Kinetics of added organic matter decomposition in a Mediterranean sandy soil

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Abstract

Carbon mineralization kinetics of 17 organic materials were studied in a Mediterranean sandy soil. These added organic matters (AOM) used in the organic fertilizer industry differed in their origin and composition: plant residues from the agri-food industry, animal wastes, manures (plant and animal origin), composts at different composting times and organic fertilizers. The mixtures AOM-soils were incubated under aerobic conditions at 28°C during 6 months. Soil moisture was maintained at 75% water holding capacity and respired-CO\textsubscript{2} was regularly trapped into alkali media in closed chambers, then checked by HCl titration. Analyses of CO\textsubscript{2} were performed in triplicate at 17 sampling occasions. The mineralized AOM fraction (MAOMF) varied according to the AOM origin: from 12-33% of added C for composts, to 65-90% for animal-originated AOM, with many intermediate patterns for plant-originated AOM.

Seven decomposition models from the literature were fitted to actual MAOMF: (a) three consecutive models with two 1st-order-kinetic compartments and three parameters (\textit{m}1, humification; \textit{m}2, exchange; \textit{m}3, decomposition), (b) three parallel models (\textit{m}4, with two compartments and three parameters; \textit{m}5, a three-compartment model with four parameters), and (c) \textit{m}7, a model with one 2nd-order-kinetic compartment and two parameters. Additionally, \textit{m}6, a simplified version of \textit{m}5 was proposed. Models \textit{m}2 and \textit{m}7 did not match with actual data or gave a poor fit. By the correlation parameters, the most simple model \textit{m}4 was chosen instead of the consecutive models \textit{m}1 and \textit{m}3. Residual sums of squares were always greater—but not significantly—in \textit{m}8 than in \textit{m}4, which confirmed the superiority of the models with two 1st-order compartments against 1st-order plus 0-order models for incubation times higher than 100 days. Model \textit{m}5 (most of its parameters being not correlated) gave the best predictions of our data. The proposed \textit{m}6 version gave predictions with similar precision as \textit{m}4 and appeared powerful with only two parameters (very labile and stable fractions of the AOM). A compromise between the precision of the predictions and the simplicity of the formulation allowed the recommendation of the well-known \textit{m}4 model, and above all the simpler \textit{m}6 model. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Decomposition models; Added organic matter; Organic fertilizers; Composted organic amendments; Organic carbon

1. Introduction

The utilization of organic amendments and fertilizers is increasing with the development of organic farming, and is even increasing among conventional farmers (Hartz et al., 2000). Indeed, such products are largely available due to: (a) a social need for healthy food produced under conditions that protect the environment and (b) a constant legislative pressure for recycling of organic wastes. Both manufacturers and farmers need tools for characterizing and evaluating such organic materials. Furthermore, environmental scientists need more precise parameters for modelling the decomposition of such added organic matter (AOM, Mueller et al., 1998) in soils. Up to now, many works have dealt with the carbon and/or nitrogen mineralization kinetics of crop residues (Janzen and Kucey, 1988; Mary et al., 1993; Recous et al., 1995; Kaboneka et al., 1997) and its modelling (Quemada and Cabrera, 1995; Whitmore, 1996; Gilmour et al., 1998; Hadas and Portnoy, 1997; Hartz et al., 2000), together with modelling investigations (Levi-Minzi et al., 1991; Saviozzi et al., 1993; Kirchmann and Bernal, 1997; Hadas and Portnoy, 1997; N’Dayegamiye et al., 1997; Bernal et al., 1998). Because laboratory techniques and model standardization is lacking, these studies are difficult to compare.
Table 1

Major characteristics (C, N, C-to-N ratio, total ashes) and doses of added organic matter (AOM) in g (C or N) kg⁻¹ dry soil, and in equivalent field dose in ton per hectare

