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From Fertilizer to Food: Tracing Nitrogen Dynamics in Conventional and Organic Farming Systems Using $^{15}$N Natural Abundance

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ABSTRACT

Synthetic nitrogen (N) fertilizers differ markedly from organic N fertilizer sources in relative isotopic composition at natural abundance levels ($\delta^{15}$N). The objective of this paper is to provide an overview of the applications of $\delta^{15}$N techniques to study the dynamics of synthetic fertilizers, animal excreta and comports in the soil-plant-atmosphere continuum. However, isotopic fractionation processes often complicate the interpretation of results. These fractionation processes and the factors affecting the $\delta^{15}$N signatures of organic N fertilizers are reviewed. Published data from short-, medium- and long-term experiments with annual crop rotations and in pastures subject to organic N inputs are also examined and analyzed with respect to changes in delta nitrogen-15 ($\delta^{15}$N) signatures of the soil, the crop or pasture, the soil biota and leachates. The use of $^{15}$N to differentiate organic and conventional plant products is briefly covered. There are few data on the dynamics of N during the storage of animal excreta or the composting of agricultural wastes as shown by $\delta^{15}$N values in the organic, inorganic or gaseous N phases. The major N loss process is ammonia (NH$_3$) volatilization. Reviewed data show significant relationships between bulk $\delta^{15}$N signatures of stored manure and cumulative NH$_3$ loss or bulk $\delta^{15}$N of livestock manure composts and N concentration. These significant relationships suggest that $\delta^{15}$N may have wider applications in estimating the efficiency of N conservation during storage or composting. In addition, the combined use of bulk $\delta^{15}$N and delta oxygen-18 ($\delta^{18}$O) signatures of nitrous oxide (N$_2$O) evolved during storage and composting, together with the isotope-derived site preference of N$_2$O, are emerging technologies for identifying N$_2$O production pathways. $\delta^{15}$N in combination with appropriate statistical analysis is a promising diagnostic tool for differentiating organic and conventional plant products.

Key words: animal excreta, compost, crop rotations, delta $^{15}$N, isotopic fractionation, pastures.

INTRODUCTION

In conventional farming systems the use of both synthetic and organic N fertilizer sources with respect to their ability to supply N for crop growth. Organic N sources must be biologically mineralized to inorganic N before they become available for plant uptake, whereas synthetic N fertilizers (ammonium and nitrate salts) are highly soluble in water and are readily available for plant uptake. Urea is the principal synthetic N fertilizer used in agriculture, and it is also quickly taken up by plants following its rapid enzymatic hydrolysis to ammonia in soil. Therefore, organic N fertilizers are often referred to as slow-release N sources, and are considered to be somewhat better synchronized with crop demand for N. However, organic fertilizers contain a mixture of both organic and mineral (NH$_4^+$ and NO$_3^-$) forms of N.

Both organic and synthetic sources are subject to several N loss processes which reduce their effectiveness to supply N for plant growth. Animal excreta must be collected and stored in intensive animal feeding operations before application to crops or pastures, and gaseous N losses (NH$_3$, N$_2$O, N$_2$, and other oxides of N (NO$_3^-$)) may occur during storage. Similar loss processes may occur during the composting of agricultural wastes. Nitrogen losses may occur following N fertilizer application to soil either via gaseous N emissions or nitrate leaching. Therefore it is important to estimate the N fertilizer use efficiency, and where possible to quantify the N loss pathways of synthetic and organic fertilizer sources during each phase of the continuum.

The use of the $^{15}$N stable isotope is a basic tool for studying the dynamics of N in farming systems (Chalk, 1997). Both naturally-occurring differences in the relative abundance of $^{15}$N in N sources, or the use of N sources artificially-enriched in $^{15}$N can be used to trace the fate of fertilizer N. The literature on the application of $^{15}$N to study N dynamics in animal excreta or compost-amended soils was reviewed by Dittert, Georges and Sattelmacher (1998) and Chalk, Magalhães and Inácio (2013), respectively. The emphasis of these reviews was on quantifying post-application N use efficiency and N transformations in soil, rather than on N transformations prior to soil application i.e. during storage or composting. The objective...
of the present paper is to provide an overview of the applications of the $^{15}$N natural abundance technique to trace N transformations that occur during pre- and post-application of animal excreta and composts. The application of $^{15}$N to differentiate organic and conventional foodstuffs is only briefly covered, as this topic was comprehensively reviewed for plant products by Inácio, Chalk and Magalhãese (2013).

### Units of $^{15}$N concentration

Stable isotopic values close to the natural abundance of the designated isotope are expressed by the notation ($\delta$) in units of parts per thousand (per mil or ‰) relative to the international standard for that element (Chalk, 1995). Since N has only two stable isotopes ($^{14}$N and $^{15}$N), then:

$$\delta^{15}\text{N} (\%) = \frac{[1^{15}\text{N}/1^{14}\text{N}]_{\text{sample}}/[1^{15}\text{N}/1^{14}\text{N}]_{\text{standard}}} - 1\right) \times 1000 \quad (1)$$

where the international standard is atmospheric N$_2$ ($\delta^{15}\text{N} = 0\%e$, by definition).

The $\delta^{15}\text{N}$ value can be either negative or positive depending whether it is depleted or enriched in $^{15}$N relative to the standard. Stable isotopic values of artificially-enriched samples are expressed as absolute abundance in units of atom %$^{15}$N (Chalk, 1995).

$$\text{Atom} \%^{15}\text{N} = \left(\text{number of} \, ^{15}\text{N} \text{atoms} / \text{total number of} \, ^{15}\text{N} + ^{14}\text{N} \text{atoms}\right) \times 100 = \left(1^{15}\text{N} / 1^{15}\text{N} + 1^{14}\text{N}\right) \times 100 \quad (2)$$

Thus as can be seen from Equation 2, it is incorrect to substitute atom %$^{15}$N for the $^{15}$N/$^{14}$N ratio in Equation 1, as is sometimes seen in the earlier literature (e.g. Selles and Karamanos, 1986), and although a close approximation will be obtained it will nevertheless be an underestimate (Chalk, 1995).

Since the absolute $^{15}$N abundance of atmospheric N$_2$ is 0.3663 ± 0.0004 atom % (Junk and Svec, 1958) then:

$$^{15}\text{N} \text{enrichment (atom} \%^{15}\text{N excess)} = \text{atom} \%^{15}\text{N} - 0.3663 \quad (3)$$

It is quite common in the literature to see atom %$^{15}$N incorrectly designated as $^{15}$N enrichment. Atom % excess values are used to trace the pathways of $^{15}$N-enriched fertilizers added to soil.

