Sensitivity analysis of C and N modules in biogeochemical crop and grassland models following manure addition to soil

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Summary

Process-based crop and grassland models estimating carbon (C) and nitrogen (N) dynamics are widely used to investigate best management practices in agriculture. They integrate several processes in a complex structure, but studies where modules corresponding to specific processes extracted from the whole model structure are assessed independently are uncommon. With the support of documented aerobic incubation trials in manure-amended soils, a sensitivity analysis was performed on the C–N cycling processes of four modules (MOD1–4), corresponding to the models APSIM, EPIC, FASSET and STICS. The results show that the parameter, 'substrate use efficiency', had the most effect on the predicted values of net CO_2 emissions and net N mineralization, together with the C/N ratio of the soil microbial biomass. They explained 74–75% on average of both output variances, whereas parameters determining manure C and N partitioning and first-order decomposition constants of manure pools explained, on average, an additional 17–19%. Efforts should be focused on calibrating these parameters for more accurate simulations. The greater sensitivity of both outputs to parameters related to manure pools in more complex modules (MOD2–4) facilitates their adaptation to specific contexts, whereas MOD1 probably requires that parameters related to soil pools are also adapted to specific applications. Parameter interactions were limited, becoming noticeable only in situations of N-limited soil organic matter decomposition. Models MOD1 and MOD 3 allowed soil microbial biomass to vary its C/N ratio temporarily, and therefore were less sensitive to mineral N availability and more easily adapted to a wide range of situations. This study provides essential information to support the development of state-of-the-art biogeochemical models.

Highlights:

- We compared four C–N modules embedded in process-based biogeochemical models.
- We used sensitivity analysis to assess the simulation of manure decomposition in soil.
- We identified a few parameters that influenced CO_2 emissions and N mineralization.
- We found that substrate use efficiency explained most of the output variance for all models.

Keywords

Animal slurry; CO_2 emissions; N mineralization; parameter calibration; soil organic matter.

Introduction

Complex dynamic agricultural and environmental models enable carbon (C) and nitrogen (N) fluxes in terrestrial ecosystems to be simulated. The simulations carried out with these models are important for estimating greenhouse gas emissions, crop productivity and leaching losses of nitrate-N under various pedo-climatic conditions and different N management scenarios. Modules (sub-models) describing the changes in C and N pools of soil and of added organic materials are essential components of these models.

In C–N modules, plant material and animal manures are generally modelled to enter the soil environment as readily decomposable (carbohydrate-like) and resistant (lignin and cellulose-like) materials (Henriksen *et al.*, 2007; Izaurralde *et al.*, 2006; Petersen *et al.*, 2005b; Probert *et al.*, 2005). The soil component consists of different pools of various residence times, varying from months for labile products of microbial decomposition to thousands of years for organic substances with strong organic–mineral bonds (Dungait *et al.*, 2012; Falloon & Smith, 2000). There are considerable differences in the understanding and interpretation of soil organic matter (SOM) processes in current C–N modules, both regarding number of pools and type of decomposition kinetics used to represent SOM turnover (Manzoni & Porporato, 2009). Equations implemented in C–N modules often require a large number of parameters, defined as quantities that remain constant within a simulation but can vary among different simulations. Typically, in C–N modules parameters are quantities related to soil or quantities related to added substrates like animal manure. The values of simulated state variables (e.g. CO_2 emissions and soil mineral N concentration) at different points in time are the model outputs of interest for the users.

Simulated C and N transformations are generally strongly nonlinear and interact with other processes (e.g. water flows and plant growth) simulated in agricultural and environmental models. Moreover, the uncertainty associated with the estimates of several parameter values increases the risk of inaccuracies in model predictions. For these reasons, results of alternative state-of-the-art terrestrial

biogeochemical models, describing the contribution of agricultural systems to C and N sequestration and source or sink status, might diverge significantly (Brilli *et al.*, 2017). It is therefore important to compare the predictions from C–N modules characterized by different structures separately from other sources of uncertainty that arise from processes simulated in the larger models in which the C–N modules are embedded.

An area where C–N modules is particularly important is animal manure management because of complex and dynamic manure–soil interactions. Liquid and solid manure application is a common practice in livestock systems, which provides an input to soils of heterogeneous materials made of decomposable compounds (in the range from slow to fast). These compounds include volatile fatty acids, colonic cells, ruminal bacteria and more resistant compounds in different proportions (Morvan & Nicolardot, 2009; Van Kessel *et al*., 2000). The C to organic N ratio (C/ON; g C g N^{-1}) of the added materials and the availability of inorganic N in the soil are two important interacting factors that profoundly affect C and N cycling following manure addition to soil. Previous aerobic incubation studies (Bechini & Marino, 2009; Morvan *et al*., 2006; Thomsen & Olesen, 2000) have shown the complexity of responses related to C respiration and N immobilization in manure-amended soils. The suitability of simulation models to reproduce, through adequate model parameterization, C and N decomposition dynamics after manure incorporation has also been shown to be difficult (Cavalli & Bechini, 2012; Gillis & Price, 2016; Petersen *et al*., 2005b; Probert *et al*., 2005).

Determining parameter values from field and laboratory measurements or calibration may require considerable effort and costs. Therefore, a sensitivity analysis might help to identify key model parameters involved in the simulation of relevant C–N processes prior to using models to assess the effects of field practices. In conventional practice, sensitivity analysis carried out before calibration reduces the number of parameters subject to calibration. In this way, optimized sets of parameters can be identified better, either specific for soil and substrate-type (Cavalli & Bechini, 2011; Gillis & Price, 2016; Petersen *et al*., 2005b) or common to all soils (Petersen *et al*., 2005a).

Sensitivity analysis provides reliable advice only if the uncertainties of the simulated outputs match the statistical distributions of the measured variables that the output represents. For this reason, the choice of the statistical distributions of model parameters is a critical issue for the analysis (Pianosi *et al*., 2016). The statistical distributions of some parameters can be derived from measured properties of soil and manure, but those of others must be obtained by calibration.

The research described here sets up a procedure that first calibrated the statistical distribution of parameters to fit the distribution of simulated outputs to a measured distribution taken from a reference data set. Then, the sensitivity analysis was done with the statistical distributions of the calibrated parameters. With the support of published results of aerobic incubation trials, this study compared four modelling approaches (C–N modules) with global sensitivity analysis to soil C and N cycles (differing in the number of parameters, pools and fluxes), applied to the decomposition of animal manures. The four modelling approaches were selected for this study because they are representative of the mechanistic models reported in the literature (Campbell & Paustian, 2015; Falloon & Smith, 2000; Manzoni & Porporato, 2009; Stockmann *et al*., 2013), and characterized by different structures and principles governing C and N turnover in soil.

Material and methods

First, we provide a brief description of the selected C–N modules, directing readers to original papers for the full details. Then, we describe the procedure used to calibrate model parameters in order to match the variation in net CO_2 emissions and net N mineralization as measured in manure amended-soils by laboratory incubation experiments (Figure 1a–c). Finally, we provide details about the procedure used to perform sensitivity analysis of model outputs for the chosen modules (Figure 1d).

C and N modules

Description and implementation

122 Four SOM models (MOD1–4; Figure 2) were derived from the C–N modules of the models STICS
123 (Brisson *et al*., 2009), APSIM (Probert *et al*., 1998, 2005), EPIC (Izaurralde *et al*., 2006) and FASSET
124 (Berntsen *et al*., 2003; Petersen *et al*., 2005a, 2005b).
125 All of the above models use interconnected multiple pools to simulate C and N dynamics. These
126 models differ in structure (number of key pools and fluxes) and total number of parameters (Table
127 1). In addition, the C to N ratio (C/N; g C g N^{-1}) in the microbial biomass of STICS (MOD1) and in
128 all the native pools of EPIC (MOD3) varies according to mineral N availability (Izaurralde *et al*.,
129 2006) and microbial biomass N requirement during SOM decomposition (Brisson *et al*., 2009;
130 Giacomini *et al*., 2007). In contrast, C/N is set to fixed values in the pools of APSIM (MOD2) and
131 FASSET (MOD4). Finally, modules implement different response functions to external factors such
132 as soil temperature, soil moisture and, for MOD3 and MOD4, texture. All models assume first-order
133 decomposition kinetics and represent soil microbial biomass explicitly. In our implementation, some
134 minor changes were made to the EPIC module (Table S1; Supporting Information).
135 *Model outputs and initialization*
136 Parameter calibration and sensitivity analysis were performed on two model outputs: accumulated
137 net CO_2 emissions and net N mineralization (NNM). The units were mg C 100 mg^{-1} manure C and
138 mg N 100 mg^{-1} manure C, respectively, to ensure consistency with the published data. We obtained
139 net CO_2 emissions from total CO_2 emissions by subtracting the amount of CO_2 emitted from
140 unamended soil. The NNM represents the variation in soil mineral N after subtracting the amount of
141 N in unamended soil compared to day 0 (Bechini & Marino, 2009). Positive NNM indicates net
142 mineralization of organic N (ON) while negative values indicate net immobilization of soil mineral
143 N. The initialization process performed during parameter calibration and sensitivity analysis is
144 reported in Table S2 (Supporting Information).
145
146 **Parameter calibration**
147 *Reference datasets*

