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REGULAR ARTICLE

Quantifying and modelling C and N mineralization kinetics of catch crop residues in soil: parameterization of the residue decomposition module of STICS model for mature and non mature residues

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Abstract C and N mineralization kinetics of 25 catch crop (CC) residues, whose organic C:N ratio varied from 9.5 to 34.0, were studied during soil incubations under controlled conditions. Decomposition rates were rather similar for the different CC residues, 59% to 68% residue-C being mineralized after 168 days incubation. C mineralized during the first weeks was mainly correlated to the soluble C content of the residue. N mineralized from CC residues was much more variable (−4.9 to +38.0 mg N g^{-1} added C at day 168), and was mainly related to the organic N content in residues. C and N mineralization kinetics were simulated with STICS residue decomposition model, using the previous parameterization mostly based on mature crop residues (Nicolardot et al. Plant Soil 228:83–103, 2001). A reasonable agreement was found between measured and simulated C kinetics but N mineralization was underestimated by the model. A new parameterization was carried out to improve N predictions. The fitting procedure was first applied independently to each CC residue in order to optimise the five parameters of the model. The relationships found between each optimised parameter and the C:N ratio of CC residues were similar to those obtained previously, indicating that the same model was applicable to all residues. The parameters of these relationships were fitted on a combined dataset including CC and mature residues. The new parameterisation lead to better simulations for CC residues, the errors of prediction (RMSE) for C and N mineralization being 32 and 1.8 mg g^{-1} added C, respectively. For the whole dataset (68 residues), the RMSE were 50 and 3.3 mg g^{-1} added C. The prediction quality is satisfactory with respect to the model simplicity and the single criterion of residue quality (C:N ratio).

Keywords Decomposition · Catch crop · Crop residues · Model · Incubation · Mineralization

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Introduction

Besides good N fertilizer management, the control of inorganic nitrogen in arable soils under temperate climates is required during the fallow period between two main crops in order to limit nitrate leaching. The

efficiency of catch crops (CC) in preventing nitrate pollution has been widely demonstrated (e.g. Meisinger et al. 1991). However, additional work is needed to optimise their management in order to simultaneously minimise water evapotranspiration and nitrate leaching and maximise N release for the next crop. Concerning this last issue, different approaches have been used to quantify N mineralization from CC residues. Field experiments carried out under different soil and climatic conditions, agrosystems and rotations have shown that the release of N derived from CC and their recovery in the succeeding crops may be highly variable (e.g. Mitchell and Teel 1977; Thorup-Kristensen 1993; Vos and van der Putten 2001; Olesen et al. 2007). Apart from the difficulty of extrapolating results to other experimental conditions, the main point raised by Thorup-Kristensen (1993) concerns the pre-emptive competition for N caused by catch crops. The N uptake by the succeeding crop may be reduced after CC because N mineralized from CC residues decomposition may not compensate the depletion in soil mineral N which occurred during CC growth. N mineralization coming from CC residues can also be studied using ^{15} N labelled CC residues in field microplots (Jensen 1992; Thomsen and Jensen 1994) or lysimeters (Chapot 1995). However, the interpretation of these experiments is hampered by pool substitution effects resulting from mineralization and immobilization occurring simultaneously (Hart et al. 1986). Another method has been proposed by Justes et al. (1999a) who studied soil N dynamics after CC residue destruction in bare soil and calculated nitrate leaching and N mineralization of catch crops using the LIXIM model (Mary et al. 1999). Mineralization of CC-N has also been studied under semi-controlled experimental conditions by using pot experiments: Thorup-Kristensen (1994) found that N release is relatively rapid and influenced by residue quality. Soil incubations under controlled conditions were conducted with a wide range of CC residues (Elers and Hartmann 1988; Quemada and Cabrera 1995; Breland 1996; Vos and van der Putten 2001; Jensen et al. 2005). These studies indicated that N mineralization of CC residues is highly variable and related to the C:N ratio and biochemical quality of the residues. Comparable findings were reported by Nicolardot et al. (1995) who studied the decomposition of ^{15} N labelled catch crop residues during soil incubations. Other studies (Wivstad 1997; Vanlauwe et al. 1997; Magid et al. 2004; Trinsoutrot et al. 2000a; Jensen et al. 2005) pointed out that CC quality may differ widely from mature plant residues, including the N content of plant tissues. These differences are expected to affect the C and N kinetics during decomposition of plant materials in soil. Nevertheless only few studies have simultaneously quantified C and N mineralization from CC residues and evaluated a simulation model.

The objective of this work was to quantify and model C and N mineralization due to decomposition of CC residues under laboratory controlled conditions, for a wide range of C:N ratio in CC residues. The CC incubation dataset was used to (i) evaluate the ability of the current decomposition module of STICS model (Brisson et al. 1998; Nicolardot et al. 2001) which had been parameterized mainly for mature residues to simulate CC decomposition, (ii) improve the model parameterization over a calibration dataset containing some of CC residues studied here and some mature residues reported by Nicolardot et al. (2001), and (iii) assess the performance of the new parameterization versus an independent dataset containing both CC and mature residues incubation data.

Materials and methods

Catch crop residues

Catch crop residues of white mustard (*Sinapis alba* L.), radish (*Raphanus sativus* L.) and Italian ryegrass (*Lolium multiflorum* L.) were collected from field experiments where different sowing dates, N fertilization and irrigation rates had been set up in order to evaluate the plant module of the soil-crop model STICS (Dorsainvil 2002). These experiments produced CC residues with a wide range of N contents which can be found in actual field conditions (Table 1). The CC residues numbered 1–16 composed the 'calibration dataset' while the nine remaining CC residues (17–25) were included in the 'validation' dataset. The aerial parts of CC were sampled in the field (1 m^2 per replicate), dried at 80°C and ground to 1 mm.