The relationship between the $^{15}$N/$^{14}$N ratio and atom %$^{15}$N is given by:

$$^{15}\text{N}/^{14}\text{N} = \text{atom} \%^{15}\text{N}/(100 - \text{atom} \%^{15}\text{N}) \quad (4)$$

For atmospheric N$_2$:

$$^{15}\text{N}/^{14}\text{N} = 0.3663/(100 - 0.3663) = 0.00367647$$

### $^{15}$N signatures of synthetic and organic fertilizers

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). A review of published data (Inácio, Chalk and Magalhãese, 2013) shows that synthetic N fertilizers have slightly positive or negative $\delta^{15}$N values within the range of –3.9 to + 5.9‰.

Organic N fertilizers are generally naturally enriched in the stable isotope $^{15}$N compared with synthetic N fertilizers. A review of published data (Inácio, Chalk and Magalhãese, 2013) shows that total N in manures and composts varies with $\delta^{15}$N values in the range of +2.0 to +16.7 and +4.9 to +45.2‰, respectively. Animal excreta consist of both solid (dung) and liquid (urine) components, except for poultry where there is no urinary component. Dung and urine components often show marked differences not only in the relative amounts and N concentrations, but also $\delta^{15}$N signatures.

Steele and Daniel (1978) reported that dairy and beef cattle urine was depleted in $^{15}$N relative to the animal diet while manure was enriched (Table 1). Sponheimer et al. (2003) reported similar data for llamas, with faeces enriched in $^{15}$N relative to both low- and high-protein diets, whereas urine was depleted in $^{15}$N (~2.1‰) relative to the low-protein diet, but was not significantly different from intake $^{15}$N on the high protein diet (Table 1). Mariappan et al. (2009) similarly reported swine urine depleted in $^{15}$N relative to diet and faeces (Table 1). More recently, Cheng et al. (2011) reported both positive and negative $\delta^{15}$N values for the urine of dairy cows, while manure was always positive (Table 1). Urine was invariably depleted in $^{15}$N relative to diet, while faeces were either similar to or enriched in $^{15}$N relative to diet (Cheng et al., 2011). A highly significant positive linear relationship was found between the $\delta^{15}$N values of the feed (range of +2 to +8.5‰) and faeces (range of +4 to +9‰) (Cheng et al., 2011).

Organic fertilizers contain both organic and inorganic (ammonium (NH$_4$)+ and nitrate (NO$_3$)-) forms of N. The inorganic N concentrations are generally low compared with the total N of the manure or compost, but $\delta^{15}$N values can be quite variable (Table 2). The inorganic N fraction is often enriched in $^{15}$N compared with the total N, indicating non-uniform labelling due to isotope fractionation processes. The unusually high $\delta^{15}$N values for inorganic N in cattle feedlot manure (Kim et al., 2008; Table 2) may be indicative of substantial N losses during storage.

### Table 1. $\delta^{15}$N signatures of animal diets and excreta

<table>
<thead>
<tr>
<th>Animal</th>
<th>Diet</th>
<th>$\delta^{15}$N (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jersey cow</td>
<td>Pasture</td>
<td>$+0.6$</td>
<td>–1.6</td>
</tr>
<tr>
<td>Angus steer</td>
<td>Silage</td>
<td>$+0.6$</td>
<td>$+2.1$ to $+2.5$</td>
</tr>
<tr>
<td>Llama</td>
<td>Alfalfa</td>
<td>$+0.4$</td>
<td>$+3.3$</td>
</tr>
<tr>
<td></td>
<td>Bermuda grass</td>
<td>$+5.8$</td>
<td>$+8.8$</td>
</tr>
<tr>
<td>Swine</td>
<td>Not specified</td>
<td>$+1.7 \pm 1.0$</td>
<td>$+2.4 \pm 0.9$</td>
</tr>
<tr>
<td>Dairy cow</td>
<td>Silage$^1$</td>
<td>$+1.8$ to $+8.4$</td>
<td>$+4.2$ to $+8.8$</td>
</tr>
</tbody>
</table>

$^1$ Nine individual silages were made from forage grasses (3 types), red clover, red clover mixed with corn or oats in different proportions.
**TABLE 2. Concentration and $^{15}$N natural abundance of total and inorganic forms of N in organic N fertilizers**

<table>
<thead>
<tr>
<th>Material</th>
<th>N fraction</th>
<th>N concentration (g/kg)</th>
<th>$^{15}$N (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cattle manure</td>
<td>Total</td>
<td>4.4–10.7</td>
<td>+7.9</td>
<td>Choi et al. (2006)</td>
</tr>
<tr>
<td>Cattle manure</td>
<td>NH$_4^+$</td>
<td>0.001–0.067</td>
<td>+9.9</td>
<td></td>
</tr>
<tr>
<td>Cattle manure</td>
<td>NO$_3^-$</td>
<td>0.007–0.009</td>
<td>+16.6</td>
<td></td>
</tr>
<tr>
<td>Cattle feedlot manure (sawdust bedding)</td>
<td>Total</td>
<td>9.5</td>
<td>+11.4</td>
<td>Kim et al. (2008)</td>
</tr>
<tr>
<td>Cattle feedlot manure (sawdust bedding)</td>
<td>NH$_4^+$</td>
<td>2.0</td>
<td>+39.8</td>
<td></td>
</tr>
<tr>
<td>Cattle feedlot manure (sawdust bedding)</td>
<td>NO$_3^-$</td>
<td>0.22</td>
<td>−426</td>
<td></td>
</tr>
<tr>
<td>Swine manure compost</td>
<td>Total</td>
<td>23.1 (1.2)</td>
<td>+15.3 (0.2)</td>
<td>Yun et al. (2011)</td>
</tr>
<tr>
<td>Swine manure compost</td>
<td>NH$_4^+$</td>
<td>0.33 (0.014)</td>
<td>+12.5 (1.3)</td>
<td></td>
</tr>
<tr>
<td>Swine manure compost</td>
<td>NO$_3^-$</td>
<td>0.12 (0.008)</td>
<td>+22.6 (0.1)</td>
<td></td>
</tr>
</tbody>
</table>