<table>
<thead>
<tr>
<th>AOM origin</th>
<th>AOM</th>
<th>g kg⁻¹ AOM (dry basis)</th>
<th>g kg⁻¹ dry soil</th>
<th>t ha⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
<td>Ashes</td>
<td>C: N</td>
</tr>
<tr>
<td>Plant</td>
<td>Coffk</td>
<td>537</td>
<td>20</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Wgrap</td>
<td>529</td>
<td>27</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>Dgrap</td>
<td>469</td>
<td>22</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>Olivp</td>
<td>469</td>
<td>20</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>Kokoa</td>
<td>437</td>
<td>45</td>
<td>91</td>
</tr>
<tr>
<td>Manure</td>
<td>Shepm</td>
<td>379</td>
<td>22</td>
<td>281</td>
</tr>
<tr>
<td></td>
<td>Chicom</td>
<td>376</td>
<td>61</td>
<td>323</td>
</tr>
<tr>
<td>Animal</td>
<td>Nfeat</td>
<td>545</td>
<td>146</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Feam</td>
<td>471</td>
<td>152</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Guano</td>
<td>175</td>
<td>156</td>
<td>433</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>Gnofer</td>
<td>273</td>
<td>95</td>
<td>404</td>
</tr>
<tr>
<td></td>
<td>Comfer</td>
<td>369</td>
<td>37</td>
<td>255</td>
</tr>
<tr>
<td>Compost</td>
<td>Compo a</td>
<td>362</td>
<td>29</td>
<td>322</td>
</tr>
<tr>
<td></td>
<td>Compo b</td>
<td>363</td>
<td>25</td>
<td>344</td>
</tr>
<tr>
<td></td>
<td>Compo e</td>
<td>288</td>
<td>27</td>
<td>404</td>
</tr>
<tr>
<td></td>
<td>Compo +</td>
<td>339</td>
<td>26</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td>Compo p</td>
<td>449</td>
<td>25</td>
<td>402</td>
</tr>
</tbody>
</table>

1 AOM bulk weight, calculated on 0–20 cm layer, mean soil bulk density (<2 mm) = 1.5, refuse (>2 mm) = 5.21% and 6.68% for the 0–10 cm and 10–20 cm layers, respectively.

Protocols differ on CO₂ measurement methods, type of soil, incubation time, temperature, soil moisture, AOM amounts, decomposition of AOM alone (specific mineralization) or simultaneous addition of mineral-N (mineralization with standardized total-N content). Most of the models used for predicting CO₂-C mineralization take into account one (the whole AOM), two, or more organic compartments of the AOM (more or less resistant to microbial attack).

The first objective of this work was to test, under standard laboratory conditions, the specific carbon mineralization of a wide range of AOM in a sandy soil with low organic matter content. The second objective was to find accurate models to describe the carbon-AOM mineralization kinetics under these standard conditions, the model parameters only depending upon AOM quality.

2. Material and methods

2.1. Soil for mineralization test

The incubation test was done with the top-layer (0–20 cm) of a sandy soil (69.3% sand, 11.5% clay), previously described by Servat and Callot (1966) and classified as fluvisol (FAO-UNESCO-ISRS, 1988) or Udifluvent (USDA, 1975). It was collected in an experimental site (Thuriès et al., 2000a) located in Théza (Eastern Pyrénées, France). This soil has pH(H₂O) 6.6, CEC 5.5 cmol c⁻¹ kg⁻¹ soil, total C and N 4.98 and 0.59 g kg⁻¹ soil, respectively. It was partially air-dried at room temperature (20°C) until it could be crushed and sieved through a 2 mm sieve, then air-dried to constant weight.

2.2. Added organic matter (AOM)

Different kinds of AOM from agri-food industry wastes and industrial-processed fertilizers (organic amendments and fertilizers) were tested. Their major characteristics are shown in Table 1. The raw materials were from (a) plant origin: wet and dry grape berry pellicles cakes (Wgrap, Dgrap), coffeecake (Coffk), cocoacake (Kokoa), olivecake (Olivp), (b) animal origin: hydrolyzed feather meal (Feam), native fine feather (Nfeat), guano (Guano), (c) manure origin (plant and animal origin): sheep manure (Shepm), chicken manure (Chicom) and (d) fertilizers: organic composted amendments (Compo series), and organic fertilizers (Gnofer, Comfer). The composted organic amendments (Compo) were made from Shepm and Coffk in periodically-turned and aerated piles, during a 10-month composting period. Samples were taken before the composting process (Compo a), and at 40 (Compo b), 120 (Compo p), and 305 (Compo e) days. Compo + was a mixture of 75% Compo e and 25% Dgrap (used for drying the compost). Gnofer was a guano-based organic fertilizer, whereas Comfer was a Compo-based fertilizer supplemented with Chicm. The AOM were air-dried at 25°C, then finely ground.

2.3. Incubation experiment

Carbon mineralization was measured as respired CO₂-C in closed chambers (28°C ± 1°C, in an incubator) with the experimental design adapted by Thuriès et al. (2000b). An exact mass (125–500 mg AOM per container) was
homogeneously incorporated in 50 g air-dried soil. These experimental AOM amounts were chosen to correspond to realistic inputs in field conditions: 7 or 14 t ha\(^{-1}\) for animal products or fertilizers, 28 t ha\(^{-1}\) for composts, plant origin products and manures (Tables 1).