Soil

The soil used for incubation came from the field experiment and was a carbonitic Lithic Rendoll which

Table 1 Dataset of catch crop residues and their field growth conditions

Dataset	Catch crop residue		Sowing — harvest date	Growth conditions in field		
	Code	CC species		N fertilization (kg N ha^{-1})	Irrigation (mm)	Biomass** ($t.ha^{-1}$)
Calibration	CC1 to CC6	White mustard	August 3–Nov. 29, 1999	0, 50, 100, 150, 200, 250	59	5.4, to 8.9
						9.8 to 9.9
Calibration	CC7 to CC8	Radish	August 3–Nov. 29, 1999	0, 150	0	3.0
					49	6.4
Calibration	CC9 to CC10	White mustard	August 6–Nov. 5, 1998	0, 200	0	1.7
					97	8.1
Calibration	CC11 to CC12	White mustard	September 11–Nov. 5,	0	0	1.1
			1998 *before frost*	200	0	1.8
Calibration	CC13 to CC14	White mustard	September 11–Dec. 3,	0	0	0.7
			1998 *after frost*	200	0	1.5
Calibration	CC15 to CC16	Italian ryegrass	August 6–Dec. 3, 1998	0	0	1.9
			after frost	175	27	3.3
Validation	CC17 to CC18	Radish	August 3–Nov. 29, 1999	0	49	3.0
				150		6.4
Validation	CC19 to CC21	White mustard	August 3–Nov. 29, 1999	0	59	5.4
			frozen and dried in lab	150		8.9
				250		9.9
Validation	CC22 – CC23	Rye	R35* and R40*	0	0	1.3
Validation	CC24	Rape	R41*	0	0	0.7
Validation	CC25	Radish	R42*	0	0	1.0

*Residue reference in Nicolardot et al. (2001)

**Total biomass (shoots plus roots sampled on 30 cm depth)

corresponds to a hypercalcareous rendosol (French soil classification, Baize and Girard 1995). Its main characteristics were: $CaCO_3$=65%, clay=9.9%, silt=20.0% and sand=5.0%; organic C=1.53%, organic N=0.17%, pH=8.3. The soil was sampled in the Ap horizon, sieved through a 4-mm mesh and stored fresh at 4°C before incubation.

Soil incubations

C and N mineralization from CC residues were studied during a 168-day soil incubation period. The amount of CC residue incorporated in soil was 8 g dry matter kg^{-1} soil. For each CC, 200 mg dry residue was mixed thoroughly with a fresh soil sample containing 25 g of dry soil, and was incubated either in a glass jar (250 mL) to determine CO_2 or in a polyethylene pot placed in a 2 L glass jar (ten pots per jar) to determine inorganic N. A treatment without addition of residues (control soil) was also performed to measure mineralization of native soil organic matter. Each treatment (i.e. control soil and residue amended soil) was replicated four times on each sampling time. Mineral nitrogen was added to the soil at the onset of incubation to ensure that decomposition would not be limited by N: the addition rate was 60 mg NO_3^--N kg^{-1} dry soil based on a previous reference (Recous et al. 1995). Soil moisture content was fixed close to field capacity (24.2% dry soil corresponding to -10 kPa) and controlled regularly by weighing and corrected, if necessary, by adding distilled water. Incubation temperature was 15.6°C. The CO_2 produced by the soil was trapped in 10 mL of 0.25 M NaOH in 250 mL jars and in 30 mL of 1 M NaOH in the 2 L jars. The traps were located on the top of the flask and changed periodically in order to renew the atmosphere in the jars and prevent saturation of the NaOH. Mineral

nitrogen extraction was performed with 1 M KCl (30 min. shaking at 20°C, soil:solution=1:4) by destructive sampling of the soil samples present in the 2 L jars. After sedimentation, soil extracts were stored at −20°C until analysis.

Analytical determinations

The total C and N concentrations of the plant residues were determined using an elemental analyzer NA 2000 (Fisons Instruments, Italy). Nitrate-N in CC residues was extracted in water for 30 min. at 20°C (100 mg dry residue in 50 mL H_2O) and measured by continuous flow colorimetry. Water soluble C and N in CC residues were also extracted in pure water for 30 min. at 20°C (200 mg dry residue in 100 mL H_2O) and determined with an auto-analyzer (1010, O.I. Analytical, USA) by oxidation at 100°C with persulfate, followed by infrared detection of the CO_2 evolved (Barcelona 1984) for C and by a TN3000 analyzer (Euroglass, Delf, Netherlands) for N (Alavoine and Nicolardot 2000).

CC residues were fractionated using a modification of the Van Soest method (Van Soest and Wine 1967). The VS soluble fraction was obtained by hot water extraction (100°C) for 30 min, followed by extraction with neutral detergent (100°C) for 60 min (Linères and Djakovitch 1993). The hemicellulose, cellulose and lignin fractions were then determined as described in the original publication. Total C and N concentrations in these fractions were determined using an elemental analyzer (NA 2000, Fisons Instruments, Italy).

The soluble polyphenols (POL) present in the crop residues (150–250 mg dry residue) were extracted at 80°C with an aqueous methanol solution (10 mL, water:methanol ratio=1:1) (Tian et al. 1995) and measured by colorimetry in the presence of Folin-Denis reagent (King and Health 1967). The results were expressed in equivalent tannic acid in % of residue dry matter.

The evolved CO_2 trapped by the NaOH was determined by continuous flow colorimetry (Alavoine and Nicolardot 2002) using an auto-analyzer TRAACS 2000 (Bran & Luebbe, Germany). The mineral nitrogen (NO_2^-, NO_3^- and NH_4^+) in the soil and the residue extracts were also measured by continuous flow colorimetry. The nitrate and nitrite were measured using an adaptation of the method proposed by Kamphake et al. (1967) and the ammonium was measured by a method derived from that of Krom (1980).

Calculation of C and N mineralization from CC residues

C mineralization and net N mineralization (or immobilization) due to the decomposition of CC residues were obtained by subtracting the C or N mineralization measured in the control soil, assuming that no priming effect occurred during the incubation. The rate of mineralization was calculated by reference to the organic fraction of the residue, obtained by difference between the measured total and mineral concentrations.

Evaluation and parameterisation of the decomposition model

C and N mineralization kinetics measured during soil incubation were compared to simulations carried out with the residue decomposition module of STICS (Brisson et al. 1998) using the current parameters established by Nicolardot et al. (2001) mainly for mature crop residues. The amount of C mineralized is calculated using the following Eq. (1):

$$C = C_{R0}\left[1 - Yh - \left(1 + \frac{Y(k-\lambda h)}{\lambda - k}\right)e^{-kt} + \left(\frac{kY(1-h)}{\lambda - k}\right)e^{-\lambda t}\right] \quad (1)$$

which is the 'apparent' C mineralization of the crop residue (mg C kg^{-1} soil), C_{R0} the amount of C in the crop residue at time 0 (mg C kg^{-1} soil), k the decomposition rate constant of the plant residue (day^{-1}), λ the decay rate constant of the zymogeneous microbial biomass (day^{-1}) decomposing the residues, Y the assimilation yield of residue-C by this microbial biomass (g g^{-1}), h the humification coefficient of the microbial C (g g^{-1}), and t the time in days.