1 Data in parentheses are standard deviations of the mean
2 Range of values over 4 yr
3 Mean values over 4 yr
4 Data are time zero at the beginning of composting for 90 d

**TABLE 3. Discrimination factors ($\Delta$) for some N cycle processes**

<table>
<thead>
<tr>
<th>Process</th>
<th>Discrimination factor (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonification (organic N $\rightarrow$ NH$_4^+$)</td>
<td>$\approx$0</td>
</tr>
<tr>
<td>Nitrification (NH$_4^+$ $\rightarrow$ NO$_2^-$ $\rightarrow$ NO$_3^-$)</td>
<td>15–35</td>
</tr>
<tr>
<td>Ammonia volatilization (NH$_4^+$ $\rightarrow$ NH$_3$↑)</td>
<td>29</td>
</tr>
<tr>
<td>Denitrification (NO$_3^-$ $\rightarrow$ NO$_2^-$ $\rightarrow$ N$_2$O↑ $\rightarrow$ N$_2$↑)</td>
<td>0–33</td>
</tr>
<tr>
<td>N$_2$O and NO production during NH$_4^+$ oxidation</td>
<td>35–60</td>
</tr>
<tr>
<td>Biological N$_2$ fixation</td>
<td>0–2</td>
</tr>
<tr>
<td>Inorganic N assimilation by plants</td>
<td>0–20</td>
</tr>
<tr>
<td>(NH$_3$↑ $\rightarrow$ N$_2$↑)</td>
<td>0–19 (NO$_3^-$)</td>
</tr>
<tr>
<td>(NH$_4^+$)</td>
<td>9–18 (NH$_4^+$)</td>
</tr>
</tbody>
</table>

1 Values given as $\Delta$ were converted to $\Delta$ by Equation 8

**Isotopic fractionation processes affecting the $\delta^{15}$N signatures of organic N fertilizers**

**Units**

Isotopic fractionation can occur as a result of physical (e.g. diffusion), chemical (equilibria or ion exchange) or biological (enzymatic) processes. It can be expressed by the fractionation factor ($\alpha$) where $\alpha = \delta_A / \delta_B$ in an equilibrium reaction, where A is a reactant and B is a product. Isotopic fractionation can also be expressed as discrimination ($\Delta$ or $\epsilon$) in units of per mil (%).

$$\epsilon(‰) = (\delta_a - \delta_p) [1 + (\delta_B 1 000)]$$

(5)

where $\delta_a$ is substrate and $\delta_p$ is product

An approximation of the above equation is

$$\epsilon(‰) = \delta_a - \delta_p$$

(6)

The fractionation factor ($\alpha$) is approximated by:

$$\alpha = (\epsilon / 1 000) + 1$$

(7)

or

$$\epsilon = (\alpha - 1) \times 1 000$$

(8)

Thus for a fractionation factor ($\alpha$) of 1.020, $\epsilon$ of the product = $\sim$20‰ relative to the substrate (Högberg, 1997).
tation is quantitatively the most significant N loss process during storage of animal excreta, the voiding of excreta on grazed pastures and during the composting of agricultural wastes.

The first step in nitrification, the enzymatic oxidation of NH$_4^+$ to NO$_2^−$ was shown to have a large fractionation factor (1.015 to 1.036) in pure cultures of *Nitrosomonas* (Högberg, 1997). Thus a decrease in NH$_4^+$ concentration with a concomitant increase in its $\delta^{15}$N signature and the production of NO$_2^−$ relatively depleted in $\delta^{15}$N all point to active nitrification (Wragge et al., 2004). According to Högberg (1997) the second step in nitrification (NO$_2^−$ $→$ NO$_3^−$) is not normally rate-limiting and should therefore not lead to further fractionation. However, this is frequently not the case in urine patches and during the composting of animal excreta where the oxidation of nitrite is inhibited by the high pH resulting in the temporary accumulation of nitrite (e.g. Clough et al., 1998; Sasaki et al., 2006).

Denitrification can be a significant fractionation process during the storage of animal excreta and the composting of agricultural wastes. The overall process or so-called “total denitrification” (NO$_3^−$ $→$ NO$_2^−$ $→$ N$_2 O$ $→$ N$_2$) has a fractionation factor of 1.028 $→$ 1.033 (Robinson, 2001) although Högberg (1997) gives a much wider range (Table 3). Robinon (2001) also shows a large discrimination factor for NO$_2$ and NO produced during nitrification, of the same order of magnitude as for NH$_3$ volatilization (Table 3).

N$_2$O production pathways have been investigated using the dual isotope measurements of $\delta^{15}$N and $\delta^{18}$O of the N$_2$O emitted from soil (e.g. Yamulki et al., 2000). Several studies have reported that $\delta^{15}$N values of soil-emitted N$_2$O can be as low as $−56%$ and as high as $+3%$, with $\delta^{18}$O values varying between $−21%$ and $+57%$ (Yamulki et al., 2001; Bol et al., 2003). The $\delta^{15}$N values of soil-emitted N$_2$O are thus lower than the corresponding tropospheric (+18.7‰) and stratospheric (+21.3‰) values (Yamulki et al., 2001; Bol et al., 2003). Nitrous oxide produced by nitrification or denitrification in soils is depleted in $\delta^{15}$N relative to its substrate (NH$_4^+$ and NO$_3^−$, respectively), but as noted above, the fractionation is larger for nitrification-derived N$_2$O. Therefore, a shift in N$_2$O production from nitrification to denitrification increases both $\delta^{15}$N and $\delta^{18}$O values up to 20–50‰ and 10–25‰, respectively (Yamulki et al., 2001; Bol et al., 2003). However, if urine is the main source of nitrification, a shift in the $\delta^{15}$N signature (but not in the $\delta^{18}$O signature) would be expected, because the oxygen in urea [CO (NH$_2$)$_2$] would be hydrolyzed to CO$_2$ (Yamulki et al., 2001).

When N$_2$O is further reduced to N$_2$ during total denitrification, $\delta^{15}$N of N$_2$O becomes more enriched relative to the N$_2$ product. Thus simultaneous measurements of the $\delta^{15}$N signatures of emitted N$_2$O and N$_2$ permits the amount of N$_2$O $→$ N$_2$ to be calculated, and hence improves estimates of the relative contribution of nitrification and denitrification to total N$_2$O emissions from soils (Bol et al., 2003).