The AOM-C ranged from 8 to 102% of initial soil C, and the AOM-N from 26 to 93% of initial soil N. Identical added quantities of AOM-N would have led to very low inputs of C for N-rich fertilizers and unrealistic high field doses for N-poor amendments. Recous et al. (1995) and Henriksen and Breland (1999) indicated that concentrations of available N (AOM-N + soil inorganic N) less than 1.2% of AOM dry matter significantly reduced the rate of C-mineralization and growth of microbial biomass. This risk does not exist in the present experiment since AOM-N concentrations alone were greater than 2% of AOM-dry matter (Table 1). For our study of specific AOM mineralization, we did not consider any mineral N addition simultaneously with AOM addition. During decomposition, the N pathway and dynamics of organic and inorganic N are not the same (Pansu et al., 1998a); the addition of mineral-N would not reduce the N heterogeneity linked to AOM addition.

Three replicates per AOM treatment, basal soil respiration and blanks were used for the experiment. Sample containers were placed in 1.2 l airtight glass jars containing a 50 ml vial with 20 ml aqueous NaOH solution 0.25 mol l\(^{-1}\) (Titrisol) for CO\(_2\)-C trapping and ~10 ml deionized water (moisture saturated atmosphere) to prevent soil desiccation. Soil moisture was checked by periodical weighting and maintained at ~75% water holding capacity (~ - 30 kPa or 16% dry weight basis) with deionized water. For each replicate of AOM, blank and control, 17 sampling occasions of CO\(_2\)-C measurements were done at days 1, 2, 3, 5, 7, 10, 14, 20, 28, 41, 61, 90, 100, 120, 130, 152 and 180.

### 2.4. Measurements

Organic carbon and total nitrogen of soil and AOM were determined by dry combustion (Carlo Erba NA 2000) with control by lost on ignition at 450°C for AOM (NFU 44160, 1985).

The respired CO\(_2\)-C was estimated by precipitating the carbonates with a solution of BaCl\(_2\) and titrating the remaining NaOH (uncarbonated) with HCl 0.25 mol l\(^{-1}\). Soil basal respiration (control unamended soil) was subtracted from the gross respiration to assess the net respiration associated to AOM mineralization (Eq. 1). The total respired CO\(_2\)-C quantities were obtained by summing the CO\(_2\)-C respired between sampling occasions (Eq. 2).

### 2.5. Data calculation and control

The fraction of added C mineralized from AOM at a sampling occasion \(i\) was estimated according to:

\[
C_{Ma} = \frac{CO_2 C_{ia} - CO_2 C_{ia}}{TAC}
\]  

(1)

\[
\bar{C}_m = \frac{1}{n} \sum_{i=1}^{n} C_{Ma}
\]

(2)

\[
MAOMF_i = MAOMF_{i-1} + \bar{C}_m
\]

(3)

Where \(C_{Ma}\) = respired fraction of organic amendment at sampling occasion \(i\) and replication \(\alpha\), \(CO_2 C_{ia}\) and \(CO_2 C_{ia}\) are the amounts of C evolved from the amended and control \(\alpha\) samples respectively, TAC is total added C expressed in the \(CO_2 C_{ia}\) unit, \(\bar{C}_m\) = mean respired fraction of AOM at sampling occasion \(i\) \((n = 3\) replicates\), \(MAOMF_{i}\) and \(MAOMF_{i-1}\) are mean mineralized AOM fractions (cumulated values of respired fractions with \(MAOMF_{0} = 0\)). The expression \(MAOMF\) is very useful for practical use since it does not depend on any unit. For example, a value \(MAOMF = 0.4\) at 150 days, means (with gross approximate of comparable mineralization conditions) that for a 10 Mg C ha\(^{-1}\) AOM application, 4 Mg C ha\(^{-1}\) will be mineralized during 5 months after spreading. Hess and Schmidt (1995) pointed out that estimations with non-cumulative data were more accurate than with cumulative ones. But they used short-term experiments with a great number of sampling occasions with the same time interval. Moreover, their estimations by the two methods where not really different. Our experiment lasted for 6 months with very different time intervals between sampling occasions. The cumulative values are also the most frequently used for parameter estimations and correspond directly to the analytical solutions of differential equations (Table 2). Nevertheless, working with cumulative values necessitate careful data control during the experiments since variances are added simultaneously with mean additions. The pooled variance of \(C_{Mi}\) is:

\[
S^2_{C_m} = \frac{1}{np - p} \sum_{i=1}^{p} \sum_{\alpha=1}^{n} (C_{Ma} - \bar{C}_m)^2
\]

(4)

where \(p\) is the total number of sampling occasions with \(n\) samples. The cumulative confidence intervals must be calculated according to Pansu et al. (1998a):

\[
MAOMF_i = MAOMF_{i\alpha} \pm t_{0.975} S_{C_m} \sqrt{\frac{1}{n}}
\]

(5)

### 2.6. Mathematical models

Our main objective was to compare the efficiency of different model formulations (Table 2) in the description of cumulative CO\(_2\)-C data. The tested models can be classified in three types: one-compartment model \((O\) in Table 2\), consecutive 1st order compartment models \((C\) in Table 2\) and parallel 1st order compartment models \((P\) in Table 2\).