148 A reference distribution of net CO_2 emissions and NNM data (Figure 1a) was obtained by taking
149 these variables from 17 published aerobic incubation experiments (Table S3; Supporting
150 Information). Different manure types were considered (faeces, solid manures, liquid manures), also
151 with respect to animal species (bovine, pig, sheep and poultry), manure storage systems and treatment
152 alternatives (fresh, anaerobically stored, anaerobically digested, separated fractions). Treatments
153 belonging to compost-amended soils were excluded.
154 We recognize that the variation in measured C respiration and NNM was not due to manure type only,
155 because different incubation conditions (soil type and temperature) were used in the experiments
156 considered. However, all the above citations (Table S3; Supporting Information), except Thomsen &
157 Olesen (2000) and Thomsen *et al*. (2003), disrupted soil structure by soil sieving (usually through 2-
158 or 4-mm mesh size), thus reducing the effect of soil type on C and N turnover. Moreover, because
159 the influence of soil type was small (even in the case of undisturbed soil), we assumed that all the
160 variation measured originated from manure properties.
161 We calibrated, separately for each treatment, two empirical models to estimate measured variables at
162 fixed dates because different dates of sampling among experiments made it impossible to compare
163 them directly. We used a double exponential model (Bechini & Marino, 2009) for net CO_2
164 measurements and a Monod-type three-parameter model (Peters & Jensen, 2011) for NNM.
165 Thereafter, two datasets (one for net CO_2 emissions and one for NNM) were created with measured
166 or simulated values at days 3, 7, 14, 28, 42, 84, 120 and 180 to obtain the frequency distributions of
167 the reference output at different stages of manure decomposition.
168
169 *Parameter distributions*
170 The statistical distributions of model parameters (Figure 1b) were derived from a literature review of
171 manure, soil and microbial biomass properties, and from model documentation (Table 1). We linked
172 the partitioning of manure C and ON to the results of proximate analysis (Henriksen *et al*., 2007;
173 Morvan *et al*., 2006; Peters & Jensen, 2011). In this way, manure pools comprised a labile (fast-

decomposable, soluble-like) pool (ML), a resistant (cellulose-like) pool (MR) and a very resistant (lignin-like) pool (MVR) (Figure 2; Table 1). Either uniform or normal distributions were considered, and for each parameter the one that approximated the data distribution best was chosen. Alternatively, first-order decomposition constants were arbitrarily assigned a normal distribution with mean μ equal to the reported reference value, and a standard deviation σ equal to 0.25μ. The distributions of all model parameters were bounded between a lower and an upper limit of $\pm 3\sigma$, respectively.

Calibration procedure for parameters

When the model was run with the initial distributions of parameters taken from the literature, relevant deviations were observed between the distributions of simulated and reference outputs. Therefore an *ad hoc* procedure (Figure 1c) was conceived to adjust the distributions of simulated outputs to the measured ones. As a result, a revised distribution was obtained for some parameters (Table 1). These were the decay constants of microbial biomass (K_{SMB} for models MOD1–3; T_{SMB2} in MOD4) and of manure pools (K_{MAN} in MOD1, K_{ML} and K_{MR} in MOD3 and MOD4, and K_{ML}, K_{MR} and K_{MVR} in MOD2). The optimization procedure (Figure S1; Supporting Information) was designed to find new values iteratively of μ for these parameter distributions that minimized the root mean squared error (RMSE) between observed and simulated output frequencies of net CO_2 emissions and NNM at the eight dates in the two reference datasets. This task was achieved by a local search method (Nelder & Mead, 1965) coupled with a global optimization genetic algorithm OMNIOPT (Deb & Tiwari, 2008) to reduce the risk of obtaining sub-optimal values of μ because of issues of local minima. With the adopted procedure, for each new value of μ found by the Nelder–Mead algorithm, σ and the lower and upper limits ($\pm 3\ \sigma$) were recalculated for the decay constants. Thereafter, the model was run repeatedly (2048 times) and all model parameters were sampled from their distributions and frequency distributions of simulated net CO_2 emissions, and NNM values were assessed.

Preliminary calibration provided values for the decomposition constants of microbial biomass that produced too large a turnover of the pool (in practice the size of the microbial biomass pool remained

close to zero). To avoid this, and because the reference data set did not include measurements of SMB, we decided to constrain the size of the SMB pool to ±50% of a reference time series (expressed as % manure C) obtained by Marino P. (University of Milan, Italy; personal communication). This was from an 180-day aerobic incubation experiment with a loamy soil amended with maize (*Zea mays* L.) stalks, pig slurry and ammonium sulphate.

Sensitivity analysis

The method of Sobol

Global sensitivity analysis methods evaluate the effect of a model parameter on given outputs, whereas all other model parameters are varied simultaneously, thus accounting for interactions among them without depending on stipulation of a nominal point as they explore the entire range of each parameter. The method of Sobol (Saltelli *et al*., 2010) relies on the decomposition of the total model output variance (V) that, for w independent model parameters (input factors), provides 2^w–1 terms of increasing order (1–w), i.e. partial conditional variances from single parameters (V_i) and interactions among them (V_{ij}, V_{ijm}, and so on):

$$V = \sum_i V_i + \sum_{i<j} V_{ij} + \sum_{i<j<m} V_{ijm} + \ldots + V_{12\ldots w}, \qquad \text{[Eq. 1]}$$

where i, j, m and w represent model parameters.

Sensitivity indices (S) are calculated as the ratios of conditional variances (V_i, V_{ij}, etc.) to total (unconditional) variance ($S_i = V_i/V$; $S_{ij} = V_{ij}/V$, and so on), and quantify portions of the total variance that is due to variation of single parameters or a combination of them (Saltelli *et al*., 2010).

In general, accurate estimation of sensitivity indices requires several model runs. To reduce computational time, only first-order effects (S_i), and not higher-order terms, are usually calculated. Instead, interactions among model parameters can be taken into account by calculating total-order indices (ST), representing the whole contribution of parameters (alone and in combination with all other parameters) to total output variance. Indeed, ST_i is the sum of all terms in Equation (1) involving

parameter i, divided by V. The quantity $ST_i–S_i$ provides an estimate of the portion of total variance due to all interactions (from order two to order w) between the ith parameter and all other parameters. Quasi-Monte Carlo estimation of first- and total-order sensitivity indices were implemented according to Saltelli *et al*. (2010) using a sample size of 2^{16}. The Sobol sequence generator was initialized with the set of direction numbers provided by Joe & Kuo (2008).

Modelling scenarios during sensitivity analysis

Sensitivity analysis (Figure 1d) was executed by varying parameter values using the distributions obtained after calibration (Table 1). Toevaluate the sensitivity of model outputs in a broad set of situations representative of possible model applications, we repeated the analysis for the 48 combinations of eight dates ● three manure C/ONs ● two initial soil mineral N contents. The eight dates corresponded to those when reference measurements were available. Selected manure C/ON values were 8, 21 and 34 (the average and $\pm 2\sigma$ of reference manure C/ON; Table 1), whrease the initial soil mineral N contents were 0.1 mg N kg^{-1} (to introduce N limitation on C decomposition for large C to N inputs) and 100 mg N kg^{-1} (to avoid any limiting effect of N on C decomposition).

Results

Parameter calibration

Reference datasets

Net CO_2 emissions from manure-amended soils occurred at exponentially decreasing rates over time (Figure S2a; Supporting Information). After six months, net CO_2 losses averaged 55% of manure C but variation was large, with total C respiration in the range 20–100% of manure C.

Nitrogen dynamics differed among treatments. In fact, some manures always induced net N immobilization, whereas others showed net N release from the first days of decomposition (Figure

S2b; Supporting Information). On average, manures promoted marked net N immobilization in the first week following their addition to soil (2.4 mg N 100 mg manure C^{-1}, corresponding to 67% of manure ON). After day 7, net mineral N concentration in soil started to increase and, after six months, NNM averaged 0.6 mg N 100 mg manure C^{-1} (5% of manure ON).

Reference frequency distributions of net CO_2 emissions and NNM are shown in Figure 3, limited to the most relevant dates. These dates included the peak of negative NNM (day 7), the switch date from faster to slower rates of net CO_2 emissions (day 14) and four additional dates exploring short–medium term decomposition dynamics (days 28, 42, 84 and 180).