The intramolecular distribution of N isotopes in N$_2$O is an emerging tool for defining the relative importance of microbial sources of this greenhouse gas (Sutka et al., 2006). Since N$_2$O has two N atoms within the asymmetric molecule (central and outer N), $\delta^{15}$N is distributed across three principal isotoptopes, $^{15}$N$_2$O, $^{15}$N$^{14}$N$^{15}$O, $^{14}$N$^{15}$N$^{16}$O. A technique developed by Sutka et al. (2006) enables the individual measurement of $\delta^{15}$N$_2$O and $\delta^{14}$N$^{15}$N$^{16}$O. The difference in $\delta^{15}$N$_2$O and $\delta^{14}$N$^{15}$N$^{16}$O is the so-called site preference ($\delta^{15}$N$_2$O $→$ $\delta^{15}$N$^{14}$N$^{15}$O $→$ $\delta^{14}$N$^{15}$N$^{16}$O, where $\delta^{15}$N$^{14}$N$^{15}$O and $\delta^{15}$N$^{15}$N$^{16}$O represent the $\delta^{15}$N/$\delta^{14}$N ratios at the centre and outer N atoms, respectively). The difference in the site preference for N$_2$O from hydroxylamine oxidation ($\sim$33‰) and nitrite reduction ($\sim$0‰) found in a pure culture study (Sutka et al., 2006) can be used to differentiate the relative contributions of nitrification and denitrification to N$_2$O emissions. Yamulki et al. (2001) considered that site preference can provide a more fundamental and sensitive analysis of N$_2$O sources and production processes compared with the bulk $\delta^{15}$N analysis of N$_2$O.

**Factors affecting the $\delta^{15}$N signatures of organic N fertilizers**

**Storage of animal excreta**

Many types of storage facilities for animal excreta exist on farms worldwide. In the UK, the principal types of storage facilities for dairy, cattle and swine excreta are middens (piles or heaps with a permeable or impermeable base), slurry tanks (below or above ground) constructed of steel or concrete, and lagoons with pervious or impermeable linings (Nicholson and Brewer, 1997).

Hristov et al. (2009) and Lee et al. (2011) studied the cumulative amounts and $\delta^{15}$N signatures of NH$_3$ emitted from dairy manure during simulated storage under laboratory conditions. $\delta^{15}$N values of NH$_3$ volatilized increased quadratically ($r^2 = 0.92; ***p < 0.001$) from $−31%$ (1 d) to $−15%$ (14 d) while the $\delta^{15}$N of total N remaining in manure also increased quadratically ($r^2 = 0.96$) from $+5.6$ to $+7.2%$ (Hristov et al., 2009). A highly significant positive linear relationship was observed between cumulative NH$_3$ loss and the $\delta^{15}$N signature of the stored manure ($r^2 = 0.76; ***p < 0.001$) over the range of $\delta^{15}$N in manure of 4 to 8%. (Hristov et al., 2009).

Ammonia volatilization was most significant during the first 2–3 d of storage and 90 percent of emitted NH$_3$ came from the urine component of the faeces as a consequence of rapid urea hydrolysis (Lee et al., 2011). A sigmoidal curve ($r^2 = 0.96; ***p < 0.001$) best described the $\delta^{15}$N of volatilized NH$_3$ during incubation for 30 d (Lee et al., 2011). NH$_3$ was highly depleted in $\delta^{15}$N at the beginning of the manure storage process, and $\delta^{15}$N values of manure reached a plateau which coincided with the decline in NH$_3$ volatilization. Therefore, $\delta^{15}$N of volatilized NH$_3$ is a promising tool for estimating cumulative ammonia losses during storage of animal excreta, but further testing is required with different excreta under different and more realistic conditions of storage.

The earthen anaerobic lagoon is a common method of on-farm storage of feedlot runoff and slurries from dairy and pig barns in mid-western USA. Mariappan et al. (2009) studied the spatial and temporal concentrations and $\delta^{15}$N signatures of total N and NH$_4^+$ within 13 anaerobic lagoons of variable volumes receiving dairy (one), cattle (two) and swine (eleven) wastes. $\delta^{15}$NH$_4^+$ varied from $+2.0$ to $+59.1%$, was spatially uniform within the top 1.5 m of the lagoon, and was not statistically different from the total $\delta^{15}$N value. Based on comparisons with feed and fresh manure and urine, most $\delta^{15}$N isotopic fractionation occurred after excretion and was affected by management and environmental factors (Mariappan et al., 2009). $\delta^{15}$NH$_4^+$ enrichment increased when NH$_3$ volatilization increased with increasing seasonal temperatures, and lagoons that were frequently pumped out and refilled with fresh waste were not characterized by the high $\delta^{15}$N values normally associated with animal wastes. Wastes must mature in lagoons in order to develop high levels of $\delta^{15}$NH$_4^+$ enrichment ($> +10%$) (Mariappan et al., 2009).

**Composting of agricultural wastes**

The $\delta^{15}$N signature of corn silage increased by $+7.9%$ during aerobic-thermophilic composting (Lynch, Voroney and Warman, 2006; Table 4). Composting created a more homogeneous bulk $\delta^{15}$N signature compared with the feedstock, as seen by the lower sub-sample standard deviation (Table 4). Kim et al. (2008) similarly observed an increase in the $\delta^{15}$N signature of cattle manure composted with sawdust bedding of $+4.2%$, and of $+3.4%$ for manure composted with rice hull bedding (Table 4).
TABLE 4. Natural $\delta^{15}$N abundance in agricultural wastes and derived composts

<table>
<thead>
<tr>
<th>Residue</th>
<th>$\delta^{15}$N (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn silage</td>
<td>$+0.3 \pm 1.3$</td>
<td>Lynch, Voroney and Worman (2006)</td>
</tr>
<tr>
<td>Corn silage compost</td>
<td>$+8.2 \pm 0.4$</td>
<td></td>
</tr>
<tr>
<td>Cattle manure</td>
<td>$+7.6$</td>
<td>Kim et al. (2008)</td>
</tr>
<tr>
<td>Cattle manure + rice hull$^1$ compost</td>
<td>$+11.0$</td>
<td></td>
</tr>
<tr>
<td>Cattle manure + rice hull$^2$ compost</td>
<td>$+11.4$</td>
<td></td>
</tr>
<tr>
<td>Cattle manure + sawdust$^2$ compost</td>
<td>$+15.6$</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ $\delta^{15}$N of rice hull = $+4.9 \pm 0.1\%$

$^2$ $\delta^{15}$N of sawdust = $+1.7 \pm 0.2\%$

According to Lynch et al. (2006), the observed compost $\delta^{15}$N enrichment is attributable to a combination of fractionation mechanisms, including microbial isotope discrimination during N turnover, a shift to more complex N compounds, and fractionation during NH$_3$ volatilization, with the relative contributions being unknown. Kim et al. (2008) reasoned that NH$_3$ volatilization would be the dominant process in the early thermophilic stage of composting of cattle manure due to the fast hydrolysis of the high concentrations of urea in livestock excreta, followed by slow or insignificant increases in $\delta^{15}$N in the latter stages. This hypothesis remains to be tested.