The first consecutive two-compartment humification model
Table 2
Model formulations for remaining AOM fraction (RAOMF = 1–MAOMF); CM = compartment model; T = model type (C = consecutive two CM, P = parallel 2 or 3 CM, O = one CM)

<table>
<thead>
<tr>
<th>T No.</th>
<th>Name</th>
<th>Flow AOM = added organic matter</th>
<th>Analytical solution RAOMF at time t</th>
<th>Parameters</th>
</tr>
</thead>
</table>
| C m1  | Consecutive humification, 1st order 2 CM, three parameters | ![Diagram](image) | \[
\frac{(k_{mL} - k_{mR})}{k_{mL} + k_{mR} - k_{mR}} e^{-\alpha_{mL} t} + \frac{k_{mL} + k_{mR} - k_{mR}}{k_{mL} + k_{mR} - k_{mR}} e^{-\alpha_{mR} t}
\] | \[k_{mL}, k_{mR}: 1\text{st order kinetic mineralization constants of labile (L) and resistant (R) compartments}
\]
| C m2  | Exchange 1st order 2 CM | ![Diagram](image) | \[
\frac{\lambda_1 + k_m}{\lambda_1 - \lambda_2} e^{\lambda_1 t} - \frac{\lambda_2 + k_m}{\lambda_1 - \lambda_2} e^{\lambda_2 t}
\] | \[k_m: humification and decomposition constants. \]
| C m3  | Consecutive decomposition 1st order 2 CM, three parameters | ![Diagram](image) | \[
P_1 e^{-k_m t} + (1 - P_1) e^{-k_m t}
\] | \[P_1: labile AOM fraction
\]
| P m4  | Parallel 1st order 2 CM, three parameters | ![Diagram](image) | \[P_1 e^{-k_m t} + (1 - P_1) e^{-k_m t}
\] | \[k_n, k_n: see m1 above, P_1: see m3 above
\]
| P m5  | Parallel 1st order 3 CM, 4 parameters | ![Diagram](image) | \[
P_1^* e^{-k_m^* t} + (1 - P_1^*) e^{-k_m^* t} + P_S
\] | \[P_1^*, P_S: very labile AOM fraction, \]
| P m6  | Parallel 1st order 3 CM, 2 parameters | ![Diagram](image) | \[
P_1^* e^{-k_m^* t} + (1 - P_1^*) e^{-k_m^* t} + P_S
\] | \[P_1^*, P_S: see m5 above. \]
| O m7  | 2nd order kinetic model | ![Diagram](image) | \[
\frac{1}{1 + k \alpha (1 - \alpha) t}
\] | \[k: 2nd order kinetic constant. \alpha: fraction of AOM becoming microbial biomass
\]
| P m8  | 1st order plus 0 order model | ![Diagram](image) | \[
P_1 e^{-k_m t} + 1 - P_1 + k_m t
\] | \[P_1, k_m: see m4 above. k_m: 0 order kinetic constant
\]
The model \( m2 \) is a two-compartment version of the three-compartment model proposed by Saggar et al. (1996). Using models \( m1 \) or \( m2 \) means that a CO2-C mineralization experiment alone cannot give a valuable information about the forms of C in soil, especially for long-term incubations. Hénin et al. (1959) and Saggar et al. (1996) presented their model with humification from organic inputs (\( L \) in Table 2) toward humified materials (\( R \) in Table 2) with consecutive direct R-mineralization (\( m1 \)) or R-decomposition toward \( L \) (\( m2 \)).

The consecutive 1st order two-compartment decomposition model (\( m3 \) in Table 2) was proposed by André and Kätterer (1997) to fit field decomposition data: the AOM input is split between labile AOM (\( L \)) which mineralizes and resistant AOM (\( R \)) which decomposes toward \( L \).

Parallel 1st order two-compartment model (\( m4 \) in Table 2) is the most commonly used to interpret incubation experiments (Gilmour et al., 1998) and was used to model climate effects (Lomander et al., 1998). It is the easiest to integrate to an analytical solution. Parallel 1st order two-compartment models (labile and resistant organic materials) regulates the C-input in most of the more complex soil organic matter models such as Phoenix (McGill et al., 1981), Ncsoil (Molina et al., 1983), Century (Parton et al., 1987), Momos (Sallih and Pansu, 1993), Rothamsted (Bradbury et al., 1993). So a better knowledge of model parameters for different organic inputs are of great interest to improve all model predictions. Non-linear fittings of models \( m1, m3 \) and \( m4 \) analytical solutions (Table 2) are equivalent. Models \( m1 \) and \( m4 \) are related by \( \{ k_{ml} \}_{m1} = \{ k_{ml} \}_{m4} \), \( \{ k_{ml} + k_{H} \}_{m1} = \{ k_{ml} \}_{m4} \) and