The amount of nitrogen mineralized is calculated from the Eq 2:

$$N = N_{R0}\left[\begin{array}{l}\left(1 - e^{-kt}\right) - \frac{W_B}{W_R}\frac{kY}{(\lambda - k)}\left(e^{-kt} - e^{-\lambda t}\right) \\ \qquad - \frac{W_H}{W_R}\frac{Yh}{(\lambda - k)}\left(e^{-\lambda t} - \lambda e^{-kt}\right) - \frac{W_H}{W_R}Yh\end{array}\right] \quad (2)$$

with N_{R0} being the amount of initial N in the crop residue (mg N kg^{-1} soil), w_R the N:C ratio of the plant

residue (g g^{-1}), w_B the N:C ratio of the newly-formed microbial biomass (g g^{-1}) and w_H the N:C ratio of the newly-formed humified organic matter (g g^{-1}).

To improve predictions of N released by catch crops during soil incubations, a new parameterisation procedure was carried out as described by Nicolardot et al. (2001), using the following steps:

Step 1. For each of the 16 CC residues of the 'calibration dataset' (CC1 to CC16), a fitting procedure was used to minimise the difference between observed and simulated values. Two parameters were fixed: the N:C ratio of the residues and N:C ratio of the humified organic matter pool. The other 5 remaining parameters (the N:C ratio of newly-formed biomass, the decomposition rate constant of plant residues and that of newly-formed microbial biomass, the assimilation yield of residue-C by microbial biomass and the humification coefficient) were optimised simultaneously but independently for each CC. All parameters were assumed constant during the incubation.

Step 2. We first checked that the variation of each of these five parameters obeyed the same type of relationships with the initial C:N ratio of CC residues than those found initially with mature residues (Nicolardot et al. 2001). The coefficients of these relationships were then optimised simultaneously against the whole calibration dataset. This dataset was composed of 16 CC residues of this study (CC1-CC16) and the 27 mature crop residues used by Nicolardot et al. (2001) and corresponding to their calibration dataset.

Step 3. The quality of prediction was evaluated using an independent dataset which was composed of 9 CC residues (CC17-CC25, this paper) and 16 mature residues corresponding to the 'validation dataset' of Nicolardot et al. (2001).

Statistical analysis

The parameter optimisation was realized with the excel solver using the Newton method. The minimised criterion was RR (relative residual):

$$\mathrm{RR} = \mathrm{RRMSE}\ (C) + \mathrm{RRMSE}\ (N) \tag{3}$$

where RRMSE (V) is the relative root mean square error for variable V (apparent C or N mineralization of catch crop residue expressed respectively in % residue-C and mg N kg^{-1} soil):

$$\mathrm{RRMSE}\ (V) = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{V_i - \widehat{V}_i}{\max(V_i) - \min(V_i)}\right)^2} \tag{4}$$

n is the number of sampling times, V_i and $\widehat{V}_i$ are the observed and simulated V values (apparent C or N mineralization). The other statistical criteria used to evaluate the model (Smith et al. 1996) are the mean difference (MD),

$$\mathrm{MD}(V) = \frac{1}{n}\sum_{i-1}^{n}\left(V_i - \widehat{V}_i\right) \tag{5}$$

and the absolute root mean square error (RMSE),

$$\mathrm{RMSE}(V) = \sqrt{\frac{1}{n}\sum_{i-1}^{n}\left(V_i - \widehat{V}_i\right)} \tag{6}$$

Results

Catch crop residue characteristics

As expected, the studied CC materials varied widely in their composition (CC1-CC16, Fig. 1). Total N in plant residues ranged from 1.36 to 4.10% dry matter, while organic C contents were comparable (41.6± 1.6% dry matter). Inorganic N content (mainly in form of NO_3^-) was noticeable for some residues and represented on average 9.2±10.8% of residue-N. The organic C:N ratio (R) varied from 10.9 to 31.6. A large part of residue-C was in the form of water soluble C (22.0±9.7% residue-C) or Van Soest soluble fraction (43.4±11.9% residue-C). Hemicellulose and cellulose fractions represented respectively 18.8±4.8 and 29.1±10.7% residue-C. CC residues contained small amounts of total soluble polyphenols (1.3±0.4% dry matter). Most of the residue-N (detailed results not shown) was recovered in water at 20°C (33.4±7.2% residue-N), Van Soest soluble fraction (49.3±13.1% residue-N) and hemicellulose fraction (36.0±10.1% residue-N). Finally, character-

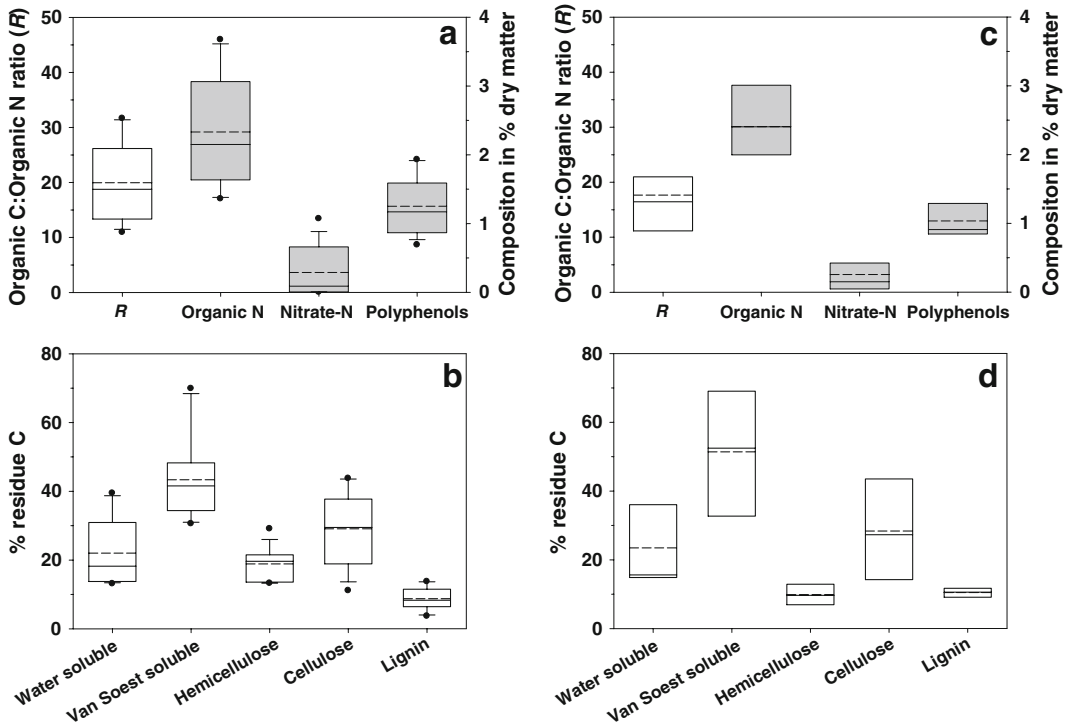


Fig. 1 Chemical composition of catch crop residues used for parameterization (CC1 to CC16) (a, b) and calibration (CC17 to CC25) (c, d). The organic C:N ratio values (*R*) are unit less. The upper and lower lines of each box correspond to the 10th and 90th percentiles and the upper and lower bars to the 5th and 95th percentiles; the horizontal continuous line in the box is the median and the broken line is the mean; closed circles are the extreme values. For Figs. 1c and 1d, 5th and 95th percentiles and extreme values are not represented since number of residues is less than 9

istics of residues used for calibration (CC1 to CC16) are close to those of residues used for validation (CC17 to CC25).

