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Nitrogen and Carbon Isotope Composition of Organic Fertilizers(1)

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ABSTRACT: Synthetic (e.g. urea) and organic fertilizers (e.g. compost) differed markedly in N isotope composition and the greater the difference between organic and synthetic fertilizer the more robust will be the differentiation of crops and vegetable grown under different farming systems. The objective of this study was to compare nitrogen and carbon isotope composition of organic fertilizers and manures available for conventional and organic farming in Brazil. Seven samples of organic fertilizer, two of organo-mineral fertilizers and two of different animal manures were analyzed for nitrogen and carbon isotope composition (δ^{15}N, δ^{13}C). Organic fertilizers and manure samples were enriched in δ^{15}N as expected. Using synthetic fertilizers as the primary material of organo-mineral fertilizer can imprint a low δ^{15}N value to the final product. Organic fertilizers, organo-mineral fertilizers and manures can have their organic feedstock differentiated using δ^{13}C. These are preliminary data of the isotopic composition of organic fertilizer in Brazil. Therefore, a wider survey of fertilizers and an experimental approach for organic- and organo-mineral fertilizer production is needed to elucidate the natural isotope variation of the array of available products.

Keywords: δ^{15}N, δ^{13}C, Natural isotope variation

INTRODUCTION

Stable isotope analysis of fertilizers has been identified as a tool for environmental studies (Vitòria et al., 2004) and for studies of nitrogen (N) dynamics in the soil-plant-atmosphere continuum (Chalk et al., 2013). Special attention has been given to the potential application of N isotope analysis in discriminating between organic and conventional plant products (Inácio et al., 2013). Synthetic (e.g. urea) and organic fertilizers (e.g. compost) differed markedly in N isotope composition (Bateman and Kelly, 2007) and the greater the difference between organic and synthetic fertilizer the more robust will be the differentiation of crops and vegetable grown under different farming systems. Plants show the nitrogen isotope composition from the N source, and degradation of plant residues causes discrimination of ^{15}N resulting in variation of isotope composition of the product i.e. soil N moieties. Carbon isotope composition of organic fertilizers and manure is a potential tool to determine the identity of the organic source material (C3 and C4 plant sources have markedly different carbon isotope composition) and to study post-application organic fertilizer degradation in soil.

The objective of this study was to compare the nitrogen and carbon isotope composition of organic fertilizers and manures available for conventional and organic farming in Brazil.

METHODS

Commercial organic fertilizer samples were sent by manufacturers, located in São Paulo State, to Embrapa. Three out of nine brands received were certified for organic farming and two brands were a mix of synthetic fertilizer with organic material, and most products were from a composting process (Table 1). Information was given by manufacturers. Horse manure sample were obtained from Teresópolis, in Rio de Janeiro State, and poultry litter sample from Rio Verde, in Goiás State, Brazil. These manures have been used as organic amendments by farmers. Horse bedding manure has been used by conventional vegetable growers and organic certified growers to make compost. Poultry litter is one of the most available organic amendments in Brazil, and is a source to organic fertilizer manufacturing by composting or themo-physical process. Samples were dried at 60°C and homogenized and milled to a fine powder in a ball mill. Total nitrogen and total carbon of samples were determined by an elemental combustion analyzer (Perkin-Elmer CHNS/O Series II 2400). Dried samples were weighed into tin capsules, and internal laboratory reference material (TBS) and samples matched to give 40 µg N (±5%) per isotope composition analysis. The isotope ratio analysis was performed in an isotope ratio mass spectrometer (Delta Plus, Thermo/Finnigan) coupled to an elemental analyzer for carbon and nitrogen (ECS 4010, Costech Instruments) by the John Day Laboratory, Embrapa Agrobiology, located at Seropédica, RJ, Brazil. Samples were analyzed in triplicate.

Isotopic composition can be expressed as an absolute abundance (atom %) or in relative units (‰ or per mil). e.g. for N: Atom % ^{15}N = 100 [(number of ^{15}N atoms) / (number of ^{15}N + ^{14}N atoms)]. The natural abundance of ^{15}N in atmospheric N_2 (standard) is 0.3663 ± 0.0004 atom %. The ^{15}N enrichment of a sample (atom % ^{15}N excess) = sample ^{15}N abundance – ^{15}N natural abundance.