\[
\left\{ \frac{k_{ml} - k_{mR}}{k_{ml} - k_{mR} + k_{H}} \right\}_{m1} = \{ P_L \}_{m4}
\]

but parameters of the two models do not have the same physical significance, except \( k_{mR} \). However, if in model \( m1, k_{mR} \approx k_{L} \), then

\[
\frac{k_{ml} - k_{mR}}{k_{ml} - k_{mR} + k_{H}} = \frac{k_{ml}}{k_{ml} + k_{H}}
\]

which can represent the AOM labile fraction (\( P_L \) in model \( m4 \)). Models \( m3 \) and \( m4 \) are related by \( k_m = k_{ml} \), \( k_D = k_{mR} \) and

\[
\left\{ \frac{P_L k_{mR} - k_{D}}{k_m - k_{D}} \right\}_{m3} = \{ P_L \}_{m4}
\]

when \( k_D \ll k_m \) models \( m3 \) and \( m4 \) are identical.

Parallel 1st order three-compartment model (\( m5 \) in Table 2) was used to regulate C-input in the Verberne et al. (1990) model and in the Daisy model (Hansen et al., 1991). The compartment S corresponds to the AOM stable fractions. It was not possible to predict its mineralization during a 6-month experiment, thus we did not mention any mineralization constant for the S compartment. In order to reduce the complexity, we proposed the \( m6 \) model (Table 2) with only two parameters: the very labile and stable fractions in AOM.

The 2nd order kinetic model (\( m7 \) in Table 2) was found better than a simple 1st order kinetic (one compartment) model by Whitmore (1996). The mixed 1st-order plus 0th kinetic model (\( m8 \) in Table 2) was chosen by Bernal et al. (1998) to fit CO2-data from a 2-month laboratory incubation and by Blet-Charaudeau et al. (1990) to fit CO2-data from field experiment.

2.7. Calculation tools

Calculations were performed using linear (\( m5 \) and \( m6 \) in Table 2) or non-linear (\( m1 \) to \( m4 \) and \( m7 \) in Table 2) fittings with optimization of parameters using the Marquardt algorithm to minimize residual sum of square (RSS). The choice of a model was based on the following statistical tests:

- Determination coefficient \( r^2 \) or percentage of variability explained by the model;
- Residue distributions: a model which explains the whole information in a given data series must have a normal residue distribution around residual mean \( = 0 \); residual tests can be performed in two ways: visual graphical observation (Hess and Schmidt, 1995) or auto-correlation Durbin-Watson test (DW);
- Correlations: our work with 17 data series allowed us to calculate correlation between parameters values; a positive test indicates a possible dependence between parameters which can be graphically observed;
- Residues comparison: the best model must have the lowest RSS; let \( RSS_a \) and \( RSS_b \) the residual sum of square of models \( a \) and \( b \) respectively; comparisons with test \( F \) must be performed as follows:

\[
F = \frac{RSS_a}{RSS_b}
\]

if \( RSS_a > RSS_b \) - otherwise:

\[
F = \frac{RSS_b}{RSS_a}
\]

if \( RSS_b > RSS_a \) - with \( p \) = number of sampling occasions, \( m \) = number of model parameters, \( \hat{y}_a, \hat{y}_b \) = measured and predicted values with \( a \) and \( b \) models respectively, at sampling \( i \). An \( F \) value (Eq. 3) greater than bilateral \( F_{(p-m),(p-m_1)} \) (statistical table) indicates that equality hypothesis must be rejected with 5% risk: \( RSS_a \) is greater than \( RSS_b \) so model \( b \) fitting is better than \( a \).

3. Results and discussion

3.1. Data from CO2 mineralization

The patterns of C mineralization are presented in
Figs. 1–3. Most of AOM from animal origins were rapidly mineralized (Figs. 1 and 3). During 6 months, 65% (Chicm), or up to 90% (Guano) of AOM-C was respired. Mineralization from plant origin-AOM was less intensive (Fig. 1) with a large range of mineralized C: from 29% for Dgrap to more than 56% for Coffk. These discrepancies occurred during the last stages of incubation (after 2 months). Some AOM have uncommon patterns. On one hand the Kokoa mineralization curve looks like a fertilizer or an animal-originated AOM (see Featm in Fig. 1) with a large very labile fraction. On the other hand, native fine feather (Nfeat in Fig. 1) was less susceptible to microbial degradation, and behaved like a recalcitrant plant material. Nfeat is composed of native proteins arranged in lamella, and is quite recalcitrant to microbial attacks (AOM manufacturer, unpublished data). Another hypothesis is the possible presence of antibiotics since Nfeat is derived from intensive duck livestock.