Kim et al. (2008) observed an increase in the $\delta^{15}$N of NH$_4^+$ from $+30.2$ to $+41.7\%$ in manure + rice hull compost, and from $+39.8$ to $+45.6\%$ in the manure + sawdust compost, while the $\delta^{15}$N of NO$_3^-$ fluctuated during composting within the approximate range of $+25$ to $+45\%$. Based on both the temporal changes in the concentrations and isotopic signatures of NH$_4^+$ and NO$_3^-$, Kim et al. (2008) concluded that loss of NH$_4^+$ in the early stages of composting through NH$_3$ volatilization and nitrification, and loss of NO$_3^-$ in the latter stage (after 60 d) through denitrification were the primary reasons for the increase in $\delta^{15}$N in the composted manure.

There are presently no data available on the $\delta^{15}$N values of NH$_3$ emissions during composting. However, a weak negative linear relationship was observed between N concentrations and $\delta^{15}$N values of livestock manure composts ($r^2 = 0.16$; *p < 0.05) over the range of 10 to 35 g N/kg and $\delta^{15}$N of $+9$ to $+22\%$ (Lim et al., 2010). It would be expected that treatments designed to conserve N during composting would exert a strong influence on the $\delta^{15}$N values of volatilized NH$_3$ and hence compost N concentrations and $\delta^{15}$N values, but data are not yet available.

In contrast to the lack of data for NH$_3$ there are a few measurements on the natural $\delta^{15}$N abundance of N$_2$O formed during composting. From 0.5 to 1.6 percent of total N was emitted as N$_2$O during the composting of livestock waste in turned and static piles, respectively, with the $\delta^{15}$N signature of N$_2$O increasing markedly from $-23.1$ to $-0.2\%$ (Yoh et al., 2003). The bulk $\delta^{15}$N signature of N$_2$O produced during thermophilic composting of cow manure with orchard grass increased from $-20$ to $-15\%$ between day 14 and day 45 (Maeda et al., 2010), but then suddenly decreased at day 45 to reach $-35\%$ at day 56. The isotopomer methodology was applied to identify the sources of N$_2$O emissions. It was found that denitrification was the main source of N$_2$O following the turning of the compost pile, with a concomitant reduction in the concentrations of N$_2$O and N$_2$O$^−$. An increased value in site preference indicated that nitrification, which occurred mainly in the surface of the pile, partially contributed to N$_2$O emissions between the turnings (Maeda et al., 2010).

$\delta^{15}$N signatures of soils, crops, soil biota and leachates under organic and conventional fertilizer regimes

Soils and plants

Experiments of short- (42 to 157 d, medium- (4 to 12 yr) and long-term (30 to 91 yr) duration have been carried out either in the glasshouse or field to compare the temporal changes in the concentrations and $\delta^{15}$N signatures of total soil N and crop N uptake.

TABLE 5. N concentration and natural $\delta^{15}$N abundance of N fertilizer sources and crop N in short-term pot and field experiments with animal excreta, composts and synthetic N fertilizer

<table>
<thead>
<tr>
<th>Crop / scale / duration</th>
<th>N fertilizer source Type$^1$</th>
<th>Total N (g/kg)</th>
<th>N rate (kg/ha)</th>
<th>$\delta^{15}$N (%) Part</th>
<th>Total N (g/kg)</th>
<th>N uptake (g/plant)</th>
<th>$\delta^{15}$N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize / pot / 70 d</td>
<td>C</td>
<td>0</td>
<td>0</td>
<td>$-2.3 \pm 0.2$ Above ground</td>
<td>1.83</td>
<td>+6.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>U</td>
<td>451</td>
<td>150</td>
<td>$+13.9 \pm 0.2$</td>
<td>3.00</td>
<td>+6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SMC</td>
<td>20.6</td>
<td>150</td>
<td></td>
<td>3.44</td>
<td>+6.7</td>
<td></td>
</tr>
<tr>
<td>Chinese cabbage / pot / 42 d</td>
<td>SMC</td>
<td>25.3</td>
<td>0</td>
<td>$+16.2$ Outer leaf$^3$</td>
<td>24.3</td>
<td>+14.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>31.1</td>
<td>+22.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5$^2$</td>
<td></td>
<td>40.9</td>
<td>+24.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0$^2$</td>
<td>$+16.2$</td>
<td>48.4</td>
<td>+24.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.5$^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maize / field / 157 d</td>
<td>C</td>
<td>0</td>
<td>700</td>
<td>$-0.7 \pm 0.1$ Grain</td>
<td>16 ± 0</td>
<td>+5.8 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CD</td>
<td>24 ± 6</td>
<td>75</td>
<td>$+13.9 \pm 0.6$</td>
<td>16 ± 0</td>
<td>+8.1 ± 1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SG</td>
<td>82 ± 9</td>
<td>200</td>
<td>$+38.1 \pm 0.6$</td>
<td>15 ± 1</td>
<td>+21.2 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ C — control; U — urea; SMC — swine manure compost; AS — ammonium sulphate; CD — camelid dung; SG — seabird guano

$^2$ Unit is g/kg

$^3$ LSD ($p < 0.05$) between N rates; Total plant N = 2.1 g/kg; $\delta^{15}$N plant material = 1.0%
under animal excreta, composts and synthetic N fertilizer regimes. A range of annual crops in short-term (single season) experiments or in medium- to long-term crop rotations has been used.

**Short-term (single season) experiments**

Choi et al. (2002) found large differences in the $\delta^{15}$N signatures of urea and swine manure compost treatments applied at the same N rate in a pot experiment, which were reflected in the $\delta^{15}$N signatures of the foliage of maize at day 30. However, these differences were short-lived and converged to the initial $\delta^{15}$N value of total soil N of +6.9 ± 0.3‰ after 70 d, despite the increasing N uptake from control, to urea to compost treatments (Table 5).