C and N mineralization of catch crop residues

The amounts of C and N mineralized in the control soil at the end of incubation (day 168) were 365 and 33 mg kg^{-1} dry soil, respectively. The addition of CC residues boosted C mineralization by a 5–6 fold factor. C mineralization derived from CC1 to CC16 residues (calculated by difference) was fast and rather comparable between the various CC residues and comparable to residues used for validation (CC17–CC25) (Fig. 2a). The cumulative C mineralized represented 59–68% of residue-C at day 168. The C mineralized at day seven was important (19–29% of residue-C) and strongly dependent on the biochemical composition of the residue. It was positively correlated to the soluble C present in the residue, either as water soluble C (r=0.84, p<0.01) or as Van Soest soluble fraction (r=0.95, p<0.01). It was also negatively related to cellulose (r=−0.91, p<0.01) or lignin content (r=− 0.62, p<0.01). No significant relationship was found between mineralized C at day 168 and C present in the different fractions of the Van Soest method.

On the contrary, the N mineralized derived from CC1 to CC16 residues was very variable between residues as they are for residues used for validation (CC17 to CC25) (Fig. 2b). At day 7, net N mineralization varied between −64 and +58 mg N kg^{-1} soil, corresponding to −58% and +20% of residue-N or −19.5 to +18.5 mg N g^{-1} residue-C. The mineral N dynamics was strongly dependent on the organic C:N ratio (*R*) of the residue: net N mineralization was positive throughout the incubation for CC residues with R<13 whereas it was always negative (net N immobilization) for CC residues with R>26. When *R* was between 13 and 20, net N immobilization occurred during the first weeks of incubation and was followed by re-mineralization leading to net N mineralization at

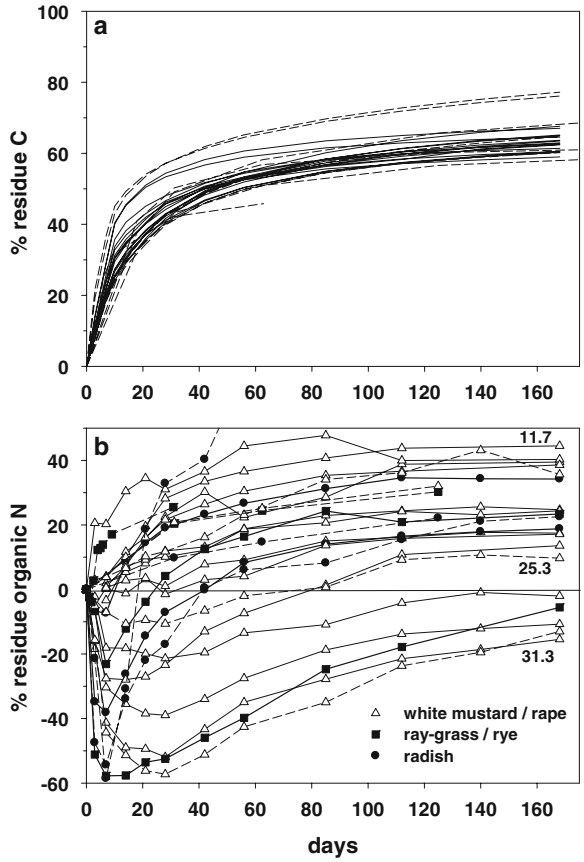


Fig. 2 Cumulative C (**a**) and N (**b**) mineralization rates of the catch crop residues (CC1 to CC16) measured during soil incubation at 15.6 . Coefficients of variation were lower than 5% for C mineralization and 10% for N mineralization. Numbers in Figure 2b indicate organic C:N ratio of CC residues. Dashed lines correspond to residues used for validation (CC17 to CC25)

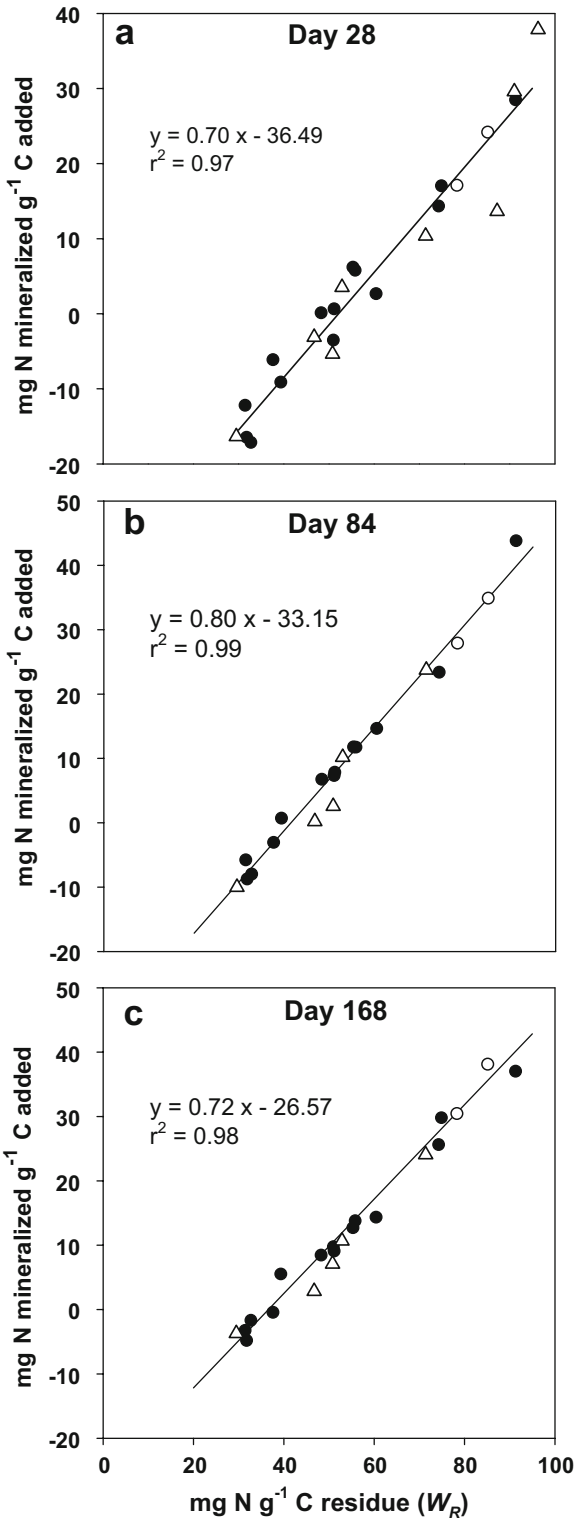
the end of incubation. Residues CC13 and CC14 were obtained from catch crops which had experienced a frost period at the end of the growing period in field. The frost apparently had no effect on decomposition of CC residues since these residues had similar C and N mineralization rates than unfrozen CC residues with a comparable C:N ratio. N mineralized was highly correlated with total N content, organic N content, C:N ratio (results not shown) and organic C:N ratio (R) at all sampling times. The best relationships (linear) were found between the N mineralized per unit of added C and the organic N:C ratio (W_R) of the residue (Fig. 3). However, the slope and intercept of these relations varied with time, due to the succession of net N immobilization and mineralization phases. In the early decomposition phase (day 7), N mineralized was negatively related to the C:N ratio of the water soluble and Van Soest soluble fractions (r=−0.83 and −0.87, respectively, p<0.01) and the polyphenols:N ratio (r= −0.84, p<0.01). At the end of incubation (day 168), N mineralization was correlated to the C:N ratio of the hemicellulose fraction (r=−0.80, p<0.01) and the (lignin + polyphenols):N ratio (r=− 0.81, p<0.01).