The relative isotopic composition of nitrogen is

δ^{15}N (‰) = 1000 [(^{15}N/^{14}Nsample – ^{15}N/^{14}Nstandard) / ^{15}N/^{14}Nstandard]

where the international standard is atmospheric N_2 (δ^{15}N = 0‰, by definition). The delta value can be either negative or positive depending whether it is depleted or enriched in ^{15}N relative to the standard. The same units of isotopic composition apply to carbon. i.e. atom % ^{13}C or δ^{13}C (‰). The international standard for carbon is V-PDB (Vienna PeeDee Belemnite). Internal laboratory reference material gave N = 1.96%; δ^{15}N = +4.5‰; C = 39.73%; δ^{13}C = -24.99‰.

RESULTS AND DISCUSSION

Results of N and C total content and δ^{15}N and δ^{13}C values of samples analyzed are reported in Table 1. Total N contents of manufactured organic fertilizers were low (<3%) as expected, and only organo-mineral fertilizers which have ammonium sulfate in the mixture show higher N content (>3%). Poultry manures show the N content as high as organo-mineral fertilizers. Total carbon content shows a wide range between the samples. However, carbon content below or near 10% was shown by products with rock powder as a component of the mixture. As expected, the highest carbon content (>30%) was shown by manures. C:N ratio around 20 or less is expected for organic fertilizer, however, one sample shows a high C:N ratio (45) which is undesirable for organic fertilizers.

Delta nitrogen-15 (δ^{15}N) values of the samples show natural enrichment (positive values) of the organic fertilizers and manures, except the one organo-mineral fertilizer (Table 1). This natural enrichment may be attributed to two main factors: (i) N loss during organic material storage, mainly manures which are susceptible to ammonia volatilization, (ii) N loss during the composting process, mainly as ammonia (Chalk et al., 2013). Ammonia volatilization has a high discrimination factor of ^{15}N in the N cycle (Robinson, 2001); therefore, ammonia volatilized, e.g. from stored manure, is depleted in ^{15}N (Lee et al., 2011). There is a highly significant positive linear relationship between cumulative ammonia loss and the δ^{15}N value of stored manure over the range of +4 to +8‰ (Hristov et al., 2009). Similarly, Kim et al. (2008), observed an increase in the δ^{15}N values of cattle manure composted with sawdust (from +11.4 to +15.6‰) and cattle manure composted with rice hulls (from +7.6 to +11.0‰). Kim et al. (2008) attributed the discrimination to N loss by ammonia volatilization and nitrification, in the early stage of the thermophilic phase of composting, and denitrification of nitrate in the latter stage. Bateman and Kelly (2007) reported values between +3.5 to +16.2‰ for farmyard manure, compost and chicken manure. These results were similar to ours. However, δ^{15}N values of chicken manure were lower (+4.8 to +8.4‰) than the value found for poultry litter (+14.9‰) which suggests a greater N loss. Lim et al. (2010) reported δ^{15}N values of manure in the range of +5.3 to 7.2‰ and cattle manure composts in the range of +9.3 to +20.9‰.

Bateman and Kelly (2007) also reported synthetic fertilizers (urea, ammonium salts, nitrates) δ^{15}N values in the range of –2.4 to +2.1, and extreme values of –5.9 and +6.6‰ for one urea sample and one ammonium sulfate sample, respectively. Similar ranges of δ^{15}N values (–1.7 to +3.9‰) for synthetic fertilizers used in Spain was reported by Vitòria et al. (2004). Lim et al. (2010) reported synthetic fertilizers δ^{15}N ranged from –3.8 to +0.5‰. Therefore, synthetic fertilizers have δ^{15}N slightly depleted or enriched in relation to atmospheric N_2 (δ^{15}N = 0 ‰).