After 6 months of incubation, the C mineralization of the industrial composts (Compo in Fig. 2) showed a gradient according to the time of composting: 33% for the initial mixture to 12% for the most composted material. The curve patterns were intermediary between the animal-origin AOM and plant-origin ones. The fertilizer with a compost base (Comfer in Fig. 3) combined the typical fertilizer pattern (strong early mineralization rate) with a more stable one.

The confidence intervals at 152 or 180 days of incubation (Figs. 1–3) are the greatest of the experiment since they are calculated with $i = 16$ or $i = 17$ respectively (Eq. 5). It is difficult to compare their amplitudes with other works since the calculation methods are not given, and results are very different: for example, very small intervals reported by Bernal et al. (1998) and wider ones by Paré et al. (1998).

The highest actual confidence intervals relate to the products with strong mineralization: guano-based fertilizer and guano (Fig. 3). In contrast, the third animal product with rapid mineralization (Featm in Fig. 1) gave a better repeatability. This feather meal is an industrial product, and has been treated at high temperature ($120^\circ$C, autoclaved); this product is finely ground and is probably more homogenous with respect to the C- and N-repartition and active sites for microbial attack.

3.2. Comparative $m_1$, $m_2$, $m_3$, $m_4$, $m_7$, $m_8$ model predictions

Models $m_2$ and $m_7$ (Table 2) did not match with this data or gave poor fittings (determination coefficients $2\% < R^2 < 97\%$, depending on the AOM). As expected, models $m_1$, $m_3$ and $m_4$ gave the same predictions. The 17 data series were well predicted with these two-compartment models (Figs. 1–3). The determination coefficients (in Table 3 and on each curve) were above 99% for 11 series.
Fig. 1. Mineralized added organic matter fraction (MAOMF) of cocoa (Kokoaj, dry and wet grape pellicle cake (Dgrap, Wgrap), olive pulp (Olivp), coffee cake (Coffk), native fine feather (Nfeat), feather meal (Featm)). Symbols represent experimental data (n = 3), and plain or dashed lines represent the predictions according to models m4, m5 and m6 (r² values from Table 4 are reported on each curve). Vertical bars represent the maximum confidence intervals at 95% for cumulated values of C mineralization.
Fig. 2. Mineralized added organic matter fraction (MAOMF) of composts (Compo a, b, c, + and Compo p). Symbols represent experimental data (n = 3), and plain or dashed lines represent the predictions according to models m4, m5 and m6 ($r^2$ values from Table 4 are reported on each curve). Vertical bars represent the maximum confidence intervals at 95% for cumulated values of C mineralization.
Fig. 3. Mineralized added organic matter fraction (MAOMF) of chicken manure (Chicm), guano (Guano), guano-based fertilized (Gnofer), compost-based fertilizer (Comfer), sheep manure (Shepm). Symbols represent experimental data (n = 3), and plain or dashed lines represent the predictions according to models m4, m5 and m6 (r² values from Table 4 are reported on each curve). Vertical bars represent the maximum confidence intervals at 95% for cumulated values of C mineralization.
Table 4
Values of the estimated parameters: \( P_L \) (no dimension), \( k_{mL}, k_{mR} \) \( (\text{d}^{-1}) \) in model m4, \( P'_L \), \( P_S \) (no dimension), \( k'_{mL}, k'_{mR} \) \( (\text{d}^{-1}) \) in models m5 and m6.

In model m4, \( P_S \) is calculated by difference \( 1-P_L \). In models m5 and m6, \( P_S \) is calculated by difference \( 1-P'_L-P_S \). ** Two exponential models \( (m1 \text{ or } m4) \)
gave low \( k_{mR} \) values with associated confidence interval including zero value, low \( k_{mL} \) values close to \( k_{mR} \) values of most products; consequently they could be considered as particular cases of models m5 with labile L compartment = 0; ** = Particular cases of model m5 where \( P_R = 0 \), could be fitted with one exponential term and a constant term with two parameters \( k_{mL} \) and \( P_S \) (with \( P'_L = 1-P_S \)). ** * = Particular cases of models m5 where \( P_S = 0 \), then fittings are those of model m4

<table>
<thead>
<tr>
<th>AOM origin</th>
<th>AOM</th>
<th>Model m4 (or m1) ( P_L )</th>
<th>Model m5 ( P'_L )</th>
<th>Model m6 ( P'_L )</th>
<th>( r^2 ) (%)</th>
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<td>0.0019</td>
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between 98 and 99% for four series and between 97 and 98% for two series.