Simulation of C and N kinetics with STICS model using the initial parameterization

C and N mineralization kinetics of the CC residues were compared to the simulations performed with the residue decomposition module of the STICS model (Nicolardot et al. 2001) using the set of published parameters (called “initial parameters”). A reasonable agreement was found between measured and simulated carbon kinetics (Table 2). The mean RMSE and MD values were respectively 4.6 and 0.7% residue-C for the 16 CC residues. However, the model overestimated the C mineralization rate during the first weeks of decomposition and underestimated it at the end of incubation (Fig. 4a). The N mineralization kinetics were not as well simulated (Figs. 5 and 6a): the mean RMSE and MD values obtained for the same dataset with 16 CC residues were 18.8 and 11.7 mg N kg^{-1} soil, respectively (Table 2). In fact the model underestimated the N mineralized at all the incubation times (Fig. 6a), except for the last date (day 168) at which simulated and observed values were in good agreement.

New parameterization of STICS model for CC residues and consequences for mature residues

The significant bias of the model observed values for N mineralization of CC residues justified a new parameterization of the decomposition module in order to simulate both mature and CC residues. Therefore the fitting procedure described previously (step 1) was applied to the calibration dataset containing both the 16 CC residues (CC1–CC16) and the 27 mature residues published by Nicolardot et al. (2001). This new optimisation resulted in a noticeable improvement in model performance since the mean RR value obtained for the 16 CC dataset was reduced by 35% (0.136 instead of 0.205 initially). The quality of fit (Table 2a) was unchanged for C mineralization (RMSE (C)=5.0% and MD (C)=3.0%



◀**Fig. 3** N mineralized per unit of added C at day 28 (**a**), day 84 (**b**) and day 168 (**c**) versus organic N:organic C ratio (W_R) of catch crop residues (CC1-CC16, open and closed circle symbols). Correlation coefficients (r) are statistically significant ($p<0.001$). Open circle symbols indicate catch crops sampled after leaf frost (CC13 and CC14). Open triangle symbols correspond to residues used for validation (CC17 to CC25) which are not used to calculate regression

of residue-C), and markedly improved for N mineralization: the RMSE (N) decreased from 19.0 to 13.2 mg N kg^{-1} soil, and the MD was reduced from 12.0 to −0.9%, indicating that the bias of the model had disappeared.

The second step of the procedure consisted in analyzing the relationships between the values of each of the five parameters of the model and the organic C:N ratio (R) of CC residues. The pattern of the parameter variation (R_b, k, λ, Y, h) versus the C:N ratio of residues was similar to that reported previously for mature residues, confirming the previous equations (Table 3). The parameters of the equations were fitted again using a new calibration dataset composed of the 16 CC residues described here and the 27 mature residues used by Nicolardot et al. (2001). The new parameters differed from the previous one in three aspects: i) the decomposition rate constant of plant residues (k) varied within a small range than previously, ii) the humification coefficient of the microbial biomass h was slightly lower, and iii) the decay rate constant of the zymogeneous microbial biomass (λ) was smaller: 0.0076 day^{-1} instead of 0.0110 day^{-1} in Nicolardot et al. (2001).

The new parameterisation slightly improved the predictive quality of C mineralization of the CC residues and even mature residues: the error (RMSE (C)) for the whole calibration dataset (43 residues) was 5.5% residue-C instead of 5.8% with the initial parameters, and the mean difference (MD (C)) was −0.8% instead of −2.5% (Table 2a). The model gave a better prediction of C dynamics during the first weeks of decomposition, but still underestimated the C mineralized during the rest of the incubation period (Fig. 4a, b). The new parameterization markedly improved the predictions of N dynamics for CC residues by simulating a smaller N immobilization particularly during the first decomposition phase (Fig. 5). Furthermore, it did not change the quality of fit of mature residues. The mean RMSE (N) for the

Table 2 Statistical criteria of evaluation of the initial (Nicolardot et al., 2001) and new parameterization of the model versus C and N mineralized

Procedure Dataset	n*	RMSE (*C*)		MD (*C*)		RMSE (*N*)		MD (*N*)	
		Initial	New	Initial	New	Initial	New	Initial	New
		% added C		*% added C*		*mg Nkg*$^{-1}$		*mg Nkg*$^{-1}$	
a. Calibration									
CC residues	(16)	4.6	5.0	0.8	3.0	19.0	13.2	12.0	−0.9
Mature residues	(27)	6.5	5.7	−4.5	−3.0	5.8	5.3	1.1	−1.2
All residues	(43)	5.8	5.5	−2.5	−0.8	10.7	8.3	5.1	−1.1
b. Validation									
CC residues	(9)	6.7	6.4	2.3	3.8	10.6	9.8	3.1	−4.3
Mature residues	(16)	7.0	6.6	−3.8	−2.8	5.8	6.1	−2.0	−3.2
All residues	(25)	6.9	6.6	−1.6	−0.4	7.6	7.5	−0.2	−3.6
c. Calibration + validation									
CC residues	(25)	5.5	5.3	0.9	2.7	12.9	8.5	7.0	−1.7
Mature residues	(43)	6.7	6.1	−4.2	−2.9	5.8	5.6	−0.1	−1.9
All residues	(68)	6.2	5.9	−2.2	−0.6	9.5	8.0	3.2	−2.0

* number of residues considered

whole calibration dataset decreased from 10.7 to 8.3 mg N kg^{-1} soil and MD (*N*) from 5.1 to −1.1 mg N kg^{-1} soil (Table 2a). Finally the simulated N mineralized derived from CC residues was slightly over-estimated whereas that derived from mature residues was unbiased (Fig. 6b, d).