Uncertainty in simulated outputs

The initial distribution of model outputs differed from that of the reference data sets for all models (Figure S3; Supporting Information). The calibration procedure effectively improved the simulation of both outputs for all models for most of the dates, which was confirmed by an average decrease in RMSEs by 6 and 4% for net CO_2 and NNM, respectively (Table S4; Supporting Information). After calibration, the RMSEs for net CO_2 (on average 8%) were smaller than for NNM (on average 21%). There were larger errors (22–34%) at the end of the incubation period, when all models tended to underestimate NNM (Figure 3).

Calibrated parameters

When multiplied by model-specific modifier factors for the simulated soil (depending on clay content, temperature and moisture), the values of decomposition constants were similar in different model pools of similar physicochemical meaning (Figure 4). Calibration provided the following mean residence time (MRT, calculated as the inverse of the first-order decomposition constant) of manure pools for models MOD2–4: 5, 201–252 (on average 228) and 213–2986 (on average 1156) days for the labile (ML), resistant (MR) and very resistant (MVR) pools, respectively. Conversely, optimized average MRT of the manure pool of MOD1 was 42 days. The MRT of soil microbial biomass did not

vary greatly among models; it ranged between 16 and 52 days (29 days on average). Finally, MRT of the stable soil pools (HUM, SLOW, PASS and NOM; Table 1) was in the order of years (72 years on average).

Sensitivity analysis

Sensitivity indices under non N-limited C decomposition

In absence of N limitation on C decomposition (large initial soil mineral N), manure C/ON did not affect the sensitivity indices of all dates and for all models; for this reason, we report them for the case of manure C/ON equal to 21 only (Figure 5). The sum of first-order indices was larger than 90% for all dates and models (Figures 5), indicating that both outputs were almost linearly dependent on parameters, and that higher-order terms (interactions) were negligible.

The substrate use efficiency (Eff) was the most important parameter, with first-order indices in the range 37–98 and 38–95% for net CO_2 emissions and NNM, respectively. The C/N of microbial biomass (CN_{SMB} for MOD1–3; CN_{SMB2} for MOD4) also contributed considerably to the variation in NNM (0–39% of NNM variance). However, while sensitivity of NNM to Eff increased over time (with the exception of MOD4), the opposite occurred for the C/N of microbial biomass whose sensitivity indices became zero after days 42–84.

A smaller fraction of output variance (2–58 and 0–25% for net CO_2 emissions and NNM, respectively) was due to variation in parameters related to manure pools. The most important ones were the fraction of manure C assigned to the resistant pool (FC_{MR}) and, solely for MOD4, of manure C and ON assigned to the manure very resistant pool (FC_{MVR} and FN_{MVR}). In addition, both outputs were sensitive to variation in the decomposition constant of manure pools (K_{MAN} for MOD1, K_{ML} for MOD2–4 and K_{MR} for MOD4). The decay constant of the labile manure pool ML (K_{ML}) contributed substantially to the output variance, mainly in the short term until the size of the pool became negligible. Sometimes, short-term effects of some other parameters were due to their indirect effects on the turnover of the ML pool. This was the case of FC_{MR} (Figure 5), which is indirectly related to

the amount of C in ML and, as a consequence, to short-term C and N dynamics. Finally, in MOD4, parameters associated with slow-decomposing pools (e.g. K_{MR}; FC_{MVR} and FN_{MVR}) had an effect that increased with time because model pools did not completely decompose in the period considered and, as the effect of other parameters diminished, they contributed to a larger fraction of the output variances.

Sensitivity indices under N-limited C decomposition

With small initial soil mineral N (0.1 mg N kg^{-1}), sensitivity indices varied depending on manure C/ON. The application of manure with a C/ON ratio of 8 rapidly increased soil mineral N concentration, thus preventing N limitation and resulting in sensitivity indices equal to those obtained in the absence of N limitation for all models (not shown). Nitrogen limitation occurred with manure C/ON ratios of 21 and 34; in this case, sensitivity analysis identified the same set of important parameters determined previously in the absence of N limitation. However, first-order sensitivity indices were usually smaller (Figure 6a; Figure S4a in Supporting Information) while interactions increased (Figure 6b; Figure S4b in Supporting Information). In MOD3, for both simulated outputs, and in MOD1 for net CO_2 only, interactions became evident only after the addition of the manure with the largest C/ON (34), whereas in MOD2 and MOD4 they were evident with a C/ON ratio of 21. For all models, interactions among parameters, whenever present (Figure 6b; Figure S4b in Supporting Information), were mainly relevant in the first period of manure decomposition (days 42–84) when they represented up to 37 and 46% of net CO_2 emissions and NNM variances, respectively.

Discussion

Simulation of net CO_2 emissions and net N mineralization

Calibrated models satisfactorily simulated experimental distributions of both variables on many dates (Figure 3), ensuring that subsequent sensitivity analyses fully resolved the effects of parameters on reliable time-dependent outputs (Pianosi *et al*., 2016)

Larger errors for NNM (average RMSE = 21%) than for net CO_2 (average RMSE = 8%), especially after day 84 (Table S4; Supporting Information), suggest that model improvements are required to simulate N turnover (Cavalli & Bechini, 2011; Mohanty *et al*., 2011; Petersen *et al*., 2005b). Even if smaller RMSEs can be obtained by focussing on N dynamics separately (Cavalli & Bechini, 2012), considering multiple outputs ensured that the results of this research are useful for model applications aimed to simulate both C and N turnover. The adopted model analysis did not enable the contribution of model structure (model type) and parameters to total output uncertainty to be separated (Wallach *et al*., 2016). However, similar distributions of the simulated outputs among models (Figure 3) suggested that model-type had less effect on the simulated outputs than the parameters.

Parameter distributions

Substrate use efficiency

The range 0.27–0.87 included most of the Eff values adopted in mechanistic models similar to MOD1–4 (Henriksen *et al*., 2007; Noirot-Cosson *et al*., 2017; Whitmore, 2007). We assumed that Eff was constant over time, independent of N availability in soil, and was equal for all C mineralization fluxes (Figure 2). This approach is frequently adopted because it simplifies model initialization and the results obtained are satisfactory (Henriksen *et al*., 2007; Petersen *et al*., 2005b). Even if variable Eff among fluxes could represent some microbial features better (e.g. metabolic costs associated with the decomposition and assimilation pathways of molecules with different chemical structure) (Manzoni *et al*., 2012; Mooshammer *et al*., 2014; Sinsabaugh *et al*., 2013), it would require

348 the explicit representation of other microbial processes, including enzyme production, maintenance
349 and overflow metabolism that increase model complexity (Manzoni & Porporato, 2009; Sinsabaugh
350 *et al*., 2013).
351
352 *Microbial biomass C/N ratio*
353 The C/N of soil microbial biomass was constrained to the values reviewed for cropland, grassland,
354 pastures and bare soils by Xu *et al*. (2013). This key parameter contributes to positive or negative
355 NNM (mg N kg^{-1}) (values in each decomposition flux (NNM_{flux}; Manzoni & Porporato, 2009):

$$\mathrm{NNM_{flux}} = K_{\mathrm{S}} \times C_{\mathrm{S}} \times \left(\frac{1}{C/N_{\mathrm{S}}} - \frac{\mathrm{Eff}}{C/N_{\mathrm{B}}}\right), \quad \text{[Eq. 2]}$$

356 where subscripts S and B represent substrates and microbial biomass pools, respectively.
357 The ratio between C/N_B and Eff determines the substrate C/N threshold above which net N
358 immobilization occurs (Manzoni & Porporato, 2009). This threshold averaged 12 (Table 1), which is
359 slightly smaller than the range 15–35 estimated from incubation experiments involving soils amended
360 with manures, organic fertilizers and crop residues (Cavalli *et al*., 2016).
361 The variation of microbial C/N across different environments is narrow with a range of 4–10 g C g
362 N^{-1} (Xu *et al*., 2013) and contrasts with that of substrates, which cover values from <10 (e.g. young
363 leaves) to >100 (e.g. cereal straw) (Henriksen *et al*., 2007). This suggests that microorganisms are
364 mostly homoeostatic, even if adaptation of their C/N was reported as a strategy to overcome resource
365 imbalances (Mooshammer *et al*., 2014). This last approach was implemented in MOD1 and MOD3,
366 that allowed the C/N ratio of SMB (and of all native soil pools in MOD3) to vary temporarily as a
367 function of N availability.
368
369 *Partitioning of C and N in manure pools*
370 The sizes of manure pools MR and MVR were initialized following the reference distribution of
371 holocellulose and lignin in manures, respectively, while ML comprised a mixture of simple soluble
372 molecules (volatile fatty acids, simple sugars, amino acids, amino sugars). This approach was has