The use of ammonium sulfate to increase the N content of organo-mineral fertilizer may explain the δ^{15}N = +0.3 found in sample F6 (Table 1). Bateman and Kelly (2007) reported ammonium sulfate δ^{15}N values in the range of –1.2 to 0.8‰, for example. However, although ammonium sulfate was present in sample F7, δ^{15}N was +6.3. There are three hypotheses for this contrasting result: (i) the composting process may explain the enrichment of δ^{15}N values. If the N loss was not controlled during the composting process, it would have led to an increase in the δ^{15}N of the product. The low N content of the organo-mineral + composting may constitute support this hypothesis; (ii) the δ^{15}N of the feedstock is being expressed over the synthetic fertilizer. Sample F3 also had sugarcane mill cake as feedstock and shows a close δ^{15}N (+6.8‰) to sample F7 (+6.3‰). However, the proportional content of different materials was not informed by the manufacturers; (iii) the ammonium sulfate used to compound product F7 has a high δ^{15}N, being not the same straight fertilizer present in sample F6. Although, the first hypothesis seems more likely than others, it would be necessary to know the δ^{15}N values of all singles components of organic- and organo-mineral fertilizer and their mixtures to draw a conclusion.

Delta nitrogen-15 values of organic- and organo-mineral fertilizers and manures also show an overlapping between fertilizer certified or permitted and organic fertilizer not permitted by organic farming standards. Besides organo-mineral sample F6 the two bio-solids (F10 and F11) show δ^{15}N values within the range found for organic fertilizers and manures. However, the use of bio-solids is not allowed by organic farming standards as well as synthetic fertilizers.

Organic fertilizers and manures can have specific carbon isotope compositions (δ^{13}C) depending on the origin of the feedstock or the animal diet e.g. δ^{13}C around –12.0‰ and –26.0‰ for crop residues having the C4 and C3 photosynthetic pathways, respectively. Our data show that it is possible to distinguish the use of C4 feedstock such as sugarcane residues to manufacturing the organic- or organo-mineral fertilizer. Samples of organic fertilizers which contain sugarcane residues showed δ^{13}C ranging from –13.6 to –14.5‰. Poultry litter also shows a δ^{13}C value (–15.5‰) which suggests that the animals were corn fed (C4 plant). and/or the presence of *Brachiaria* (C4 pasture) as bedding material. *Brachiaria* is a widespread C4 pasture in Brazil. In contrast, horse bedding manure sample shows a typical C3 signature (δ^{13}C). Intermediate δ^{13}C values of organic fertilizers may be result of a mixture of C3 and C4 source materials, or even a contribution of CAM photosynthetic pathway plant material (e.g. Pineapple).

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CONCLUSIONS

The δ^{15}N values of organic fertilizers, organo-mineral fertilizers and manures measured in this study are similar to published data.

Some organic– and organo-mineral fertilizers not allowed by organic farming standards can show δ^{15}N values within a range of permitted organic fertilizers and manures.

Using synthetic fertilizer as primary material of organo-mineral fertilizers can imprint a low δ^{15}N value to the final product; however, composting can alter the δ^{15}N value of organo-mineral fertilizer by N loss.

Organic fertilizers, organo-mineral fertilizers and manures can have their organic feedstock (e.g. plant residue) differentiated using δ^{13}C value.

These are preliminary data of the isotopic composition of organic fertilizer in Brazil. Therefore, a wider survey of fertilizers and an experimental approach for organic- and organo-mineral fertilizer production is needed to elucidate the natural isotope variation of the array of available products and soil amendments.

REFERENCES

BATEMAN, A. S. & KELLY, S. D. Fertilizer nitrogen isotope signatures. Isotopes in Environmental and Health Studies, 43:237-247, 2007.

CHALK, P. M., MAGALHÃES, A. M. T. & INÁCIO, C. T. Towards an understanding of the dynamics of compost N in the soil-plant-atmosphere system using ^{15}N tracer. Plant and Soil, 362:373-388, 2013.