Validation of the new parameters for CC and mature residues

The quality of prediction of the newly parameterized model against the validation dataset (9 CC and 16 mature residues) was only slightly lower than that obtained on the calibration dataset (Table 2b). Surprisingly, it was also comparable to that obtained with the initial parameters, both for CC and mature residues. The new parameterization is validated on this dataset without further improvement relative to the initial model.

When the whole dataset (25 CC + 43 mature residues) was considered, the mean error on C mineralized represented 5.9% and the mean difference −0.6% of added C (Table 2c). The RMSE (*N*) was 8.0 mg N kg^{-1} soil and the MD (*N*) was −2.0 mg N kg^{-1} soil, corresponding to 4.2 and −1.4 mg N g^{-1} added C, respectively. Finally, it appears that the new parameters allowed a better simulation of C and N kinetics of CC residues and an equal prediction of mature residues, using a unique set of parameters.

Sensitivity analysis

In the previous analysis, we assumed that the two parameters Y and λ were constant and independent on the residue quality defined by its organic C:N ratio (R), in accordance with the results obtained by Nicolardot et al. (2001). However, some authors suggested that these parameters might vary with residue quality or C:N ratio of decomposers (e.g. Russell and Cook 1995; Marumoto et al. 1982). These hypotheses were tested by introducing a variation of Y or λ versus R either with a linear or hyperbolic relationship and restarting the optimisation procedure. The quality of fit obtained by varying Y was equal or poorer than that obtained with a constant value (results not shown). The best fits were always obtained with high values of Y, i.e. equal or greater than the value 0.62 already set in the model. When λ varied with R, a slight improvement of the quality of fit was obtained: the improvement consisted in a reduction of the microbial decay rate λ when the organic C:N ratio of the residue (R) increases. However the improvement was small since the RMSE(C) and RMSE(N) were reduced only by 4% and 3%, respectively. These results indicate that the model in its present state was not significantly improved by these refinements, at least on our datasets, and we kept the same formalism than that proposed by Nicolardot et al. (2001).

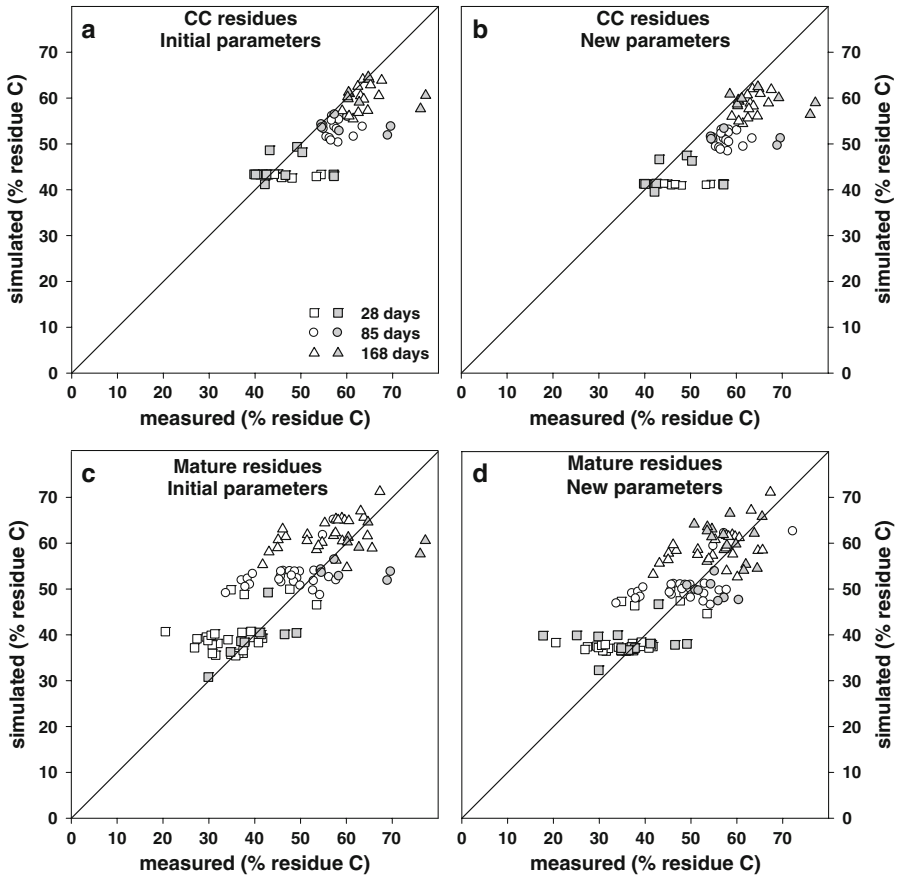


Fig. 4 Observed vs. simulated C mineralization of catch crop residues (CC1-CC25) using initial (**a**) and new parameterization (**b**) and the 43 mature residues using initial (**c**) and new parameterization (**d**). The symbols refer to three sampling dates. The white symbols and grey symbols correspond to residues used for calibration and validation, respectively. The thin line corresponds to y=x

Discussion

Different levels of N fertilization in our field experiment were chosen to obtain a wide range in quality of catch crop residues, at least with respect to their C:N ratio. The effect of N fertilization on N concentration in mature crop residues has been shown by different authors (e.g. Justes et al. 1999b; Trinsoutrot et al. 2000b; Thorup-Kristensen et al. 2003; Magid et al. 2004). This is equally true for catch crops, as reported by Wallgren and Linden (1994). Available N also influences the inorganic N content of catch crops, as reported here. Thorup-Kristensen et al. (2003) found that nitrate-N may represent up to 25% of total plant N. We observed that the biochemical composition of CC residues was also affected by N fertilization. Trinsoutrot et al. (2000b) found changes in hemicellulose, cellulose and lignin contents of oilseed rape residues with N rate. Handayanto et al. (1995) reported that N fertilization affected polyphenols content but not lignin.

The catch crop characteristics of our study were rather different from those of the crop residues sampled at maturity stage (Trinsoutrot et al. 2000a). Wivstad (1997) showed that N content generally decreases with plant age. Biochemical composition is equally affected by plant age (Vanlauwe et al. 1997). Cell wall and lignin contents generally increase in older plants (Wivstad 1997). Magid et al. (2004) observed that water soluble contents were greater in catch crop than in mature plant residues, confirming our results.

