Characterisation of the organic matter pool in manures


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Abstract

In this research, different types of animal manure were evaluated with respect to organic matter (OM), total organic carbon (Cot), total N (Nt), Cot/Nt ratio, water-soluble organic carbon (Cw), organic N (Norg), carbohydrates, Cw/Norg ratio, humic acid-like carbon (Ch), fulvic acid-like carbon (Cf), humification index ((Ch/Cot)×100) (HI) and the Ch/Cf and NH4+-N/NO3--N ratios.

In comparison with the limits set by the Spanish legislation for organic fertilisers, most of the manures had high OM contents, moderate Norg concentrations (except in the case of the chicken and pig manures where this parameter was high) and Cot/Nt ratios above the value stated in the legislation. The study of the different fractions of organic matter showed that the horse, pig and rabbit manures had the greatest content of Cot. However, the fraction of easily-biodegradable organic compounds (Cw) was significantly higher in the horse, goat and chicken manures. The study also showed that, in most cases, the percentage of fulvic acid-like C was greater than that of the humic acid-like C, indicating that the organic matter of these wastes is not completely humified. Values of HI ((Ch/Cot)×100) and Ch/Cf ratio in the studied manures were not significantly different. Regarding the parameters related to the organic matter stability such as Cw, carbohydrates and the Cot/Nt, Cw/Norg and NH4+-N/NO3--N ratios, it has been determined that the organic matter of these materials was not completely stabilised. The heterogeneity in OM composition of the studied manures did not allow the formulation of simple equations for evaluation of the composition of these wastes from easily-determined parameters.

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Keywords: Animal manure; Organic matter pools; Humic-like substances; Organic matter stability

1. Introduction

Farms generate an enormous amount of manure. During recent years, the manure production of Spain has been approximately 190×106 t year−1 (European Commission, 2001). The disposal of these wastes is one of the main environmental problems related to intensive livestock production.

A number of techniques have been utilised for both the disposal and beneficial use of manures. Some examples include land application, methane gas (biogas) production, evaporation, NH3 production, solid separation, hydrolysis, hydrogenation, composting, animal refeeding and use as a substrate in plant and microbial protein synthesis (Mikkelsen, 2000). However, the use of manures as organic fertiliser can benefit agriculture and can be, potentially, an inexpensive way for society to protect the environment and to conserve natural resources.

Manures contain high OM and Nt contents and significant amounts of other plant nutrients (Cegarra et al., 1993), favouring their use as a soil fertiliser. Eck and Stewart (1995), based on a review of the literature, stated that animal manure increased soil OM content, soil aggregate stability, water-holding capacity, water infiltration and hydraulic conductivity and decreased bulk density and evaporation rate. However, the nature, stability and dynamics of this type of residue are very heterogeneous, especially regarding the organic pool. Bernal et al. (1998b) found that the degradation of raw animal manure in the soil led to a higher CO2 production than that of composted animal manure, which could cause anaerobic and reducing conditions in the soil, due to the decreased O2 level. Also, intermediate products such as volatile fatty acids and ammonia, produced during the raw organic waste degradation, are
### Table 1
Different fractions and stability parameters of organic matter in the studied manures (dry weight basis)