373 been used successfully used in previous research (Henriksen *et al*., 2007; Mohanty *et al*., 2011;
374 Probert *et al*., 2005) and enabled the number of parameters to be calibrated to be reduced, which
375 limited the risk of finding parameter sets that performed equally. Nevertheless, real turnover of SOM
376 depends on other processes also (e.g. physical protection within soil macroaggregates, chemical
377 sorption to clay minerals and Fe and Al oxides) and the status of the soil (e.g. temperature, moisture
378 content) (Campbell & Paustian, 2015 and in Dungait *et al*., 2012). Therefore, chemically
379 homogeneous model pools are expected to decompose heterogeneously in soil (Derrien & Amelung,
380 2011; Glanville *et al*., 2012). To overcome this limitation, alternative methods can be used to define
381 manure pools kinetically. They assign C and N contents to model pools that optimize the simulation
382 of experimental dynamics (Gillis & Price, 2016; Mondini *et al*., 2017; Noirot-Cosson *et al*., 2017;
383 Petersen *et al*., 2005b), and assume implicitly that fast- and slow-decay pools are chemically
384 heterogeneous mixtures of molecules.
385
386 *Decay of manure pools*
387 Most decay constants of manure pools were comparable to those reported for APSIM (Mohanty *et*
388 *al*., 2011), a modified version of RothC (Mondini *et al*., 2017), MOTOR (implementing a model
389 similar to RothC) (Whitmore, 2007), NCSOIL (Noirot-Cosson *et al*., 2017), CN-SIM (Cavalli &
390 Bechini, 2011 and 2012; Petersen *et al*., 2005b) and the model of Henriksen *et al*. (2007). Indeed,
391 MRT of ML varied from 4 to 9 days for crop residues and animal manures. The range for MR was
392 wider, and the MRT values were as small as 20 days in APSIM and MOTOR, and as large as 1.1–2.7
393 years for the modified RothC (Mondini *et al*., 2017) and NCSOIL (Noirot-Cosson *et al*., 2017).
394 Models also differed in the turnover of MVR: those similar to MOD4 (Henriksen *et al*., 2007;
395 Petersen *et al*., 2005b) and MOD3 (Mondini *et al*.; 2017) adopted an MRT of 3–50 years, whereas
396 studies using APSIM (Mohanty *et al*., 2011; Probert *et al*., 2005) used a smaller value (105 days), in
397 accordance with the results of MOD2.

398 The MRT of manure pools sometimes deviated from incubation and field measurements that traced
399 the fate of ^{13}C- and ^{14}C-labelled substrates in soil (indicated by numbered boxes in Figure 4) including
400 low molecular weights compounds (average MRT = 21 days; Glanville *et al*., 2012), cellulose (MRT
401 in the range 0.9–1.6 years; Fioretto *et al*., 2005; Gunina & Kuzyakov, 2015) and lignin (MRT from
402 1.5 to 7.8 years; Derrien & Amelung, 2011; Fioretto *et al*., 2005).
403

404 **Sensitivity of model outputs**

405 Sensitivity analysis showed that only a few parameters effectively influenced net CO_2 emissions and
406 NNM (Figure 5 and 6; Figure S4 in Supporting Information). The most important parameters common
407 to all models were related to soil microbial biomass and to manure pools: the substrate use efficiency
408 (Eff), the C/N of microbial biomass (CN_{SMB} or CN_{SMB2}), the fraction of manure C allocated to the
409 resistant pool (FC_{MR}) and the manure decomposition constant K_{MAN} for MOD1, or K_{ML} for MOD2–
410 4. Such parameters should be adjusted when simulating specific soil ● manure combinations. Ideally,
411 it would be reasonable that when different manures are applied to the same soil, a single set of
412 parameters related to soil and microbial biomass pools is shared among simulations, while parameters
413 describing manures are varied. The opposite can be postulated when the same manure is applied to
414 different soils.

415 However, sensitivity of both outputs to the variation in parameters linked to manure pools increased
416 as model complexity increased (from MOD1 to MOD4), especially in the medium term (after day
417 42). This result suggests that simple models like MOD1 necessitate the adjustment of all parameters
418 (both those related to soil, SMB and manure pools) for each manure type to obtain satisfactory
419 predictions, even when the same manure is applied on different soils. For example, the parameters
420 K_{MAN}, but also Eff and CN_{SMB}, are set according to the manure C/N ratio in the STICS model (Brisson
421 *et al*., 2009; Giacomini *et al*., 2007). Conversely, more complex models that represent organic inputs
422 with multiple pools (MOD2–4) could differentiate soil or manure related parameters only, as required
423 by the specific conditions of the simulation (Petersen *et al*., 2005a and 2005b; Probert *et al*., 2005).

Results of sensitivity analysis depended on the amount of mineral N in soil (Figure 6b; Figure S4b in Supporting Information). Positive or negative NNM depended mainly on the combination of five parameters (those reported in Equation (2) plus the fractions of manure C and ON allocated to the manure pools). However, MOD3 reduced N limitation by temporarily increasing the C/N ratio of SMB, and for this reason the interactions among parameters were weak. Similarly, MOD1 allowed SMB to vary its C/N ratio temporarily according to microbial N requirement, but this strategy was not enough to balance the N deficit fully. For this reason, interactions in MOD1 were similar to MOD2 and MOD4, which had microbial pools with a fixed C/N ratio when N limitation became relevant (especially with manure C/ON ratio of 34). Fewer interactions among parameters could reduce calibration efforts of models like MOD1 and MOD3, characterized by variable C/N ratios in their pools, because the first-order effects of parameters are less influenced by soil mineral N concentration.

Results of sensitivity analysis depended on the statistical distribution of the parameters that we chose, the simulation scenarios (combinations of decomposition time, soil mineral N concentration and manure C/ON) and the model outputs considered (Pianosi *et al.*, 2016). However, for calibration purposes, where the interest is in parameters ranking according to first-order indices, sensitivity analysis appears quite robust to alternative assumptions about the distributions of parameters, as suggested by previous analyses with the ICBM/2BN (similar to MOD2) and CN-SIM (same implementation as MOD4) models (Cavalli & Bechini, 2011; Cavalli *et al.*, 2016).

Limitations of the study and future developments

Sensitivity analysis considered model outputs, net of the contribution of unamended soils, simulated over six months. This approach is valuable to study manure turnover because decomposition is mostly a fast process and, at the end of a six-month period, simulated C and N dynamics are often similar to those of unamended soils. Model applications including C and N released from native SOM would require longer simulation periods to fully appreciate the decomposition of soil pools with a slow

turnover. However, after defining additional parameter distributions to initialize soil native pools (Dungait *et al*., 2012; Falloon & Smith, 2000) the proposed methodology can be extended to the sensitivity analysis of gross outputs (i.e. CO_2 and mineral N from both manure and soil pools). Considering that the mineralization of native SOM produces a relevant fraction of total CO_2 emitted from manure-amended soils (about 50%; Bechini & Marino, 2009), it is likely that the sensitivity of gross outputs to variation of parameters related to soil pools will be larger than that of net outputs to variations of the same parameters.

Conclusions

This study was the first in which the controls on C and N dynamics in modules of detailed structures (crop and grassland models) have been assessed and compared. The chosen modules derived from similar principles (discrete compartmental soil organic matter representation, first-order decomposition kinetic), but differed in the complexity of their regulation (number of parameters, pools and fluxes) of N and C turnover (fixed or variable C/N of model pools). The complexity of responses related to C respiration and N immobilization were taken into account in manure-amended soils with the support of incubation experiments. The study showed that all considered modelling approaches might provide a reasonable representation of the statistical distribution of soil fluxes (notably, net CO_2 emissions and net N mineralization) measured after the addition of manure. Furthermore, sensitivity analysis indicated that variation in the two output responses was mostly affected by a few influential parameters (microbial substrate use efficiency, C/N ratio of the soil microbial biomass, manure pools decomposition constants, partitioning factors of manure C among model pools).

The effect of parameters linked to manure pools increased with model complexity (in the order from MOD1 to MOD4), suggesting that calibration strategies could vary depending on the type of model. Models similar to MOD1 (with a single manure pool) probably require specific soil ● manure parameterization, whereas more complex models (with multiple manure pools, like MOD2–4) could require only soil- or manure-specific calibrations, depending on model applications.

The results of sensitivity analysis also showed that interactive effects among parameters tended to become more pronounced when C respiration rates deviated from potential rates because N limited soil organic matter decomposition. It appears that approaches similar to MOD1 and MOD3, implementing variable C/N ratios in their pools, were less sensitive to variation in soil mineral N availability and can be easily applied to a broad range of situations when properly calibrated.