Thorup-Kristensen et al. (2003) found that the decomposition of CC residues in soil was related to their biochemical composition. In our study, the C mineralization kinetics of CC residues were rather

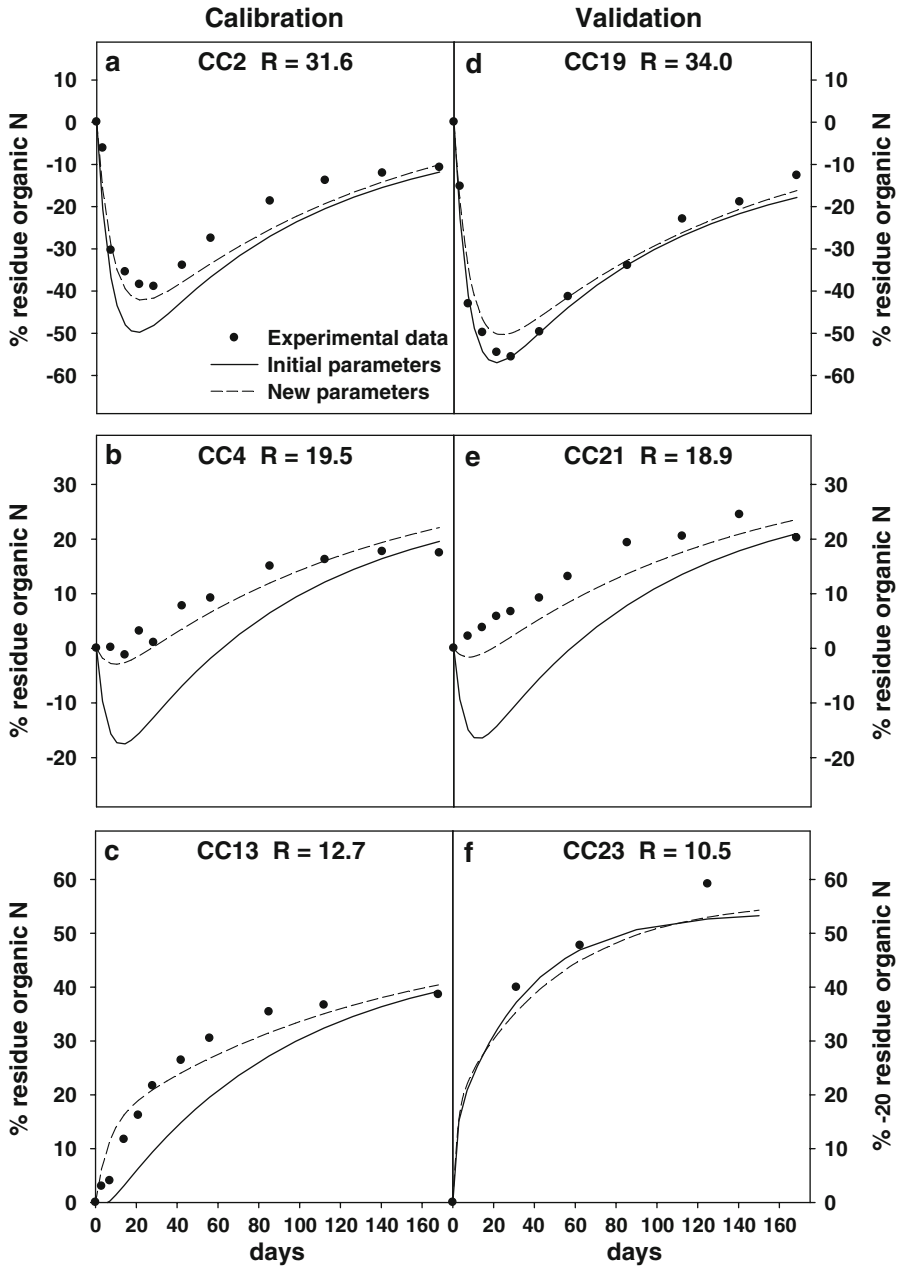


Fig. 5 Observed and simulated N mineralization kinetics of six CC residues in soil using either the initial or the new parameterization: a-c), CC residues used for calibration, d-f) CC residues used for validation

homogeneous and varied much less than those observed for mature residues (Trinsoutrot et al. 2000a; Jensen et al. 2005). Indeed the variability of biochemical composition of our CC residues was lower than that observed by the previous authors for mature residues. In these studies, lignin content represented up to 20–23% of total C in mature crop residues; it represented only 13% of CC residues in our study. The water soluble C content varied from 2 to 47% of total C in the mature residues of Trinsoutrot et al. (2000a), from 3 to 57% in the residues of Jensen et al. (2005) and from 13 to 39% in our catch crop residues. Despite this lower variability, correlations were established between residue-C mineralized at a given decomposition time and biochemical composition, similar to those obtained earlier for mature crop residues. C mineralized during the first phase of decomposition (0–2 weeks) was mainly positively