<table>
<thead>
<tr>
<th>Manure</th>
<th>OM (%)</th>
<th>C&lt;sub&gt;ot&lt;/sub&gt; (%)</th>
<th>N&lt;sub&gt;org&lt;/sub&gt; (%)</th>
<th>C&lt;sub&gt;ot&lt;/sub&gt;/N&lt;sub&gt;t&lt;/sub&gt;</th>
<th>C&lt;sub&gt;w&lt;/sub&gt; (%)</th>
<th>Carbohydrates (%)</th>
<th>C&lt;sub&gt;a&lt;/sub&gt; (%)</th>
<th>C&lt;sub&gt;ha&lt;/sub&gt; (%)</th>
<th>HI (%)</th>
<th>C&lt;sub&gt;ha&lt;/sub&gt;/C&lt;sub&gt;a&lt;/sub&gt;</th>
<th>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;/NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
<th>Average values in a column followed by the same letter are not significantly different at P &lt; 0.05 (Tukey test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horse</td>
<td>69.7 c</td>
<td>41.5 b</td>
<td>1.9 a</td>
<td>20.8 b</td>
<td>2.15 b</td>
<td>0.18 ab</td>
<td>1.10 c</td>
<td>1.35 c</td>
<td>3.38 a</td>
<td>1.02 a</td>
<td>0.82 ab</td>
<td>R.Mor et al. / Bioresource Technology 96 (2005) 153–158</td>
</tr>
<tr>
<td>Cow</td>
<td>39.6 a</td>
<td>22.5 a</td>
<td>1.5 a</td>
<td>14.2 ab</td>
<td>0.78 a</td>
<td>0.10 a</td>
<td>0.47 a</td>
<td>0.93 a</td>
<td>2.85 a</td>
<td>0.98 a</td>
<td>0.32 ab</td>
<td></td>
</tr>
<tr>
<td>Pig</td>
<td>67.7 bc</td>
<td>40.7 b</td>
<td>2.1 ab</td>
<td>19.1 b</td>
<td>1.17 ab</td>
<td>0.15 ab</td>
<td>0.82 bc</td>
<td>1.33 a</td>
<td>3.80 a</td>
<td>1.10 a</td>
<td>0.48 ab</td>
<td></td>
</tr>
<tr>
<td>Sheep</td>
<td>51.3 abc</td>
<td>31.4 ab</td>
<td>1.8 a</td>
<td>17.7 ab</td>
<td>1.37 ab</td>
<td>0.14 ab</td>
<td>1.01 bc</td>
<td>1.80 ab</td>
<td>3.56 a</td>
<td>0.74 a</td>
<td>0.15 ab</td>
<td></td>
</tr>
<tr>
<td>Goat</td>
<td>54.6 abc</td>
<td>29.5 ab</td>
<td>1.9 a</td>
<td>13.2 ab</td>
<td>1.97 b</td>
<td>0.16 ab</td>
<td>0.74 a</td>
<td>0.94 a</td>
<td>1.15 a</td>
<td>0.29 a</td>
<td>0.32 ab</td>
<td></td>
</tr>
<tr>
<td>Rabbit</td>
<td>65.0 bc</td>
<td>36.5 b</td>
<td>1.7 a</td>
<td>20.4 b</td>
<td>1.24 ab</td>
<td>0.17 ab</td>
<td>1.07 ab</td>
<td>2.31 ab</td>
<td>3.56 a</td>
<td>1.20 a</td>
<td>0.69 ab</td>
<td></td>
</tr>
<tr>
<td>Chicken</td>
<td>52.5 abc</td>
<td>32.6 ab</td>
<td>2.9 b</td>
<td>11.1 a</td>
<td>2.16 b</td>
<td>0.24 b</td>
<td>0.74 a</td>
<td>0.98 a</td>
<td>1.15 a</td>
<td>0.29 a</td>
<td>0.32 ab</td>
<td></td>
</tr>
<tr>
<td>Ostrich</td>
<td>45.6 ab</td>
<td>27.8 ab</td>
<td>1.6 a</td>
<td>17.0 ab</td>
<td>1.13 ab</td>
<td>0.13 ab</td>
<td>1.07 ab</td>
<td>2.31 ab</td>
<td>3.56 a</td>
<td>1.20 a</td>
<td>0.69 ab</td>
<td></td>
</tr>
</tbody>
</table>

OM: organic matter; C<sub>ot</sub>: total organic C; N<sub>t</sub>: total N; N<sub>org</sub>: organic N; C<sub>w</sub>: water-soluble organic C; C<sub>a</sub>: fulvic acid-like C; C<sub>ha</sub>: humic acid-like C; HI: humification index.

Average values in a column followed by the same letter are not significantly different at P < 0.05 (Tukey test).

* AV: average value (n = 4).
toxic to plants. The increase of activity or amount of microbial biomass could also promote the degradation of the natural soil organic matter (Kuzyakov et al., 2000). An initial inorganic N immobilisation immediately after raw animal manure addition to soil has been found by several authors (Sørensen and Jensen, 1995; Morvan et al., 1997; Sørensen and Amato, 2002) and a rapid release of nutrients such as nitrate is then produced, increasing the contamination of subsurface water due to its leaching (Vervoort et al., 1998). On account of this, a sustainable use of animal manure for fertilising purposes must start with a complete characterisation of the aspects outlined above.