Yun and Ro (2009) found a highly significant positive linear relationship between the N uptake of Chinese cabbage in a pot experiment and the N application rate of swine manure compost, which had a $\delta^{15}$N value of total N of +16.2‰. There were small differences in the N concentrations between outer (older) and inner (younger) leaves, and the N concentration increased with N rate (Table 5). However, the $\delta^{15}$N values were significantly higher for outer compared with inner leaves, which often exceeded the $\delta^{15}$N value of the total N of the applied compost (Table 5). This apparently anomalous result was due to the non-uniform $\delta^{15}$N label between the organic and inorganic components of the compost. The higher $\delta^{15}$N values of the compost NH$_4^+$ and NO$_3^-$ pools exerted a stronger influence than the total compost N.

In contrast to the previous short-term pot experiments, the $\delta^{15}$N signatures of maize application rate in a field experiment mirrored the $\delta^{15}$N signatures of the organic N inputs (Szpik et al., 2012). The grain in the ammonium sulphate treatment had a lower $\delta^{15}$N value than the control, while the grain in the dung and guano treatments had much higher $\delta^{15}$N signatures than the control (Table 5). The authors claimed that the guano had the highest $\delta^{15}$N value (+38.1 ± 0.6‰) for an organic N fertilizer reported to date (2012), but Choi et al. (2007) previously reported similar values of +40.1 ± 3.4‰ and +45.2 ± 4.1‰ for two compost samples.

**Medium-term crop rotations**

Choi et al. (2006) applied variable rates of swine manure slurry, cattle manure and urea to a soil in each of four yr (Table 6). There were no significant effects on surface soil total N or its $\delta^{15}$N natural abundance compared to the control. In contrast, Zhao, Maeda and Ozaki, (2002) found the annual addition of swine manure compost for six yr increased both total soil N and its natural $\delta^{15}$N abundance compared with the control at site 1, while at site 2 annual addition of cattle manure for 12 yr resulted in increasing soil total N and its $\delta^{15}$N signatures with increasing rates of manure (Table 6).

**Long-term crop rotations**

Total soil N did not differ between control and animal manure treatments after 91 yr (Bol et al., 2005), whereas it was significantly higher in the manure treatment compared with the control after 42 yr (Gerzabek, Haberhauer and Kirchmann, 2001), and between livestock manure compost and the control after 30 yr (Nishida et al., 2007). In addition, total N either decreased (Gerzabek, Haberhauer and Kirchmann, 2001) or remained unchanged over time in the control or synthetic N fertilizer treatments (Nishida et al., 2007), whereas it increased in manure and compost treatments (Table 7). These differences are most likely due to differences in climatic and edaphic factors as well as the intrinsic differences in the characteristics and rates of addition of the organic N sources.

The $\delta^{15}$N signatures of total N in surface soil (Table 7) did not differ significantly between control and manure treatments (Gerzabek, Haberhauer and Kirchmann, 2001) but they were higher in manure (Bol et al., 2005), compost and ammonium sulphate treatments (Nishida et al., 2007). The last crop of sugar beet (1985) also had higher $\delta^{15}$N values in the tops of the manure (+6.5‰) compared with the control (+2.0‰) treatment (Bol et al., 2005). Nishida et al. (2007) found that the $\delta^{15}$N signatures of total N in surface soil decreased in the control and ammonium sulphate treatments over time, but increased in the compost treatment (Table 7). Therefore there were no consistent trends in the relative long-term temporal changes in total soil N and the corresponding $\delta^{15}$N signatures (Table 7).

---

**TABLE 6. N concentration and natural $^{15}$N abundance of annual fertilizer amendments and total N in surface soil in medium-term field experiments (crop rotations) with animal excreta, composts and synthetic N fertilizer**

<table>
<thead>
<tr>
<th>Annual fertilizer amendment</th>
<th>Soil</th>
<th>Time (yr)</th>
<th>Total N (g/kg)</th>
<th>N rate (kg/ha)</th>
<th>$\delta^{15}$N (%)</th>
<th>Depth (cm)</th>
<th>Total N (g/kg)</th>
<th>$\delta^{15}$N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Initial Final</td>
<td>Initial Final</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>56.0</td>
<td>800</td>
<td>14.3</td>
<td>0</td>
<td>0–20</td>
<td>3.8</td>
<td>+6.62</td>
</tr>
<tr>
<td>SMC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>163</td>
<td>4.8</td>
<td>+9.42</td>
<td></td>
</tr>
<tr>
<td>CM</td>
<td>12</td>
<td>25.3</td>
<td>325</td>
<td>+19.1</td>
<td>650</td>
<td>4.9</td>
<td>+10.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.8</td>
<td>+10.42</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>2.6 – 4.64</td>
<td>58–172</td>
<td>+4.7 – + 5.6</td>
<td>0–30</td>
<td>1.6</td>
<td>+4.1</td>
<td></td>
</tr>
<tr>
<td>SMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
<td>+4.1</td>
<td>+4.4</td>
</tr>
<tr>
<td>CM</td>
<td></td>
<td>4.4 – 10.7</td>
<td>82–397</td>
<td>+6.8 – + 8.5</td>
<td>0–30</td>
<td>2.0</td>
<td>+3.9</td>
<td>+4.3</td>
</tr>
<tr>
<td>U</td>
<td></td>
<td>466</td>
<td>39–90</td>
<td>–0.6 – + 1.9</td>
<td></td>
<td>1.7</td>
<td>+3.9</td>
<td>+4.0</td>
</tr>
</tbody>
</table>

---

1 C — control; SMC — swine manure compost; CM — cattle manure; SMS — swine manure slurry; U — urea
2 All values are means of 2 or 3 replicates with a standard error within ± 0.3‰
3 Unit is g/L
4 Yr 1–3 (no slurry was applied in year 4)
and NH
+3.9 ± 0.1‰, respectively, while earthworms had
denitrification enriches
of fractionation during formation or consumption. For example,
tion and climates. Dijkstra
across a cattle manure gradient extending 100 m from a reservoir in
ɷ
(+3.8‰) than ancient forests (0.0‰) or previous pastures (+1.4‰).