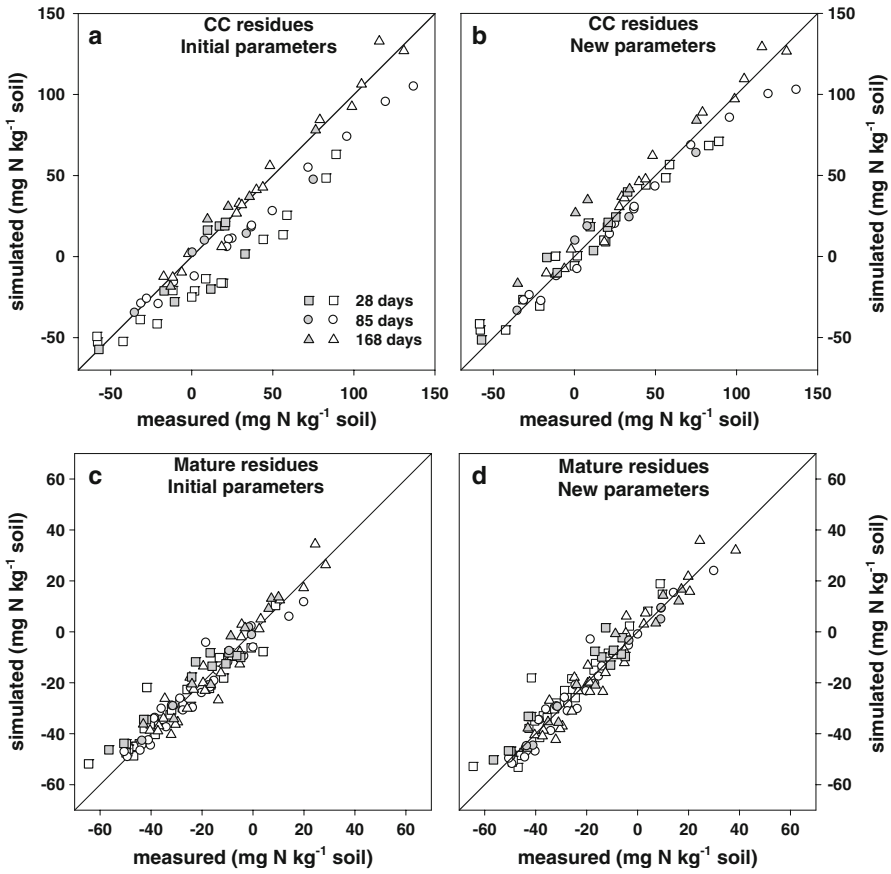


Fig. 6 Observed vs. simulated N mineralization for the 25 catch crop residues using initial (**a**) and new parameterization (**b**), and the 43 mature residues using initial (**c**) and new parameterization (**d**). The symbols refer to three sampling dates. The white symbols and grey symbols correspond to residues used for calibration and validation, respectively. The thin line corresponds to $y = x$

related to soluble forms of C and negatively related to cellulose content, confirming previous studies (Cogle et al. 1989; Collins et al. 1990; Trinsoutrot et al. 2000a; Jensen et al. 2005). As for mature crop residues, when decomposition proceeds, the amount of soluble compounds has no longer influence on C mineralization rate because this fraction is to a great extent already degraded (Trinsoutrot et al. 2000a).

Table 3 Relationships between model parameters and the organic C:N ratio of residue (R), and values used in the initial and new calibration

Parameter	Relationship	Initial calibration	New calibration
C:N ratio of zymogeneous microbial biomass (g g^{-1})	$R_b = a - \frac{b}{R}$,	a=16.1	a=15.4 (± 0.6)[2]
		b=123	b=76 (± 13)
	$R_b \geq R_{bmin}$	R_{bmin}=7.8	R_{bmin}=7.8
Decomposition rate of plant residue (nday^{-1})[1]	$k = c + \frac{d}{R}$	c=0.070	c=0.098 (± 0.020)
		d=1.94	d=0.76 (± 0.76)
Decomposition rate of microbial biomass (nday^{-1})	$\lambda = \lambda_0$	λ_0=0.0110	λ_0=0.0076 (± 0.0004)
Assimilation yield of residue-C by microbial biomass (g g^{-1})	$Y = Y_0$	Y_0=0.62	Y_0=0.62
Humification rate of microbial biomass	$h = 1 - \frac{eR}{f+R}$	e=0.69	e=0.73 (± 0.07)
		f=11.2	f=10.2 (± 4.7)

[1] nday = days at 15°C and optimum water content; [2] standard deviation calculated using the best 20 optimisations during the calibration procedure.

This indicates that intrinsic residue quality factors that play a role in decomposition are comparable for young and mature crop residues.

By contrast, N mineralization associated with CC residues decomposition varied considerably among CC as it was observed for mature crop residues (Trinsoutrot et al. 2000a). The main factor explaining net N mineralization (in % of added-N, positive or negative) was the residue-N content and its organic C:N ratio (*R*). Numerous authors have found significant relationships between N mineralization of catch crop and green manure residues and their N contents (Franzluebbers et al. 1994; Thorup-Kristensen 1994; Wivstad 1999) or their C:N ratio (Franzluebbers et al. 1994; Quemada and Cabrera 1995; Clement et al. 1998; Jensen et al. 2005). No relationship was found between N mineralization and biochemical characteristics (contents in parietal compounds and polyphenols), which confirms the findings of Thorup-Kristensen (1994) and Clement et al. (1998). However, significant relationships have been established with composite quality factors, such as C:N ratio of biochemical fractions, polyphenols:N ratio, (lignin + polyphenols):N ratio or lignin:N ratio (Vanlauwe et al. 1997; Wivstad 1999; Trinsoutrot et al. 2000a).

The C:N ratio of plant residues has been extensively used to parameterize models in order to predict the N mineralization of mature crop residues (e.g. Whitmore and Handayanto 1997; Hasegawa et al. 1999; Bruun et al. 2006) or catch crop residues (Torstensson and Aronsson 2000; Blombäck et al. 2003; Müller et al. 2006). The close relationship between N mineralization of CC residues and their C:N ratio in our study justifies its use to parameter the residue decomposition module of the STICS model (Brisson et al. 1998) to simulate C and N mineralization kinetics, as done previously for mature crop residues (Nicolardot et al. 2001). However, the set of parameters established previously was not suitable to predict satisfactorily N mineralization of our catch crop residues, probably because the dataset used by Nicolardot et al. (2001) to parameterize the model was mainly constituted of mature crop residues. The fitting procedures applied first on the CC residues dataset and secondly on the whole dataset showed that it was possible to simulate decomposition of both young and mature crop residues with a new and unique set of parameters.

Our results indicated that the best fit between observed and simulated values of C and N mineralized were obtained with high values of the microbial growth yield, i.e. greater or equal to 0.60. The value retained here (0.62) is consistent with the results of Mary et al. (1998) who calculated *Y* around 0.60 for straw decomposition and Thiet et al. (2006). Using the difference method to calculate C mineralization rate, these authors found that the microbial yield for glucose decomposition was between 0.59 and 0.62. The new parameter for microbial decay rate was found at 0.0076 day^{-1} in the reference conditions of the model, i.e. at 15°C and optimal soil water content. This parameter can be compared to that used in ROTHC (0.66 yr^{-1}) under the reference conditions of Rothamsted (Coleman and Jenkinson 1999). If we apply these reference conditions (mean temperature = 9 , mean water content of a bare soil) to STICS model using its temperature and moisture functions (Brisson et al. 2008), the decay rate will be multiplied by the temperature coefficient (0.50) and the moisture coefficient (0.74), giving an actual decay rate of 0.0028 day^{-1} or 1.02 yr^{-1}. This value is therefore about 50% greater than ROTHC value. The difference may be due to the fact that the decay rate only concerns the zymogeneous biomass in our model whereas it applies to the whole microbial biomass in ROTHC.

Finally we retained the formalism proposed by Nicolardot et al. (2001) without any modification in the equations, *Y* and λ remaining constant. The new parameterization provided both a better prediction of catch crop decomposition and an equal prediction of C and N mineralization of mature residues. The new version of the model is applicable to various types of plant residues (gramineous and cruciferous) either young or mature in a range of C:N ratios varying between 10 to 150. The model needs to be further evaluated for its ability to predict C and N dynamics over rotations or decades, particularly in long term experiments.

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