HRISTOV, A. N., ZAMAN, S., VANDER POL, M., NDEGWA, P., CAMPBELL, L. & SILVA, S. Nitrogen losses from dairy manure estimated through nitrogen mass balance and chemical markers. Journal of Environmental Quality, 38:2438-2448, 2009.

INÁCIO, C. T., CHALK, P. M. & MAGALHÃES, A. M. T. Principles and limitations of stable isotopes in differentiating organic and conventional foodstuffs: 1. Plant products. Critical Reviews in Food Science and Nutrition, 2013 (in press).

KIM, Y-J., CHOI, W-J., LIM, S-S., KWAK, J-H., CHANG, S.X., KIM, H-Y., YOON, K-S. & RO, H-M. Changes in nitrogen isotopic compositions during composting of cattle feedlot manure: effects of bedding material type. Bioresource Technology, 99: 5452–5458, 2008.

LEE, C., HRISTOV, A.N., CASSIDY, T. & HEYLER K. Nitrogen isotope fractionation and origin of ammonia nitrogen volatilized from cattle manure in simulated storage. Atmosphere, 2: 256–270, 2011.

LIM, S-S., LEE, S-M., LEE, S-H. & CHOI, W-J. Nitrogen isotope compositions of synthetic fertilizer, raw livestock manure slurry, and compost livestock manure. Korean Journal of Soil Science and Fertilizer, 43: 453–457, 2010.

ROBINSON, D. δ^{15}N as an integrator of the nitrogen cycle. Trends in Ecology & Evolution, 16: 153–162, 2001.

VITÒRIA, I., OTERO, N., SOLER, A. & CANALS, ÀNGELS. Fertilizer characterization: Isotopic data (N, S, O, C and Sr). Environmental Science & Technology, 38:3254-3262, 2004.

Table 1. Total nitrogen and carbon and isotopes composition of commercial organic fertilizers and livestock manures

	Fertilizer type	Feedstock	Source	N, %	C, %	δ^{15}N, ‰	δ^{13}C, ‰
F1	Organic	Not informed	Technes-Agrícola	0.6 ±0.0	27.0 ±0.7	+2.5 ±0.1	–27,8 ±0.1
F2	Organic			1.1 ±0.0	12.3 ±0.2	+5.5 ±0.4	–22,5 ±0.1
F3	Organic	Sugarcane mill cake + rock powder + composting	Nutrisafra	0.7 ±0.0	6.3 ±0.1	+7.4 ±0.0	–14,0 ±0.0
F4	Organic	Sugarcane mill cake and bagasse + ash + rock powder + composting	Nutrisafra	1.3 ±0.0	11.5 ±0.1	+6.8 ±0.0	–13,6 ±0.0
F5	Organic	Peat	Nutrisafra	1.1 ±0.1	20.9 ±0.5	+5.8 ±0.6	–17,2 ±0.2
F6	Organo-mineral	Peat + ammonium sulfate + potassium chloride	Nutrisafra	5.2 ±0.1	5.8 ±0.3	+0.3 ±0.0	–18.3 ±0.1
F7	Organo-mineral	Sugarcane mill cake + rock powder + ammonium sulfate + potassium chloride + composting	Nutrisafra	3.6 ±0.1	4.8 ±0.1	+6.3 ±0.3	–14,5 ±0.1
F8	Organic	Bio-solid	Genfertil	1.2 ±0.0	16.4 ±0.1	+11.8 ±0.5	–19.1 ±0.3
F9	Organic	Bio-solid + composting	Biossolo	2.5 ±0.1	27.7 ±0.8	+8.1 ±0.1	–25.8 ±0.4
F10	Manure	Horse bedding manure		1.8 ±0.1	44.5 ±0.7	+11.8 ±0.2	–27.5 ±0.1
F11	Manure	Poultry litter		4.2 ±0.2	31.5 ±1.1	+14.9 ±0.3	–15.5 ±0.6

Note: Total nitrogen and total carbon and δ^{15}N and δ^{13}C were determined by an Isotope Ratio Mass Spectrometer (IRMS) coupled to an elemental combustion analyzer. Data are expressed as means ± standard deviation of triplicates.