Values for 2002 and 2003 samples
5 Calculated assuming the tabulated moisture content (0.703–0.811 g/g) was on a dry weight basis
6 Six samples from individual yr in the 1980s–1990s
7 Soil depth was 0–20 cm except for Nishida et al. (2007) where it was 0–15 cm
ever, Koerner et al. (1999) found that soil δ15N signatures could be
used to identify past agricultural land use where fields had reverted to
forests during the past 70–100 yr. Previous garden soils with a history of
manure inputs had significantly higher δ15N signatures on average (+3.8‰) than ancient forests (0.0‰) or previous pastures (+1.4‰).

Soil biota
Dijkstra et al. (2006a) found that on average the soil microbial bio-
mass had a consistently higher δ15N value (+9.7‰) compared with
the total soil N (+6.6‰) across a broad range of soil types, vegeta-
tion and climates. Dijkstra et al. (2006b) similarly found consistently higher δ15N values of microbial N compared with total soil δ15N across a cattle manure gradient extending 100 m from a reservoir in a semi-arid, high-desert grassland, and whereas the total N increased closer to the reservoir the δ15N value of the total N remained relatively constant (∆+10‰), while the microbial δ15N increased closer to the reservoir from ∆+14 to ∆+18‰.

Schmidt and Ostle (1999) similarly found that soil invertebrates
(earthworms) had higher δ15N signatures compared with total soil N in an experiment where cattle slurry (δ15N = +13.2 to +17.0‰) and NH4NO3 (δ15N = −2.0 to +0.5‰) were individually applied to plots for three consecutive yr. Soil total N (0–10 cm) in organic- and synthetic-fertilized plots had δ15N signatures of +5.9 ± 0.6‰ and +3.9 ± 0.1‰, respectively, while earthworms had δ15N signatures of +6.5 ± 0.2‰ and +5.2 ± 0.3‰, respectively.

Leachates
Choi, Lee and Ro (2003) highlighted the difficulties of identifying sources of NO3− contamination of groundwater using δ15N signatures, since the δ15N value is not only a function of source but also of fractionation during formation or consumption. For example, denitrification enriches 15N in nitrate, and if this process is significant it could mask predicted differences between sources such as synthetic fertilizers which are relatively more depleted in 15N compared with animal excreta and composts. In a survey of wells monitored over a 3–y period within defined agricultural management systems, Choi et al. (2007) were able to correlate the nitrate concentrations and δ15N signatures of well water with applications of compost, compost + urea fertilizer or no soil amendment.

δ15N signatures have proven to be a valuable tool in identifying
leakages of animal wastes stored and treated in anaerobic lagoons as well as from land application of the lagoon effluent by spray irrigation onto adjacent fields (Karr et al., 2001 and Karr, Showers and Jennings, 2003; Israel et al., 2005). Nitrate generated from commercial application of swine waste within a catchment was discharged to surface waters by ground water passing beneath the sprayfields and adjacent riparian buffers (Karr et al., 2001). Median values of δ15N of +15.4 ± 0.2‰ were measured in situ in the liquid total N of the waste lagoons, and in nitrate in shallow ground water beneath and adjac-
ent to sprayfields, a stream draining sprayfields and waters ups to 1.5 km downstream. Israel et al. (2005) pointed out that the study of Karr et al. (2001) was carried out on a site that had received lagoon effluent for 20 yr prior to the more stringent regulations on land application of animal waste imposed in 1993, and concluded that the riparian buffer was overwhelmed either due to the nitrate concentration in the ground water moving to the stream or to its rapid flux and shallow flow path.

Karr, Showers and Jennings (2003) further demonstrated the sensi-
tivity of δ15N monitoring where low-level export of nitrate from
confined dairy farming could be detected even when stream nitrate
concentrations were low and derived predominantly from natural soil sources.

δ15N signatures in the soil-plant-atmosphere continuum in pastures subject to organic N inputs
Long-term (32–36 yr) measurements were made of δ15N in soils
and plants inside and outside enclosures in an area subject to native ungulate grazing (Frank and Evans, 1997). Across six topographically diverse sites, δ15N of soil (0–20 cm) inside enclosures was 0.7‰ higher on average than inside enclosures, while plant N was 0.7‰ less on average under grazing. Soil δ15N of urine and dung patches were significantly higher than control areas. Frank and Evans (1997) concluded that grazing probably led to an increase in soil δ15N by promoting N losses (NH3 volatilization, etc). In a later study, Frank,
Evans and Tracy (2004) measured $\delta^{15}N$ in soil, plants and NH$_3$ volatilized from simulated ungulate urine patches. $\delta^{15}N$ of acid-trapped NH$_3$ increased from –28‰ (day 1) to –0.3‰ (day 10) from urine that originally had a $\delta^{15}N$ value of +1.2‰. The isotope data showed that shoots absorbed $^{15}$N-depleted NH$_3$ volatilized from the soil, which confirms the results obtained by Denmead et al. (1976) using chemical and micro-meteorological techniques.

The natural $^{15}$N abundance of plants and soils in medium- to long-term experimental plots (8–50 yr) maintained under different management practices were measured in a montane grassland (Watzka, Buchgraber and Wanek, 2006). Plots differed in the types of N inputs (mineral fertilizer, cattle slurry, stable manure) and rates of application (0–200 kg-N·ha$^{-1}$·y$^{-1}$). $\delta^{15}$N of topsoil and plants increased with N fertilizer rate, and the $\delta^{15}$N signatures reflected the higher values for the organic compared with the mineral inputs. N balances were calculated from N inputs (fertilizer, atmospheric deposition, biological N$_2$ fixation) and outputs in harvested material. Strong positive correlations were found between $\delta^{15}$N of topsoil and N balance (range –60 to +120 kg·N·ha$^{-1}$·y$^{-1}$). The authors concluded that the different $\delta^{15}$N signals in topsoil were due to isotopic fractionation arising from increased N losses (mineral fertilizer induced) and to both increased N losses and preservation of the $\delta^{15}$N input signal (organic fertilizers).

In another long-term experiment (20 yr), Krizan et al. (2009) measured changes in the concentration and $\delta^{15}$N values of total soil N in a lysimeter experiment where cattle slurry ($\delta^{15}$N = +8.9 ± 0.5‰) and calcium ammonium nitrate ($\delta^{15}$N = –1.0 ± 0.2‰) were applied at 0 and 480 kg-N·ha$^{-1}$·y$^{-1}$ to temperate grassland. Total N remained unchanged during the experiment and leaching losses were small. The $\delta^{15}$N of topsoil increased on average from +1.8 ± 0.4‰ to +6.0 ± 0.4‰ and that of the plants from –1.2 ± 1.3‰ to +4.8 ± 1.2‰ with increasing N fertilizer rate, with samples from slurry plots being relatively more enriched in $^{15}$N. The results suggested that part of the fertilizer $\delta^{15}$N signal was preserved in the soil, but that isotope fractionation of up to 1.5‰ added to the $\delta^{15}$N values in soils and plants, indicative of long-term inefficient N usage and past N management.