This study has gone beyond the multi-model ensembles, which simulate crop and grassland systems in their integrated structure, but whose scope was not intended to be an exhaustive assessment of key processes. Although the modelling approaches we selected are only a subset of all available C–N modules, they represent a reasonable balance of contrasting approaches, which were implemented in several agricultural system models used worldwide. Our results will be useful for model improvements because modelling approaches are increasingly used to investigate changes in net terrestrial–atmosphere C–N exchanges, and thus evaluate mitigation options to reduce the emissions of greenhouse gases in crops and grasslands.

Supporting Information

Table S1. Main changes applied to the EPIC C–N module.

Table S2. Initialization of models during calibration and sensitivity analysis.

Table S3. List of papers used to define distributions of model parameters (Table 1) and to obtain measured data (Figure S2).

Table S4. Relative root mean squared errors between frequencies of measured and simulated net CO_2 emissions (mg C 100 mg manure C^{-1}) and net N mineralization (mg N 100 mg manure C^{-1}) before and after parameters calibration.

Figure S1. Schematic procedure used to calibrate parameters of models.

Figure S2. (a) Reference datasets of net CO2 emissions and net (b) N mineralization measured in laboratory incubation experiments from manure-amended soils. Continuous black line and symbols indicate the average of all treatments (labels indicate the number of data used to estimate means); dashed black lines indicate 5th and 95th percentiles; continuous grey lines indicate individual treatments (taken from the literature sources reported in Table S3); error bars indicate standard error of the mean.

Figure S3. (a) Uncertainty of net CO_2 emissions (mg C 100 mg manure C^{-1}) and (b) net N mineralization (mg N 100 mg manure C^{-1}) prior to calibration of parameters. On the x-axis the central value of each class is reported.

Figure S4. (a) Sobol first-order sensitivity indices and (b) interaction terms for net CO_2 emissions and net N mineralization calculated for eight dates over the period days 3–180. Results refer to a small initial soil mineral N concentration and manure C to organic N ratio of 34. Only model parameters with at least one first-order index or interaction term >10% are shown. The symbol 'Σ' indicates the sum of first-order sensitivity indices. See Figure 2 for names of the pools and Table 1 for a description of model parameters.

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Figure 1. Flowchart of model analysis by sensitivity analysis. Lower dashed box: traditional approach, consisting of running a sensitivity analysis prior to model calibration. Upper continuous box: work carried out in this study (see the text for details).

Figure 2. Structure of the four models. Rectangles represent C pools, valves represent C rates, arrows represent C flows and dot-ended arrows represent CO_2 emissions. Eff, microbial substrate use efficiency; *FC*, fraction of manure C allocated to labile (FC_{ML}), resistant (FC_{MR}), and very resistant (FC_{MVR}) manure pools. For a description of model parameters refer to Table 1.

Figure 3. (a) Uncertainty of net CO_2 emissions (mg C 100 mg manure C^{-1}) and (b) net N mineralization (mg N 100 mg manure C^{-1}) after calibration of parameters. On the x-axis the central value of each class is given.

Figure 4. Values of first-order decomposition constants for all pools of the four models. The values shown were obtained after multiplying the calibrated values by model-specific modification factors for the specific soil conditions. See Figure 2 for names of the pools. Areas with numbers 1–3 limit the interval of decomposition constants derived from MRT of low molecular weight compounds (1; Glanville *et al*., 2012), cellulose (2; Fioretto *et al*., 2005; Gunina & Kuzyakov, 2015) and lignin (3; Derrien & Amelung, 2011; Fioretto *et al*., 2005).

Figure 5. Sobol first-order sensitivity indices (% of total output variance) for net CO_2 emissions (mg C 100 mg manure C^{-1}) and net N mineralization (NNM; mg N 100 mg manure C^{-1}) calculated for eight dates over the period days 3–180. Results refer to large initial soil mineral N concentration and manure C to organic N ratio equal to 21. Only model parameters with at least one first-order index or interaction term larger than 10% are shown. The symbol 'Σ' indicates the sum of first-order sensitivity indices. See Figure 2 for names of the pools and Table 1 for a description of model parameters.

Figure 6. (a) Sobol first-order sensitivity indices and (b) interaction terms for net CO_2 emissions (mg C 100 mg manure C^{-1}) and net N mineralization (NNM; mg N 100 mg manure C^{-1}) calculated for eight dates over

the period days 3–180 with models MOD1–4. Results refer to small initial soil mineral N concentration and a manure C to organic N ratio equal to 21. Only model parameters with at least one first-order index or interaction term >10% are shown. The symbol 'Σ' indicates the sum of first-order sensitivity indices. See Figure 2 for names of the pools and Table 1 for a description of model parameters.

Figure 1

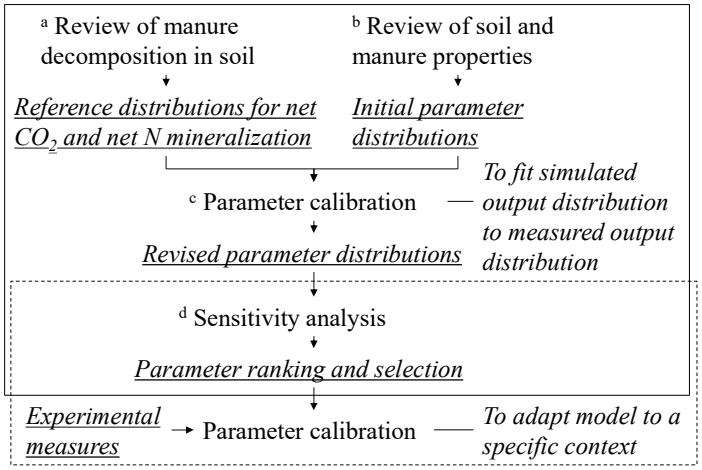
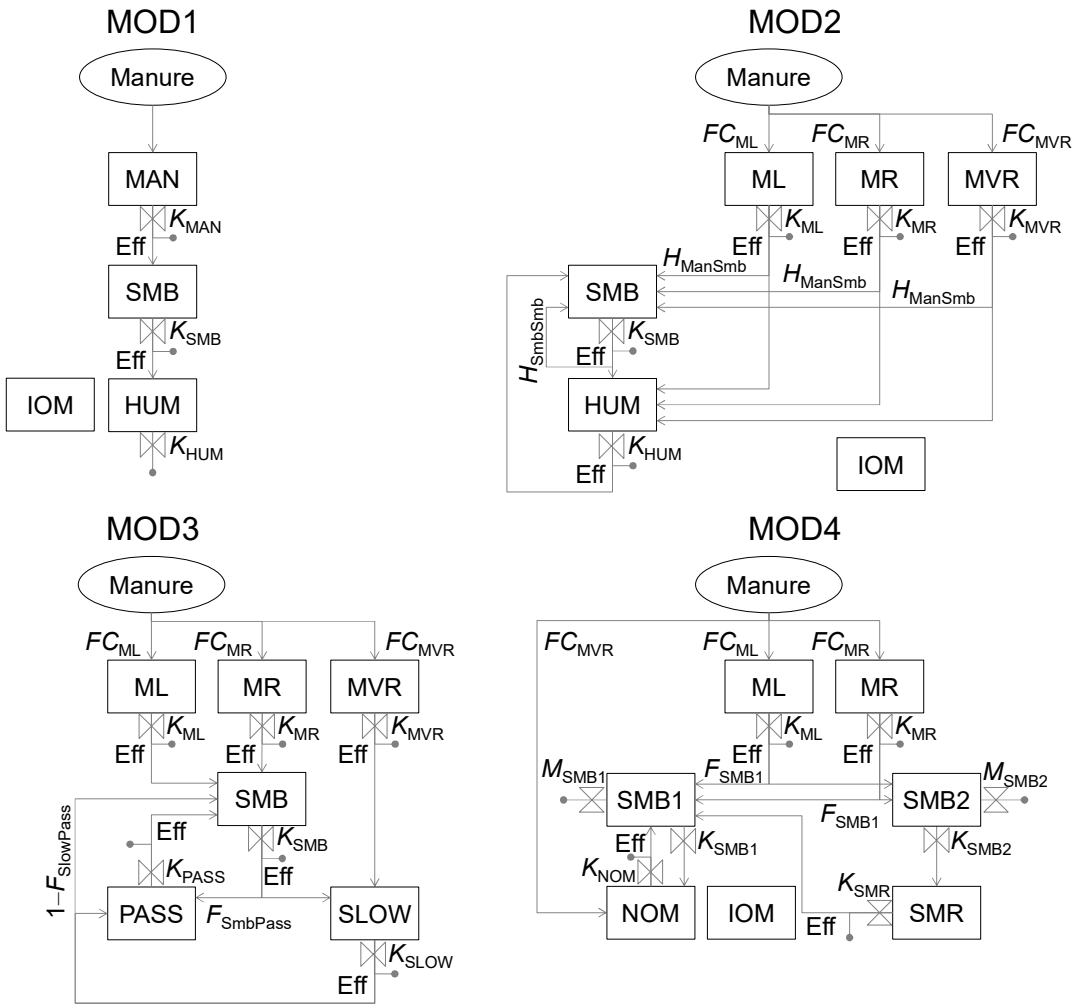