Model m8 gave also good predictions; differences between model m8 and models m1, m3 or m4 (Table 3) were not significant at 5% level \( (F \text{ values, Eq. 6)} \). Nevertheless, in all cases (except the curve for Guano) the trends were the same: \( F \text{ values (Eq. 6).} \)

greater than 1 indicated that models m1, m3 and m4 gave a better prediction than model m8. These model behaviors can be easily explained since 1st order kinetic constants for the 2nd exponential in models m1, m3 and m4 were found to be relatively small (Table 4). So resistant organic material \( (R \text{ in Table 2}) \) mineralization curves were flattened for small incubation times, like the straight line of the zero order kinetics in model m8. Blet-Charaudeau et al. (1990) indicated that the use of the double exponential model is superfluous unless the duration of incubation experiments exceeds 100 days\'; Bernal et al. (1998) found 1st-order plus 0-order kinetics from 70 days incubation experiments. Our 180 day experiments began to show a better prediction by the double exponential model but with no significant differences. The differences would become more significant for greater incubation times. Our experimental data confirmed the superiority of double exponential model compared to 1st-order plus 0-order model. This is satisfactory in mechanistic terms, since a constant R mineralization rate even when \( R = 0 \) is not realistic.

The comparison between models m1, m2, m3, m4, m7 and m8 (Table 2) indicated that the 1st order two-compartment models m1, m3 and m4 should be retained. Unfortunately, most of the correlation coefficients between the parameters found with models m1, m3 and m4 from these 17 data series were significant. But graphical representation (Fig. 4) showed that there was no evident relationship between the different parameters. Nevertheless, actual data could not allow a real choice between the three models. The model m4 can be selected for the relative simplicity of its formula (Table 2). The model m3 \( k_0 \) or model m4 \( k_{mR} \) fitted values were found small in comparison to \( k_m \) or \( k_{mL} \) fitted values (Table 4). Model m3 \( P_L \) were found close to model m4 \( P_L \) and the two models were almost identical: the parallel 1st order two-compartment model \( (m4 \text{ in Table 2}) \) can be seen as a m3 decomposition model.

3.3. Comparative m4 and m5 model predictions

Despite good predictions given by models m1, m3 or m4 with determination coefficients higher than 97% (Figs. 1–3), the residues (predicted minus measured values) were not randomly distributed. The DW tests (Table 3) showed significant autocorrelation in residues from all data series except for the animal products Guano, Gnofr and Nfeat: two
exponential models cannot describe the whole information in most of the data.

The use of model m5 improved all predictions with $r^2$ values higher than 99.7% for 14 data series and higher than 98.4 for the three other data series (animal products with strong mineralization rates: Guano, Gnofer and Featr). Tests $F$ (Eq. 6, Table 3) showed a significant improvement at 5% level for ten data series, at 1% level for seven data series included in the former ten series. The improvements are shown in Figs. 1–3, especially with a better fitting of the intermediate points (between 30 and 120 days) for nine curves (Kokoa, Coffk, Olivp, Wgrp, Compo a, Compo b, Compo +, Chinc, Comfer). At the end of the 6-month incubation, the slopes of model m5 curves were smaller than model m4 curve slopes, tending to the asymptotic lines given by the $P_S$ ($m5$ in Table 2) values (Table 4).

The correlation between the four parameter values of model m5 predictions for the 17 data series were not significant except the correlation between $P'_L$ and $P_S$ values; but this correlation did not appear as an evident relation (Fig. 4). The model m5 explained the whole information in 11 data series as shown by DW autocorrelation test in residual values (Table 3); in three other cases residual autocorrelation in model m5 were smaller than in model m4; model m5 did not match for the three

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**Fig. 4.** Correlation between estimated parameters for models m1, m3, m4, m5 and m6. Only significant correlations are shown, other values (model m5) are $r_{m5PS} = -0.01$ ($p = 0.96$), $r_{m5PLC} = 0.24$ ($p = 0.41$), $r_{m5PLP} = 0.18$ ($p = 0.54$), $r_{m5LAMHI} = 0.11$ ($p = 0.71$), $r_{m5LPL} = -0.40$ ($p = 0.17$).
other cases concerning animal products Guano, Gnofer and Nfeat. In products with high mineralization rates, Guano and Gnofer, the stable S compartment was not found. In the 3rd high mineralization animal product, Featm, models m4 and m5 gave the same predictions. In Nfeat the intermediary compartment H was not found. This may be related to the particular biochemical structure of this product.

