THE ISOTOPIC COMPOSITION ($\delta^{15}N$, $\delta^{13}C$) OF AGRICULTURAL WASTES AND DERIVED COMPOSTS

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ABSTRACT: The aim of this study was to measure variations in the isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) during the composting of different agricultural wastes using bench-scale bioreactors. Four different feedstocks of agricultural wastes (Horse bedding manure + legumes residues; Dairy manure + Jatropha mill cake; Dairy manure + sugarcane residues; Dairy manure) were used for aerobic-thermophilic composting. During composting no significant differences were found between the $\delta^{13}C$ values of the source material and the compost, except for Dairy manure + sugarcane residues. $\delta^{15}N$ values increased significantly in composts of Horse bedding manure + legumes residues and Dairy manure + Jatropha mill cake. $\delta^{15}N$ values of composts may be related to NH_3 volatilization during the composting process. Isotopic signatures ($\delta^{13}C$, $\delta^{15}N$) can be used to differentiate composts from different feedstock sources and $\delta^{15}N$ values may be a quantitative indicator of NH_3 volatilization during composting. Use of bench-scale bioreactors is a promising apparatus to study the dynamics of C and N and stable isotopes signatures during composting, but future adjustments regarding sampling methodology are necessary.

Keywords: composting, organic wastes, organic fertilizers, bioreactor, $\delta^{15}N$, $\delta^{13}C$

INTRODUCTION

Brazil produces enormous quantities of agricultural and agro-industrial wastes such as poultry litter and pig slurry which can be made into granulated organo-mineral fertilizer (Benites et al., 2010). These tonnages and volumes represent a valuable reservoir of plant nutrients in organic forms, particularly nitrogen (N), phosphorus (P) and sulphur (S). However, before it is possible to use such materials as fertilizers, they must be converted into a stable product free of odour and pathogens, and in a physical form suitable for application to soil. Aerobic-thermophilic composting is a proven technology that can achieve these objectives and to promote redistribution of nutrients both locally and regionally (Westerman and Bicudo, 2005).

Composts can have specific isotopic signatures ($\delta^{13}C$, $\delta^{15}N$) depending on the origin of the feedstock e.g. $\delta^{13}C$ around –12.0 ‰ and –26.0 ‰ for crop residues having the C4 and C3 photosynthetic pathways, respectively. During composting changes take place in the stable isotopic composition of organic nitrogen (^{15}N: ^{14}N) and carbon (^{13}C: ^{12}C). For example, the $\delta^{15}N$ of cattle feedlot manure increased during composting with rice hulls or sawdust by 2.3 – 2.9 ‰ in 10 days, due to N losses by ammonia (NH_3) volatilization and denitrification of nitrate (NO_3^-) to N_2O and N_2, processes which discriminate against ^{15}N in favour of the lighter ^{14}N isotope (Kim et al., 2008). Composts can be significantly enriched in ^{15}N (e.g. 17.4 ± 1.2 ‰, Choi et al., 2003) compared with manufactured fertilizers which can be depleted in ^{15}N (e.g. –1.6 ± 1.5 ‰, Choi et al., 2003). Likewise soils which have a long history of compost addition are enriched in ^{15}N compared with soils fertilized with manufactured fertilizers (Choi et al., 2003). The natural ^{15}N enrichment of composts can be used as a qualitative tracer to follow the fate of the organic N fertilizer source in the soil-plant-atmosphere system, whereas it is necessary to use composts artificially-enriched in ^{15}N to obtain quantitative estimates of fertilizer recovery by crops (Chalk et al., 2012). N losses can also be determined indirectly by ^{15}N mass balance. The aim of this study was to measure variations in isotopic composition (^{13}C and ^{15}N) during the composting of different agricultural wastes using bench-scale aerobic bioreactors.

MATERIAL AND METHODS

Measurement of isotopic composition

An isotope-ratio mass spectrometer is required for precise measurement of isotope ratios i.e. the ratio of $^{15}N/^{14}N$ or the ratio of $^{13}C/^{12}C$ in plant or soil samples (Chalk, 1995). 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 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

$$\delta^{15}N\ (‰) = 1000\ [(^{15}N/^{14}N_{sample} - {}^{15}N/^{14}N_{standard}) / {}^{15}N/^{14}N_{standard}]$$

The same units of isotopic composition apply to carbon. i.e. atom % ^{13}C or $\delta^{13}C$ (‰) (Chalk, 1995). The isotope ratio mass spectrometry analysis was performed by Embrapa Agrobiology laboratory, located at Seropédica, RJ, Brazil. Plant samples were dried at 60°C and milled to a fine powder in a ball mill.

Experimental apparatus

Twelve bench-scale cylindrical bioreactors (volume = 3L) of polypropylene were used to contain the composting process. These bioreactors have forced aeration flow control by fluxometers (1 to 10l/h) (ASA®, Italy) and a system of controlled temperature differentials (Controller Microsol® II plus, Sitrad® software, FullGauge®, Brazil). Biological activity within each vessel was monitored by a respirometric method using an in-line O_2-zirconia sensor and CO_2 infra-red sensor (SST Sensing, Scotland). Sampling of the exhaust gas was made by a multi-sampler equipped with solenoid valves. The air inlet was humidified prior to entry into the vessel and the air outlet was dried with a condenser and a silica gel filter prior to gas sensing.