[a] Review of manure decomposition in soil
[b] Review of soil and manure properties
Reference distributions for net CO_2 and net N mineralization
Initial parameter distributions
[c] Parameter calibration
To fit simulated output distribution to measured output distribution
Revised parameter distributions
[d] Sensitivity analysis
Parameter ranking and selection
Experimental measures
Parameter calibration
To adapt model to a specific context

Figure 2



Abbreviations:
MAN, manure; ML, manure labile; MR, manure resistant; MVR, manure very resistant; SMB, soil microbial biomass; SMB1, autochthonous SMB; SMB2, zymogenous SMB; SMR, residues of SMB; HUM and NOM, active (native) stable SOM; SLOW, slow stable SOM; PASS, passive stable SOM; IOM, inert SOM

Figure 3

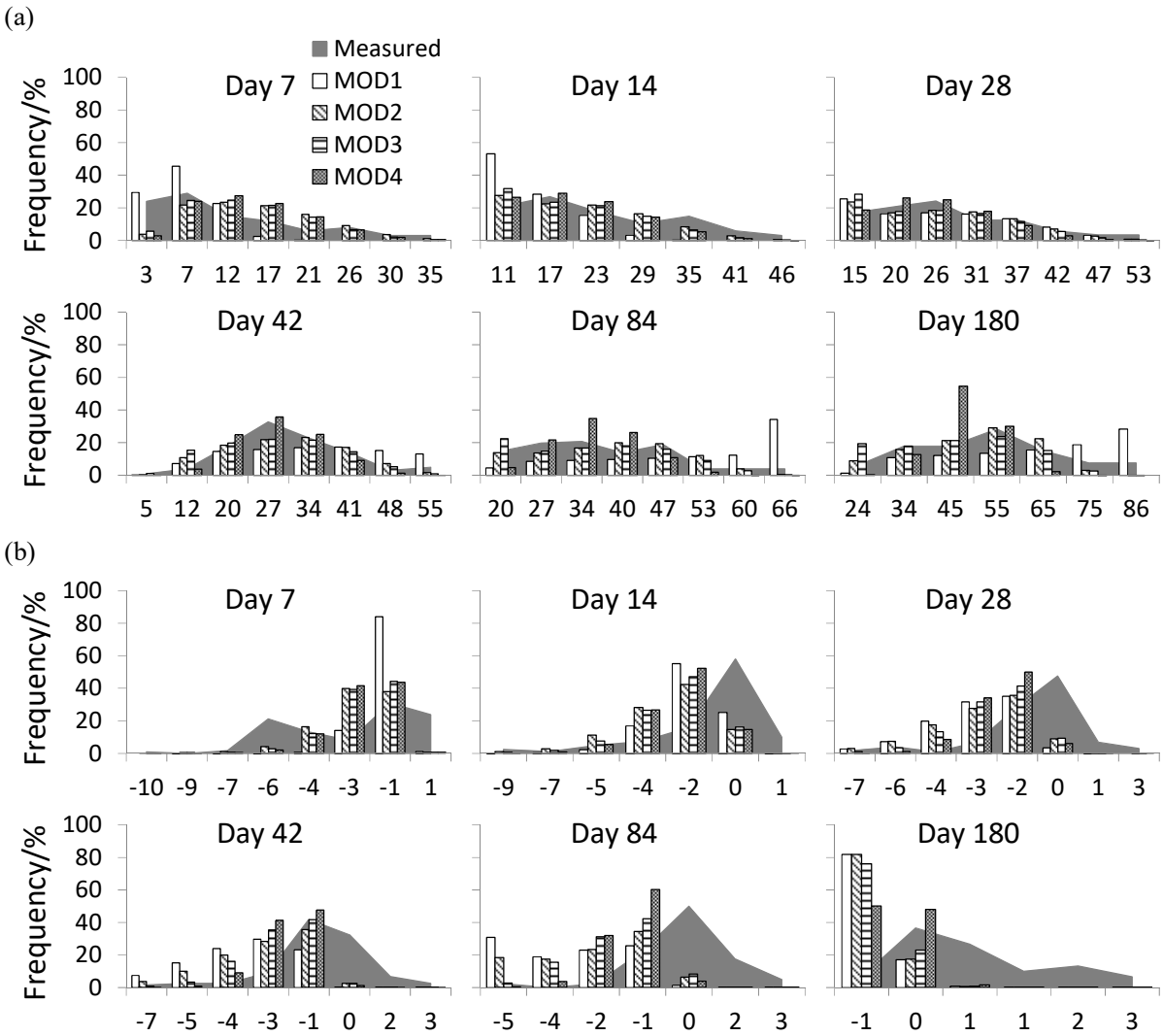
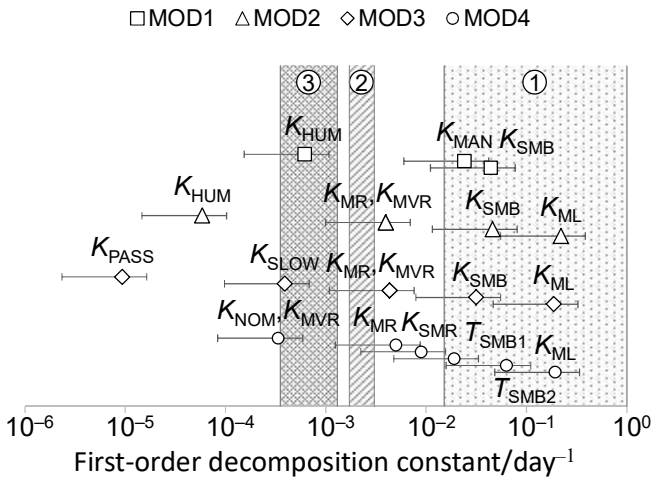

(a)
Measured
MOD1
MOD2
MOD3
MOD4
Frequency/%
Day 7
Day 14
Day 28
Day 42
Day 84
Day 180
(b)
Day 7
Day 14
Day 28
Day 42
Day 84
Day 180

Figure 4


□MOD1 △MOD2 ◇MOD3 ○MOD4
③
②
①
K_{HUM}
K_{MAN} K_{SMB}
K_{HUM}
K_{MR}, K_{MVR}
K_{SMB} K_{ML}
K_{PASS}
K_{SLOW} K_{MR}, K_{MVR}
K_{SMB} K_{ML}
K_{NOM}, K_{MVR}
K_{MR} K_{SMR} T_{SMB1} K_{ML}
T_{SMB2}
10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0}
First-order decomposition constant/day^{-1}

