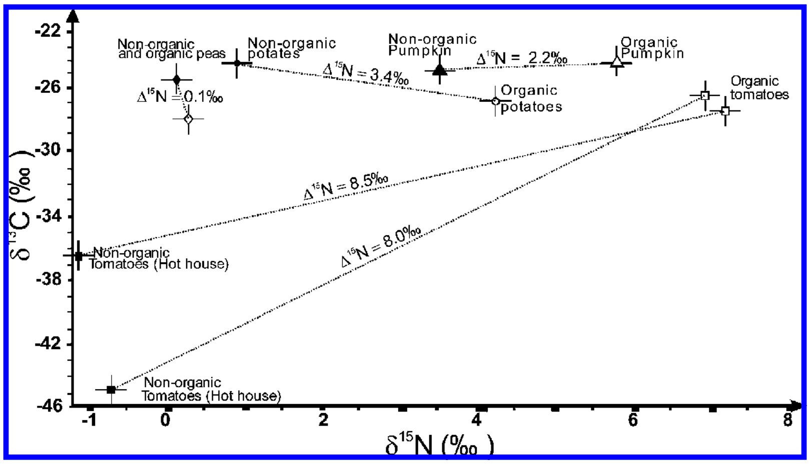

Figure 2. Plot of carbon and nitrogen isotopes from several types of vegetables showing $\Delta^{15}N_{[org-nonorg]}$ between organic and nonorganic vegetables and highlighting differences in $\delta^{13}C$ values of hothouse conditions.

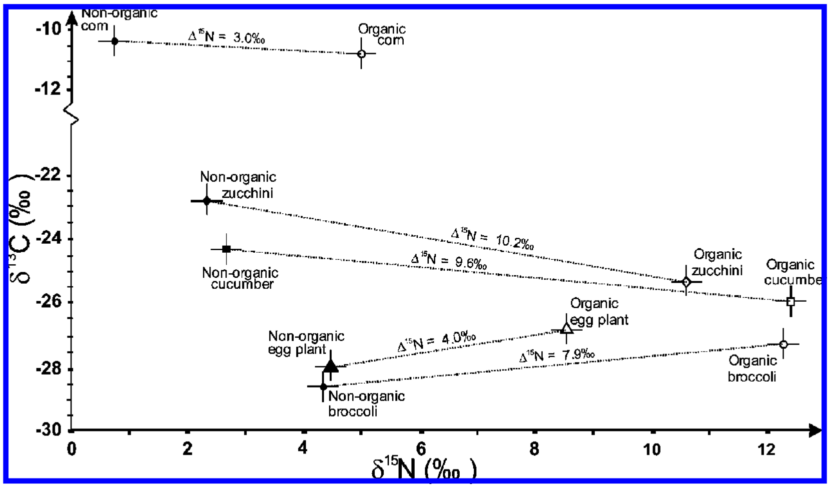

Figure 3. Plot of carbon and nitrogen isotopes from several types of vegetables showing $\Delta^{15}N_{[org-nonorg]}$ between organic and nonorganic vegetables and highlighting differences in $\delta^{13}C$ values of C_3 and C_4 plants.

analyzed in this study. Studies of plant nutrient uptake in natural N-limited systems suggest there is negligible fractionation (*18, 30*), although in higher nutrient conditions, uptake of excess ^{15}N by plants could result in a few per mil fractionation between plants and the nitrogen-rich manure (*18, 31*).

Nitrogen-Fixing Legumes. Peas grown under organic and nonorganic regimens show low $\delta^{15}N$ values near 0‰ (**Table 2**). The isotopic difference ($\Delta^{15}N_{[org-nonorg]}$) between organic and conventionally grown peas is very small, around 0.1‰ (**Figure 2**). Peas are nitrogen-fixing legumes, removing nitrogen from the air ($\delta^{15}N_{air} = 0‰$), which is fixed into the soil, rather than using nitrogen reserves from the soil. Therefore, in the case of nitrogen-fixing legumes such as peas, it is not possible to determine an organic growing regimen using nitrogen isotopes.

Faster versus Slower Growing Crops. Crops with different growth rates were investigated to determine the effects of growing time on nitrogen isotope fractionation (**Table 2**). In general, organic vegetables that are faster to mature (50−80 days to harvest) tend to have more positive $\delta^{15}N$ values and have bigger $\Delta^{15}N_{[org-nonorg]}$ values ranging between 7.9 and 10.2‰ (excluding nitrogen-fixing crops such as peas) than organic crops that are slower to mature (90−120 days to harvest) and have smaller $\Delta^{15}N_{[org-nonorg]}$ values ranging between 2.2 and 4.0‰ (**Figures 2** and **3**).

In general, plants will preferentially use ammonium, whereas soil nitrate is preferentially assimilated by tree roots relative to soil ammonium (*18*). As ammonification is the first step of urea conversion, the relative level of ammonia available for plant uptake is likely to be more abundant in overfertilized soils, and the corresponding ^{15}N signature of organic produce will reflect more positive $\delta^{15}N$ values of the added, enriched manure rather than the soil N pool. In faster growing produce, the uptake of ^{15}N-enriched organic manure and their elevated $\delta^{15}N$ values reflect the available ammonia, which will have had less time to volatilize and return to isotopic equilibrium with the soil N (which has a less positive $\delta^{15}N$ value). Therefore, more positive $\delta^{15}N$ values in faster growing organic produce (zucchini, cucumber, broccoli, and tomatoes; 6.9−12.2‰) reflect higher $\delta^{15}N$ values of the available nutrients. However, it may not always be true that more positive $\delta^{15}N$ values in organic vegetables reflect "overfertilization" with organic manure during the crop's growth and may, in fact, be related to an excess of ^{15}N-enriched ammonia previously accumulated in soils and fresh waters from past fertilizer applications. Volatilization of ^{15}N-depleted ammonia derived from manure would further enrich the residual ammonia in the soil and also suggest a higher level of organic N contribution from manure than is necessary. Therefore, whereas organic produce has more positive $\delta^{15}N$ values, it could be regarded as being less environmentally sustainable, due to the likelihood of excess N leaching into surface and ground waters.