3.4. Comparative m4, m5 and m6 model predictions

The three-compartment model m5 (in Table 2) gave the best predictions. But this model need four parameters against three for the two-compartment models m4. An examination of \( k'_{\text{LR}} \) and \( k'_{\text{LL}} \) fittings showed less variable values in model m5 than \( k_{\text{LR}} \) and \( k_{\text{LL}} \) values in models m4 (Table 4). For 14 data series (except the animal products Guano, Gnofer and Featm) the mean \( k'_{\text{LL}} \) value was 0.40 (±0.21 sd) \( \text{d}^{-1} \), the mean \( k'_{\text{LR}} \) value was 0.014 (±0.007) \( \text{d}^{-1} \). There was one extraneous value in \( k_{\text{RL}} \) distribution for Olipv (\( k_{\text{RL}} = 0.90 \)). The elimination of Olipv gave normal distribution (kurtosis and skewness tests, normal probability plot) for \( k'_{\text{LL}} \) with a mean value = 0.36 (±0.15). There were two extraneous values in \( k'_{\text{LR}} \) distribution for Comfer (\( k'_{\text{LR}} = 0.036 \)) and Shepm (\( k_{\text{LR}} = 0.002 \)). Their elimination gave \( k_{\text{LR}} \) normal distribution with mean \( k_{\text{LR}} \) value = 0.014 (±0.003). The corresponding half lives of the two parallel 1st order compartment models were 1.8 days for labile compounds L and 49 days for resistant compounds R.

Gilmour et al. (1998) reported for different crop residues incubated at 25°C, the first order rate constants for labile compartment in the range 0.09–0.43 \( \text{d}^{-1} \) with a mean value of 0.21 (±0.02) and for stable compartment in the range 0.0026–0.016 \( \text{d}^{-1} \) with a mean value of 0.008 (±0.0052). Vanlauwe et al. (1994) found 0.4 and 0.012 \( \text{d}^{-1} \) for labile and stable kinetic constants respectively, of maize residue incubated at 25°C.

Model m6 predictions with mean mineralization rate values (Table 2) \( l = -0.4 \text{d}^{-1} \) and \( r = -0.014 \text{d}^{-1} \) and the \( P_{\text{L}} \) and \( P_{\text{S}} \) fittings are shown in Figs. 1–3. The accord with data series remained valuable with \( r^2 \geq 99.5\% \) for seven series, \( 99 < r^2 < 99.5 \) for five series, \( 98 < r^2 < 99 \) for two series and \( 93 < r^2 < 98 \) for the three animal products Guano, Featm and Nfeat. Tests F (Eq. 6, Table 3) showed no significant difference between model m5 and model m6 predictions for five data series. However, significantly better predictions were found for model m5 compared to model m6 at 5% risk for one data series and at 1% risk for eight other data series. As mentioned above, the three-compartment models were less appropriate than two-compartment models for the animal products Guano, Gnofer and Nfeat.

Despite satisfactory data fittings, residual checks (Table 3) showed that model m6 did not explain the whole information in data series, contrarily to model m5. Durbin Watson tests gave significant autocorrelation except for one composted matter (Compo e).

Precision of model m6 predictions was found close to the precision of model m4 (or m1 or m3) ones. Tests F (Eq. 6, Table 3) showed that predictions with model m6 were better than model m4 ones for nine data series, with significant difference for three data series only (two at 5% risk and one at 1% risk). Model m4 predictions were better than model m6 ones for eight data series but differences were significant only for five data series (at 1% risk). For nine data series, the model m6 and m4 predictions were equivalent.

3.5. Conclusion

This work dealt with the mineralization kinetics of various AOM and not of soil organic matter (SOM). The higher proportion of mineralized AOM-C (~65–90% added C) was found in the animal-originated AOM rich in N. That from composts was of a lesser importance (~12–33% added C), and depended on their composting time. The majority of the plant-originated AOM had an intermediary C mineralization behavior, with a great discrepancy between that of animal-originated AOM and composts. The values of the very labile fractions \( P_{\text{L}} \) stable fractions \( P_{\text{S}} \) (Table 4) and resistant fractions (1-\( P_{\text{L}} - P_{\text{S}} \)) illustrated these mineralization behaviors.

For the wide variety of AOM tested in this experiment, the CO2-C mineralization were not predicted very well by the single compartment models. Additionally, this data did not justify the choice for the consecutive models for their more complex formulation than parallel ones.

In general, a better simulation was provided by the three-compartment model m5 as compared to model m4 (two compartments); furthermore, the correlations between the m5 parameters were less significant than between the m4 ones. Model m6 was adapted by simplification of model m5. Under controlled conditions, the mineralization rate of the very labile compounds was found approximately constant (half life 1.8 days), as was the mineralization rate of the resistant ones (half life 49 days). The simplified model m6 gave satisfactory predictions with only two parameters: the very labile AOM fraction and the very stable one. This did not affect negatively the quality of the predictions since the predictions of m6 were not very different than those of model m5, and sometimes better than those of m4. From the eight models tested, m4, m5 and m6 could be recommended at this time-scale. The m5 model with four parameters must be useful in fluctuating conditions, over longer time-scale. The m6 model was powerful and simple enough to be chosen but the m4 one could not be completely rejected. This work shows that it is possible to find accurate and simple parameters to describe the C mineralization kinetics of AOM with very different C mineralization behavior.
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