Therefore, the aims of this study were: (i) the characterisation of the different organic matter pools in animal manures; (ii) the evaluation of organic matter stability in animal manures and finally, (iii) to find relationships for the evaluation of the different OM fractions of these wastes, from easily-determined parameters.

2. Methods

Four samples of each manure (horse, cow, pig, sheep, goat, rabbit, chicken and ostrich) were collected from heaps at the margins of different farms in the south-east of Spain. For all manures, the collected samples had a storage time in the heaps of less than one month, except cow manures whose storage time ranged from one to three months. The studied manures were made up of the faeces and urine mixed with different proportions of straw, in horse, pig and rabbit manures, or straw and sawdust in cow, sheep and goat manures, although the fowl manures had only the faeces. Also, these manures did not undergo any stabilisation treatment, except the natural biodegradation process during their storage in the heaps. The samples were taken by mixing seven subsamples from seven sites of the small heaps (<2500 kg of weight), spanning the whole profile (from top to bottom of the heap) (Métodos Oficiales de Análisis en la Unión Europea, 1998). All samples were dried in a forced-air oven at 60 °C and ground to 0.5 mm for analysis. Organic matter (OM) was determined by loss on ignition at 430 °C for 24 h (Navarro et al., 1993), total organic carbon (Cot) and water-soluble organic carbon (Cw) by oxidation with K2Cr2O7 in H2SO4, according to Yeomans and Bremner (1989), and carbohydrates by the anthrone method (Brink et al., 1960). The 0.1 M Na4P2O7-extractable organic carbon (Cex) and fulvic acid-like carbon (Cfa), the latter after precipitation of the humic acid-like carbon (Cha) at pH 2.0, were measured by spectrophotometric determination of Cr3+, after oxidation with K2Cr2O7 (Sims and Haby, 1971). The Cha was calculated by subtracting the Cfa from the Cex. NH4+-N was extracted with 2 M KCl and determined colorimetrically by the phenol salt method (Honeycult et al., 1991). NO3--N was determined by second-derivative spectroscopy in a 1:30 (w/v) water extract (Sempere et al., 1993; Simal et al., 1985). Total nitrogen (Nt) and organic nitrogen (Norg) were calculated as the sum of Kjeldahl-N and NO3--N and as the difference between Nt and inorganic nitrogen (sum of NH4+-N and NO3--N), respectively.

Mean values of each parameter were tested for statistically significant differences, using the Tukey test at P < 0.05. Also, Pearson correlation was performed between the different fractions of OM of all manures and a multiple regression analysis with stepwise selection of variables was carried out in order to find simple equations to estimate the OM composition of these wastes from easily-determined parameters.

3. Results and discussion

The analyses of the manures are summarised in Table 1. The average OM content ranged from 39.6% to 69.7%, with, statistically, the horse and cow manures having highest and lowest OM concentrations, respectively. However, all manures had OM contents higher than the limit set by the Spanish legislation for organic fertiliser (30% OM) (BOE, 1998).

Regarding the different fractions of OM, the values of Cot were significantly higher in horse, pig and rabbit manures. The Norg concentration ranged from 1.5% to...
Table 3
Parameters of the multiple linear regression (stepwise method), correlation coefficient ($R$) and adjusted $R$-square ($R^2_a$) values between the different OM fractions of the studied manures ($n = 32$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>OM (%)</th>
<th>Cot (%)</th>
<th>Norg (%)</th>
<th>Cw (%)</th>
<th>Carbohydrates (%)</th>
<th>Cfa (%)</th>
<th>Cha (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model 1</td>
<td>Model 1</td>
<td>Model 1</td>
<td>Model 2</td>
<td>Model 3</td>
<td>Model 4</td>
<td>Model 1</td>
</tr>
<tr>
<td>Constant</td>
<td>3.745NS</td>
<td>0.482NS</td>
<td>0.826***</td>
<td>0.574*</td>
<td>0.370NS</td>
<td>0.026NS</td>
<td>-0.031NS</td>
</tr>
<tr>
<td>OM</td>
<td>1.585***</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Norg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cfa</td>
<td>0.343*</td>
<td>0.473**</td>
<td>0.897***</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cha</td>
<td>0.017*</td>
<td>0.001*</td>
<td>0.024***</td>
<td>0.346**</td>
<td>0.475***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>0.959</td>
<td>0.959</td>
<td>0.695</td>
<td>0.749</td>
<td>0.804</td>
<td>0.857</td>
<td>0.869</td>
</tr>
<tr>
<td>$R^2_a$</td>
<td>0.916</td>
<td>0.916</td>
<td>0.466</td>
<td>0.531</td>
<td>0.609</td>
<td>0.695</td>
<td>0.748</td>
</tr>
</tbody>
</table>