Conventionally grown tomatoes from this study have a nitrogen isotopic value of around −0.7 to −0.9‰, indicating that they are fertilized primarily by synthetic fertilizers (*29*) and are most likely raised hydroponically, as there does not appears to be a soil nitrogen contribution typical after several weeks equilibration between inorganic fertilizer N (~ -1‰) and soil N (~ 5‰). Organic tomatoes have more positive δ^{15}N values of around 7.5‰, consistent with the use of an organic manure fertilizer. The organic tomatoes have δ^{13}C values compatible with other C_3 vegetables grown outdoors, at around −29‰. However, this study found that the two types of conventionally grown tomatoes had more negative δ^{13}C values, of around −36 and −45‰. Although the growing environment of the conventionally grown tomatoes was unknown before the study, the ^{13}C-depleted nonorganic tomatoes were most probably grown in a hothouse, heated by combusting natural gas (primarily methane; CH_4), which in New Zealand has depleted δ^{13}C values up to −48‰ (*32*). Combustion of depleted $^{13}CH_4$ converts to depleted $^{13}CO_2$,and further respiration by plants provides a unique screening tool to identify produce grown in hothouses heated by depleted natural gas.

Conventionally grown corn has δ^{15}N values of around 1‰, suggesting the use of inorganic fertilizers. Organically grown corn has a δ^{15}N value of around 4.2‰, which appears to be relatively low in comparison to other organically grown vegetables. Corn is a slow growing crop (120+ days), and it is likely any organic fertilizer applied at planting has equilibrated with the soil N. There is also a possibility that some residual inorganic nitrogen from past fertilizer applications remains in the soil, especially if the land has been recently converted to organic crops in the past few years. Alternatively, mineralization of the soil organic matter may induce nitrification and, indeed, if nitrogen fixers (commonly used in crop rotation) had previously been grown before corn, there may have been more depleted nitrogen already fixed into the soil.

Using EA-IRMS techniques, it was possible, on the limited data set presented, to discriminate between organic and conventionally grown supermarket produce using nitrogen isotopes due to the isotopic difference between synthetic and organic fertilizers. Organically grown produce had consistently more positive δ^{15}N values than its corresponding conventionally grown produce by up to 10‰, apart from nitrogen-fixing legumes such as peas.

The main conclusions of this study are as follows:

1. It is possible to use nitrogen isotopes to differentiate between organic and conventionally grown vegetables, as long as the vegetables are not nitrogen-fixing plants that removed nitrogen from the air rather than the soil.

2. Most produce grown under an organic regimen can be identified due to its more positive δ^{15}N values, typical of animal manure addition to soil organic matter. Faster growing crops, such as zucchini, tomatoes and broccoli had greater $\Delta^{15}\mathrm{N}_{[\mathrm{org-nonorg}]}$ between organic and nonorganic varieties, suggesting faster growing vegetables rapidly assimilate the nitrogen isotopic signature of their growth medium. Slower growing crops such as corn, eggplant, pumpkin, and potatoes showed smaller $\Delta^{15}\mathrm{N}_{[\mathrm{org-nonorg}]}$ between organic and conventionally grown produce. This is attributed to their longer growing period and hence the use of ^{15}N by soil microbes, which would take place in situ. Alternatively, the crop might have been grown on soil that previously had a nitrogen-fixing crop such as peas or beans, providing a more negative nitrogen source to the soil, or the crop had some additional inorganic fertilizer added before or during its growth to enhance growing conditions.

3. More positive δ^{15}N values of faster growing organic produce (cucumber, zucchini and broccoli) than the average soil N composition indicate that there is enriched ammonium available to plants or that more enriched fertilizing material is available to the plants than is naturally found in soils. Regardless, the primary cause is likely to be due to overfertilization, which is not considered to be environmentally acceptable for organic farming.

4. Hydroponically grown vegetables can be identified using isotope analysis as they directly use available added nutrients (normally inorganic fertilizers between −2 and 0‰), rather than soil N, and have δ^{15}N values closely associated with these nutrients. Vegetables grown in soils will usually have δ^{15}N values that lie between the δ^{15}N value of the applied fertilizer and the δ^{15}N value of the soil nitrogen.

5. Vegetables raised in hothouses heated by fossil fuels can be identified by carbon isotopes if they have significantly depleted δ^{13}C values (up to −45‰), which are indicative of natural gas combustion used to heat some New Zealand hothouses.

Hence, stable nitrogen and carbon isotopes can be used as a rapid, low-cost screening tool to identify the organic growing regimen of vegetables (especially those with faster growth rates of <80 days) from their conventionally grown counterparts. For slower growing organic produce (maturity time to harvest of >80 days), the technique does not discriminate the growing regimen with as much certainty and further tests would be required to understand isotopic variations and fractionation effects between plants and soil over time. The technique also appears to be useful for detecting potential overfertilization with organic manure, raising issues of sustainability in organic farming practices.

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