Organic wastes and composting

Aerobic-thermophilic composting was carried out for 14 days in a complete randomized design with three replicates of four different mixtures of organic wastes. Table 1 shows the main characteristics of the four initial feedstocks.

RESULTS AND DISCUSSION

Some characteristics of the agricultural wastes and composts are shown in Table 1. The isotopic signatures ($\delta^{13}C$, $\delta^{15}N$) of the organic wastes are given in Table 2, while the isotopic signatures ($\delta^{13}C$, $\delta^{15}N$) of the source materials and composts are presented in Table 3.

The $\delta^{13}C$ values of agricultural wastes show two distinct groups according to C4 and C3 metabolism of the plant source i.e. sugarcane residues (C4), dairy manure (C4 tropical pasture) and *Jatropha curcas* (C3), legumes (C3) and horse bedding manure (predominant source material of C3 plant residues). $\delta^{15}N$ values differentiate alfalfa due to the influence of biological N_2 fixation (BNF). However, the same was not found for Gliricidia, probably because a low BNF input. During composting no significant differences were found between the $\delta^{13}C$ values of the initial and final materials (except for Dairy manure + sugarcane residues) which reflected the $\delta^{13}C$ values of the source materials. $\delta^{15}N$ values increased significantly in derived composts of Horse bedding manure + legume residues and Dairy manure + Jatropha mill cake mixtures. $\delta^{15}N$ values of derived composts are related to NH_3 volatilization, and therefore we can infer that N loss was greater for the above two mixtures of agricultural wastes than for Dairy manure + Sugarcane residues and Dairy manure alone. Many factors affect NH_3 volatilization during composting; inorganic-N content and biodegradable N (ammonification) of the feedstock are two relevant factors which can explain the results. Horse bedding manure had high NH_4^+/NH_3 content. Mixture of Dairy manure + Jatropha residues showed a higher temperature than Dairy manure alone during composting (data no shown) due to a much higher biodegradability. Some high standard deviations were found for parameters such total N content which limited the N mass balance calculation. For future work it will be necessary to adjust the sampling intensity from bench-scale bioreactors due to the amount of sample and material heterogeneity.

CONCLUSIONS

Isotopic signatures ($\delta^{13}C$, $\delta^{15}N$) can be used to differentiate composts from different feedstock sources and $\delta^{15}N$ values may be a quantitative indicator of NH_3 volatilization during the composting process. Use of bench-scale bioreactors is a promising apparatus for the study of C and N dynamics during composting. However, future adjustments regarding sampling protocols are necessary.

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Table 1. Some characteristics of agricultural wastes and composts derived in a bench-scale aerobic bioreactor with a controlled temperature differential.

Material	DM[a] (g)	Moist.[b] (%)	C[c] (g/kg)	N[c] (g/kg)	C/N
Horse bedding manure + Gliricidia + Alfalfa	244±11	71±0.0	403±6.0	4.2±1.5	104±34
Compost	184±22	74±0.6	183±4.7	7.2±0.4	25±0.1
Dairy manure + Jatropha mill cake	853±4.0	51±0.6	396±1.3	4.6±1.4	71±28
Compost	617±19	57±1.7	158±14	9.3±2.4	17±4.7
Dairy manure + Sugarcane bagasse and cake	409±3.0	51±0.0	397±2.8	4.1±1.9	111±42
Compost	357±12	51±0.4	133±5.8	8.6±1.4	16±2.6
Dairy manure	508±1.7	53±2.7	403±4.8	5.3±1.5	81±28
Compost	449±13	48±2.5	119±5.3	7.9±0.7	15±0.1

*Mean and standard deviation (n= 3)

[a] Initial total dry matter

[b] Sample dried at 60°C

[c] Perkin-Elmer CHN elemental analyzer

Table 2. Relative ^{15}N and ^{13}C abundance of agricultural wastes

Waste	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
Gliricidia	+6.7	–26.6
Alfalfa	+1.2	–28.3
Jatropha mill cake	+8.6	–26.6
Sugarcane bagasse	-	–12.4
mill cake	+5.3	–10.3
decanter cake	+5.4	–12.5
Dairy manure	+9.3	–14.7
Horse bedding manure	+8.6	–25.7

Table 3. Relative ^{15}N and ^{13}C abundance of agricultural wastes and derived composts

Material	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
Horse bedding manure + Gliricidia + Alfalfa	+5.9±0.1a	–27.2±0.2a
Compost	+8.2±0.5b	–27.3±0.1a
Dairy manure + Jatropha mill cake	+9.5±0.2a	–22.8±0.2a
Compost	+12.8±0.7b	–21.3±1.2a
Dairy manure + Sugarcane bagasse and cake	+8.9±0.5a	–13.6±0.2a
Compost	+9.0±0.4a	–14.4±0.2b
Dairy manure	+9.3±0.2a	–14.7±0.2a
Compost	+9.6±0.2a	–14.7±0.3a

*Means and standard deviation (n = 3). Each initial material and compost derived followed by common letter(s) are not significantly different from each other at p≤0.05 (Student's t Test).