698 Figure 5

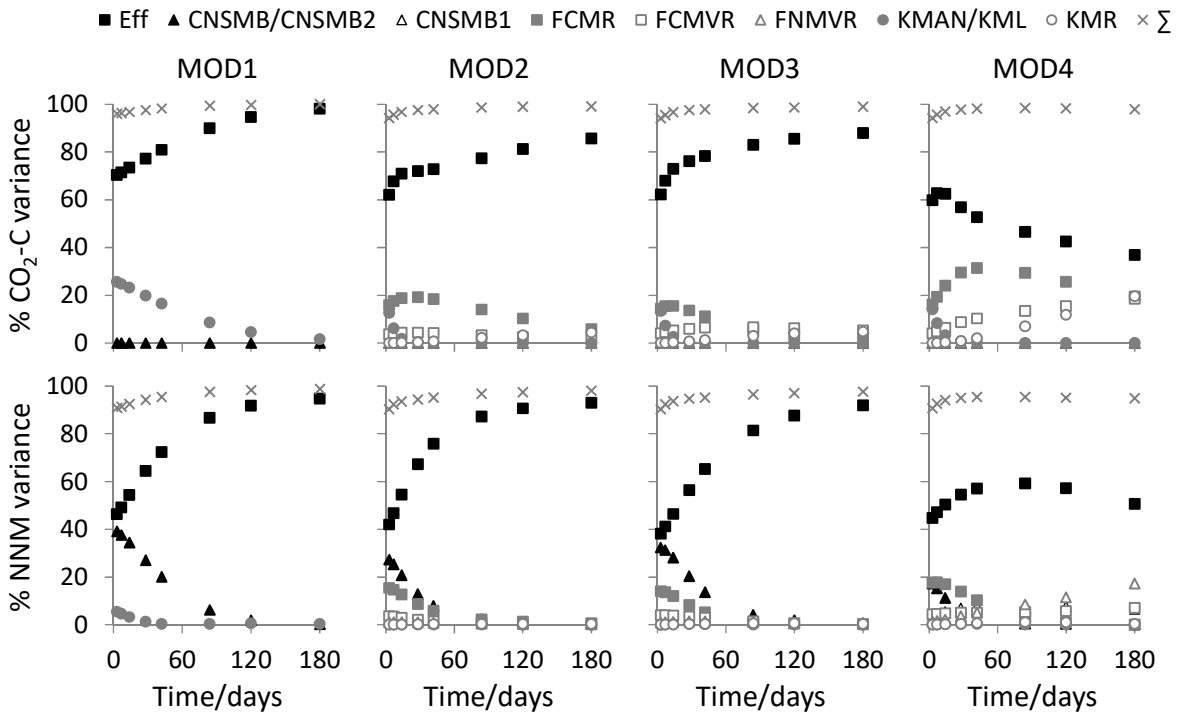


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Figure 6

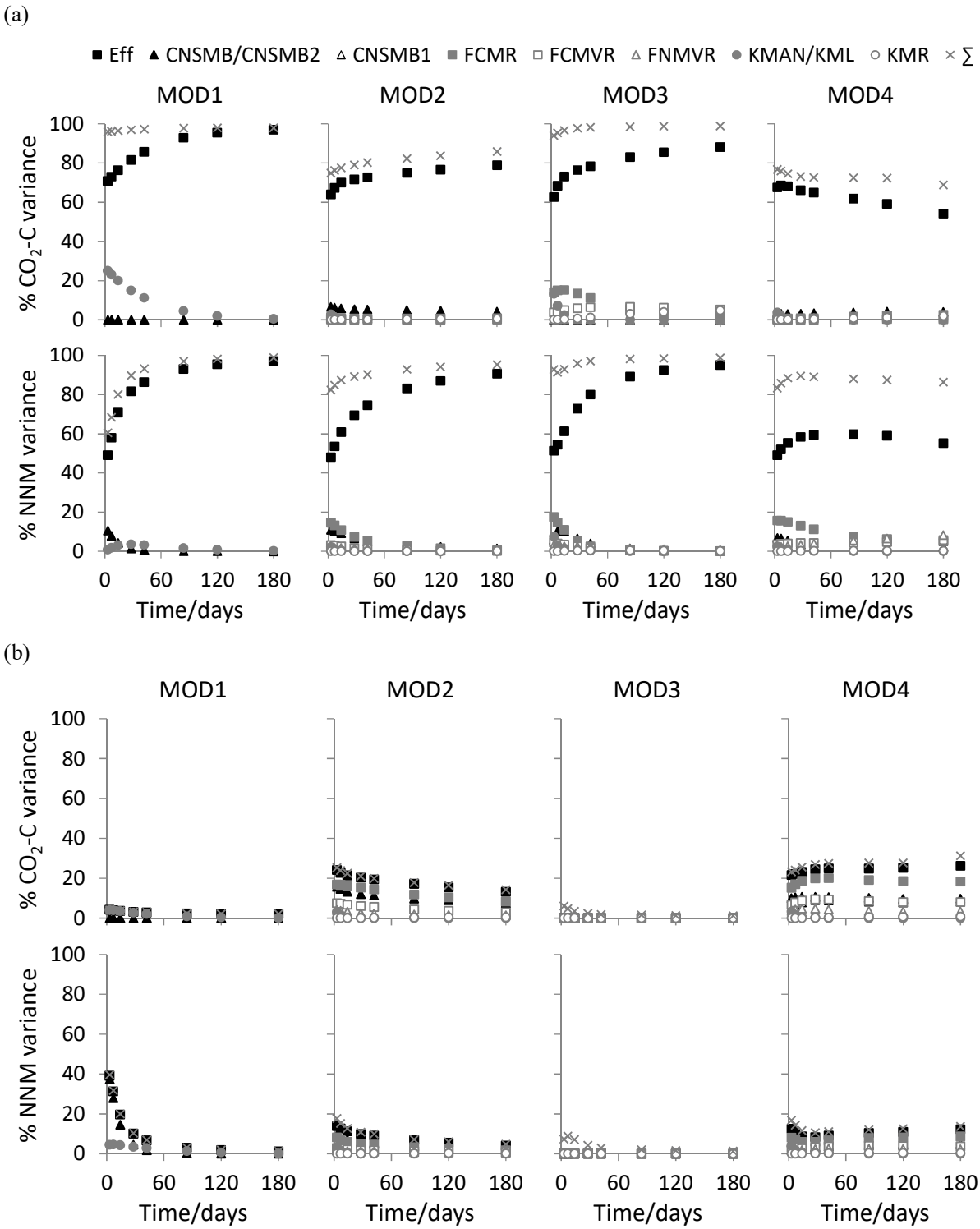

(a)
Eff
CNSMB/CNSMB2
CNSMB1
FCMR
FCMVR
FNMVR
KMAN/KML
KMR
∑
MOD1
MOD2
MOD3
MOD4
% CO_2-C variance
% NNM variance
Time/days
(b)
MOD1
MOD2
MOD3
MOD4
% CO_2-C variance
% NNM variance
Time/days

Table 1. Parameters of the four models compared and their sampling distributions after calibration. For a description of C pools refer to Figure 2.

Parameter	Name	References[a]	Model			
			MOD1	MOD2	MOD3	MOD4
Parameters of soil microbial biomass pools						
Substrate use efficiency / mg C mg C^{-1}	Eff	l	$U(0.25–0.87)$[b]	$U(0.25–0.87)$	$U(0.25–0.87)$	$U(0.25–0.87)$
C to N ratio / mg C mg N^{-1}						
SMB	CN_{SMB}	z	$N(6.54,2.46)$[c]	$N(6.54,2.46)$	$N(6.54,2.46)$	–
SMB1	CN_{SMB1}	Z	–	–	–	$N(6.54,2.46)$
SMB2	CN_{SMB2}	z	–	–	–	$N(6.54,2.46)$
First-order decomposition constant / day^{-1}						
SMB	K_{SMB}	Optimized	$N(2.79\cdot10^{-2},4.85\cdot10^{-5})$	$N(1.18\cdot10^{-1},8.75\cdot10^{-4})$	$N(7.36\cdot10^{-2},3.39\cdot10^{-4})$	–
SMB1 (total turnover)	T_{SMB1}	e,q	–	–	–	$N(1.26\cdot10^{-2},9.90\cdot10^{-6})$
SMB2 (total turnover)	T_{SMB2}	Optimized	–	–	–	$N(4.17\cdot10^{-2},1.09\cdot10^{-4})$
SMB1 (decay)	K_{SMB1}	q,r	–	–	–	Calculated[d]
SMB2 (decay)	K_{SMB2}	q,r	–	–	–	Calculated[d]
SMB1 (maintenance)	M_{SMB1}	q,r	–	–	–	Calculated[d]
SMB1 (maintenance)	M_{SMB2}	q,r	–	–	–	Calculated[d]
Turnover ratio of SMB1	R_{SMB1}	q,r	–	–	–	Calculated[d]
Turnover ratio of SMB2	R_{SMB2}	r	–	–	–	$N(5.29\cdot10^{-1},1.94\cdot10^{-3})$
Parameters of native ("humified") soil organic matter pools						
C to N ratio / mg C mg N^{-1}						
HUM	CN_{HUM}	d,t	$N(9.52,0.91)$	$N(6.00,0.36)$	–	–
SLOW	CN_{SLOW}	k	–	–	$N(12.00,1.44)$	–
PASS	CN_{PASS}	k	–	–	$N(7.00,0.49)$	–
SMR	CN_{SMR}	e,r	–	–	–	$N(7.16,0.51)$
NOM	CN_{NOM}	q	–	–	–	$N(10.00,1.00)$
First-order decomposition constant / day^{-1}						
HUM	K_{HUM}	d,t	$N(3.48\cdot10^{-4},7.58\cdot10^{-9})$	$N(1.50\cdot10^{-4},1.41\cdot10^{-9})$	–	–
SLOW	K_{SLOW}	k	–	–	$N(5.00\cdot10^{-4},1.56\cdot10^{-8})$	–
PASS	K_{PASS}	k	–	–	$N(1.20\cdot10^{-5},9.00\cdot10^{-12})$	–
SMR	K_{SMR}	e,r	–	–	–	$N(3.54\cdot10^{-3},7.83\cdot10^{-7})$
NOM	K_{NOM}	q	–	–	–	$N(1.33\cdot10^{-4},1.10\cdot10^{-9})$
Fraction of decomposed manure directed to SMB / mg C mg C^{-1}	H_{ManSmb}	t	–	$U(8.10\cdot10^{-1}–9.90\cdot10^{-1})$	–	–