* *, **, *** Significant at $P < 0.05$, 0.01 and 0.001, respectively. NS: not significant.
For abbreviations, see Table 1.
2.9%, with only the chicken and pig manures showing values of this parameter above the limit set by the Spanish legislation for organic fertiliser (2% Norg) (BOE, 1998). The chicken manure had the lowest Cwa/Nw ratio value, due to its Norg content being the highest. Most of the manures showed a Cwa/Nw ratio greater than the range of values set by the Spanish legislation for organic fertilisers (Cwa/Nw = 3–15) (BOE, 1998). The concentration of easily-biodegradable organic compounds was significantly greater in horse, goat and chicken manures, as indicated by their higher Cwa values. The average Cfa and Cfa values were in the range 0.93–2.55% and 0.43–1.35%, respectively. In most cases, the Cfa percentage was greater than that of Cfa, indicating that the organic matter of these wastes was not completely humified. The humic-like substances content, as assessed by the humification index (HI = (Cfa/Cwa) × 100) values, and the polymerisation level of humic-like substances, calculated as Cwa/Cfa, did not differ significantly among in the studied manures.

The OM of these manures might have started its biodegradation process during the storage in heaps at the margins of the farms. Therefore, parameters related to the organic matter stability were studied. In all manures, except for chicken manure, the Cwa/Nw ratio was over 12, which is the maximum value for mature composts prepared with a wide range of organic wastes (Bernal et al., 1998a). The mean Cw, carbohydrates and Cw/Norg ratio values ranged from 0.78% to 2.16%, 0.10–0.24% and 0.47–1.10%, respectively. The cow manure had significantly lower values of these parameters and, therefore, was closer to the limits set for municipal waste composts (carbohydrates <0.1%, García et al., 1992) and composts from different organic wastes (Cw <1%, Hue and Liu, 1995; and Cw/Norg <0.55, Bernal et al., 1998a). However, only the goat manure had NH4+-N/NO3--N ratio values <0.16, the acceptable value for mature compost, as suggested by Bernal et al. (1998a).

Correlations between the different fractions of OM of the studied manures are shown in Table 2. In most cases, the correlation between the OM fractions was statistically high (P < 0.01). However, only Cw was correlated with all studied OM fractions, which means that this parameter could be the best independent variable of the equations with respect to estimation of the concentrations of the different OM fractions of the studied manures.

Table 3 shows the values for the coefficient of correlation (R), the adjusted R-square (R2a) and the parameters of the multiple linear regression equations. In most cases, the R values were high (R > 0.800), indicating a good fit of the experimental data to the proposed equations. However, only OM and Cwa could be estimated from equations with a single independent variable (model 1). The rest of the OM fractions had to be calculated using equations with at least two independent variables (models 2, 3 or 4) to predict 90% of the variation in the independent variable, as assessed by the R2 values. Therefore, only the Cwa content could be calculated from easily-determined parameters, by multiplying the concentration of OM by the slope, since the intercept (0.482) was not statistically significant (Cwa (%) = 0.580 OM (%)).

4. Conclusions

According to the results obtained, it can be concluded that all the studied manures can be used as amendments in agricultural soils, to achieve both their disposal and the improvement of soil properties, due to their very high organic matter contents. However, in most cases, the organic matter stabilisation process will start after application to soil, since only the manures which had undergone the beginning of the stabilisation process, due to their greater storage time, showed values of the parameters related to OM maturity within or close to the established limits for mature organic materials.

The great variation in the storage time of animal manures on the farms in the south-east of Spain and the heterogeneity in OM composition mean that they should be characterised fully before they are used for agricultural purposes. These findings did not allow the formulation of simple equations for the evaluation of the composition of these wastes from easily-determined parameters, since only the Cwa content could be ascertained easily, by determining the OM concentration and using the highly significant correlation observed between these two parameters.

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References