Yamulki et al. (2000) found that cattle excreta patches were an important source of atmospheric N$_2$O, with emissions significantly greater from urine than from dung. Flux patterns showed a marked diurnal variation with maxima in early morning or late afternoon, which were not in phase with soil temperature changes. $\delta^{15}$N and $\delta^{18}$O of the N$_2$O emitted from soil indicated that denitrification was the major loss pathway, and after a heavy rainfall the larger $\delta^{15}$N and $\delta^{18}$O values suggested a consumption of N$_2$O by reduction to N$_2$. In contrast, Tilsner et al. (2003) found no unequivocal evidence of the source of N$_2$O emitted in an extensively managed grassland involving an unfertilized control, a synthetic fertilizer treatment and a slurry treatment based on the $^{15}$N and $^{18}$O natural abundance data for emitted N$_2$O. They concluded that the $\delta^{15}$N values of emitted N$_2$O were not only influenced by source processes but also by the microbial reduction of N$_2$O to N$_2$ and that a minimum a flux of 3.4 mmol N$_2$O m$^{-2}$·h$^{-1}$ was required to obtain accurate isotope data.

Yamulki et al. (2001) showed that the temporal intra-molecular distribution of $\delta^{15}$N and $\delta^{18}$O in N$_2$O emitted from urine patches, together with the preferential values for N$_2$O using the isotopomer methodology, were indicative of a process shift during the measurement period. Using the same methodology, Köster et al. (2011) found a rapid shift from denitrification-derived N$_2$O to N$_2$O production via nitrification after three weeks following the exhaustion of labile C compounds originating from the addition of biogas fermentation residue to a grassland soil. On the other hand, Cardenas et al. (2007) found that the isotopomer signatures for N$_2$O in control and sheep slurry treatments (lucerne diet) indicated that denitrification was the main process responsible for N$_2$O emissions from a grassland soil. Based on the majority of the above-mentioned results, it appears that bulk $\delta^{15}$N, $\delta^{18}$O and isotopomer signatures are promising tools for separating pathways of N$_2$O production in grassland soils.

### Table 8. Range of $\delta^{15}$N values of plant products according to production system (Inácio et al., 2013)

<table>
<thead>
<tr>
<th>Production system</th>
<th>$\delta^{15}$N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional$^1$</td>
<td>–2.5 to +8.7</td>
</tr>
<tr>
<td>Organic$^2$</td>
<td>+0.3 to +14.6</td>
</tr>
</tbody>
</table>

1Synthetic and organic N fertilizers permitted  
2Synthetic N fertilizers excluded

### Differentiating conventional and organic plant products using $\delta^{15}$N

Because organic and synthetic fertilizer sources often differ markedly in $\delta^{15}$N composition, it would appear to be a promising marker to distinguish organically- and conventionally-fertilized plant products. The greater the difference between organic and synthetic fertilizer the more robust will be the differentiation. However, different crops show greater or smaller differences between $\delta^{15}$N values of organic and conventional products, and a certain degree of overlap can occur (Table 8). For example, organic tomatos showed greater differences in $\delta^{15}$N values compared with conventional production (+8.1 ± 3.2‰ vs. –0.1 ± 2.1‰, respectively), whereas differences between lettuce were smaller (+7.6 ± 4.1‰ vs. +2.9 ± 4.3‰, respectively), although still statistically significant (Bateman, Keely and Woolfe, 2007). However, $\delta^{15}$N values of organic and conventional carrots (+5.7 ± 3.5‰ vs. +4.1 ± 2.6‰) were not significantly different. Perennial crops tend to show smaller but significant differences in $\delta^{15}$N between mode of production, such as orange fruit (+7.3 to +7.9‰ for organic vs. +5.1 to +6.1‰ for conventional) (Camin et al., 2011).

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, and (v) marketing of organic products as conventional products (Inácio et al., 2013).

For animal products, $\delta^{13}$C might be the most promising marker for mode of production in temperate regions because of its relationship to diet, i.e. differences between C4 maize grain used in intensive animal feeding operations and C3 pasture grasses and legumes available under free-range conditions. However, $\delta^{13}$C seems unlikely to be useful in tropical regions for grazing animals due to abundant C4 pasture grasses, e.g. Brachiaria spp. (Inácio et al., 2013).

### CONCLUSIONS

The $^{15}$N natural abundance of animal excreta and composts is a useful tool for following the fate of organic N sources in the soil-plant-atmosphere continuum. The alternative approach of using organic fertilizers artificially-enriched in $^{15}$N is time-consuming, expensive and inefficient, with the attendant risks of non-uniform labelling and perturbation of the system under study. However, fewer studies have been conducted at the level of natural $^{15}$N abundance compared with artificially-enriched materials, and $\delta$ values have generally been
used as qualitative rather than quantitative measures of N processes at the system level.

Nevertheless, recent results showing significant positive and negative linear relationships during storage of animal excreta, between the bulk $^{15}\text{N}$ signature and cumulative NH$_3$ loss and between bulk $^{15}\text{N}$ of composts and N concentration, respectively, suggest that $^{15}\text{N}$ may have wider applications in estimating the efficiency of N conservation during storage or composting. The combined use of bulk $^{15}\text{N}$ and $^{18}\text{O}$ signatures of N$_2$O evolved during storage and composting, together with the isotopomer-derived site preference of N$_2$O, are powerful tools for identifying the processes of N$_2$O formation in order to enable formulation of mitigation strategies.

Finally, it has been demonstrated that $^{15}\text{N}$ signatures could play a role in differentiating organic and conventional plant products provided each of the two populations for each product has been adequately described by a frequency distribution that enables a statistical analysis of a sample. The potential use of stable isotopes in differentiating conventional and organic animal products remains to be addressed. In addition, a review and analysis of the post-1998 literature on animal excreta artificially enriched in $^{15}\text{N}$ needs to be undertaken to complement and extend the results obtained with $^{15}\text{N}$ natural abundance reported here.

REFERENCES