Parameter	Name	References[a]	Model			
			MOD1	MOD2	MOD3	MOD4
Fraction of recycled dead SMB / mg C mg C^{-1}	H_{SmbSmb}	t	–	$U(5.40\cdot10^{-1}–6.60\cdot10^{-1})$	–	–
Fraction of decomposed SMB directed to PASS / mg C mg C^{-1}	$F_{SmbPass}$	k	–	–	0.0094/Eff	–
Fraction of decomposed SLOW directed to PASS / mg C mg C^{-1}	$F_{SlowPass}$	k	–	–	0.0048/Eff	–
Fraction of decomposed manure directed to SMB1 / mg C mg C^{-1}	F_{SMB1}	q	–	–	–	$N(3.16\cdot10^{-1},6.23\cdot10^{-3})$
Parameters of manure pools						
C to ON ratio / mg C mg ON^{-1}	CN_{MAN}	a–c,f–j,m–p,s,u–y	$N(21.00,40.96)$	$N(21.00, 40.96)$	$N(21.00, 40.96)$	$N(21.00, 40.96)$
Manure C partitioning / mg C mg manure C^{-1}						
ML	FC_{ML}	a–c,f–j,m–p,s,u–y	–	$1–FC_{MR}–FC_{MVR}$	$1–FC_{MR}–FC_{MVR}$	$1–FC_{MR}–FC_{MVR}$
MR	FC_{MR}	a–c,f–j,m–p,s,u–y	–	$N(0.440,0.007)$	$N(0.440,0.007)$	$N(0.440,0.007)$
MVR	FC_{MVR}	a–c,f–j,m–p,s,u–y	–	$N(0.170,0.002)$	$N(0.170,0.002)$	$N(0.170,0.002)$
Manure ON partitioning / mg N mg manure ON^{-1}						
ML	FON_{ML}	a–c,f–j,m–p,s,u–y	–	$1–FON_{MR}–FON_{MVR}$	$1–FON_{MR}–FON_{MVR}$	$1–FON_{MR}–FON_{MVR}$
MR	FON_{MR}	a–c,f–j,m–p,s,u–y	–	$N(0.170,0.002)$	$N(0.170,0.002)$	$N(0.170,0.002)$
MVR	FON_{MVR}	a–c,f–j,m–p,s,u–y	–	$N(0.140,0.002)$	$N(0.140,0.002)$	$N(0.140,0.002)$
First-order decomposition constant / day^{-1}						
MAN	K_{MAN}	Optimized	$N(1.51\cdot10^{-2},1.43\cdot10^{-5})$	–	–	–
ML	K_{ML}	Optimized	–	$N(5.65\cdot10^{-1},2.00\cdot10^{-2})$	$N(2.40\cdot10^{-1},3.59\cdot10^{-3})$	$N(7.66\cdot10^{-2},3.67\cdot10^{-4})$
MR	K_{MR}	Optimized	–	$N(1.02\cdot10^{-2},6.45\cdot10^{-6})$	$N(1.28\cdot10^{-2},1.03\cdot10^{-5})$	$N(1.98\cdot10^{-3},2.44\cdot10^{-7})$
MVR	K_{MVR}	Optimized	–	$N(1.02\cdot10^{-2},6.45\cdot10^{-6})$	Equal to K_{MR}	Equal to K_{NOM}

[a]References listed in Table S3 (Supporting Information): a, Althaus *et al*. (2013); b, Amon *et al*. (2007); c, Bechini & Marino (2009); d, Brisson *et al*. (2009); e, Cavalli & Bechini (2011); f, Cavalli *et al*. (2014; 2016; 2017); g, Chadwick *et al*. (2000); h, Fuccella *et al*. (2012); i, Kirchmann & Lundvall (1993); j, Kyvsgaard *et al*. (2000); k, Izaurralde *et al*. (2006); l, Manzoni *et al*. (2012); m, Marino *et al*., 2008; n, Morvan *et al*. (2006); o, Morvan & Nicolardot (2009); p, Peters & Jensen (2011); q, Petersen *et al*. (2005a); r, Petersen *et al*. (2005b); s, Powell *et al*. (2006); t, Probert *et al*.

(1998); u, Reeves III & Van Kessel (2002); v, Sørensen (1998); w, Sørensen & Fernández (2003); x, Sørensen *et al*. (2003); y, Triolo *et al*. (2011); z, Xu *et al*. (2013).

[b]Uniform distribution; lower and upper limits are indicated in parenthesis.

[c]Normal distribution; mean and variance are indicated in parenthesis.

[d]Calculated according to Petersen *et al*. (2005a and 2005b).

Table S1. Main changes applied to the EPIC C–N module.

Model pool	Change
Structural litter pool (MR + MVR)	The pool was split into two pools, representing the lignin-like and cellulose-like fractions, respectively. As in the original module (Izaurralde *et al*., 2006), rate of turnover of both pools was affected by the percentage of the lignin-like fraction in 'structural litter' (MR + MVR; Figure 2).
Leached organic matter pool	The LEACH pool (Izaurralde *et al*., 2006), which estimates the fraction of C lost by leaching, was not used, given the closed system in which C and N fluxes are assessed in this study.
Microbial biomass (SMB), slow (SLOW) and passive (PASS) stable organic matter	Parameters (decomposition constants and partitioning factors) of the fluxes from microbial biomass to SLOW and PASS pools and CO_2, and from SLOW to PASS and CO_2 (Figure 2) were redefined according to original parameter values to obtain fluxes with a common structure.

Table S2. Initialization of models during calibration and sensitivity analysis.

Parameter or variable	Value / unit	Notes
Soil water content	–0.05 / MPa	No limitation to microbial activity. Soil water potential was used instead of soil water content because it is frequently the reference variable used by models to describe water availability to microbes.
Soil temperature	20 / °C	Average value from reviewed experiments.
Soil texture	Loam / –	To achieve an average effect of soil texture on SOM decomposition.
Manure C applied	1000 / mg C kg^{-1} soil	–
All soil C and N pools	0 / mg C and N kg^{-1} soil	Model results were net of unamended soil (manure was the only source of C and ON, according to the definition of net model outputs), and the occurrence of priming effects was excluded.
Soil mineral N	100 / mg N kg^{-1} soil	If not differently specified, the addition of 100 mg N kg^{-1} soil avoids the limiting effect of N shortage on C decomposition.
Time step	0.25 / days	–

Table S3. List of papers used to define distributions of model parameters (Table 1) and to obtain measured data (Figure S2).

Reference	Note[a]
Alburquerque, J.A., de la Fuente, C. & Bernal, M.P. 2012. Chemical properties of anaerobic digestates affecting C and N dynamics in amended soils. *Agriculture, Ecosystems & Environment*, **160**, 15–22.	b
Althaus, B., Papke, G. & Sundrum, A. 2013. Technical note: use of near infrared reflectance spectroscopy to assess nitrogen and carbon fractions in dairy cow feces. *Animal Feed Science and Technology*, **185**, 53–59.	a
Amon, T., Amon, B., Kryvoruchko, V., Zollitsch, W., Mayer, K. & Gruber, L. 2007. Biogas production from maize and dairy cattle manure–Influence of biomass composition on the methane yield. *Agriculture, Ecosystems & Environment*, **118**, 173–182.	a
Atallah, T., Andreux, F., Choné, T. & Gras, F. 1995. Effect of storage and composting on the properties and degradability of cattle manure. *Agriculture, Ecosystems & Environment*, **54**, 203–213.	b
Bechini, L. & Marino, P. 2009. Short-term nitrogen fertilizing value of liquid dairy manures is mainly due to ammonium. *Soil Science Society of America Journal*, **73**, 2159–2169.	a,b
Brisson-Cohen, N., Launay, M., Mary, B. & Beaudoin, N. 2009. Nitrogen transformations. In: *Conceptual Basis, Formalisations and Parameterization of the Stics Crop Model* (eds N. Brisson, M. Launay, B. Mary & N. Beaudoin), pp. 141–166. Versailles Cedex, France.	a
Calderón, F.J., McCarty, G.W. & Reeves III, J.B. 2005. Analysis of manure and soil nitrogen mineralization during incubation. *Biology and Fertility of Soils*, **4**, 328–336.	b
Cavalli, D. & Bechini, L. 2011. Sensitivity analysis and calibration of CN-SIM to simulate the mineralisation of liquid dairy manures. *Soil Biology & Biochemistry*, **43**, 1207–1219.	a
Cavalli, D., Cabassi, G., Bechini, L., Ditto, D. & Marino, P. 2014. Release of plant available nitrogen from the solid fraction of two digestates. In: *The Nitrogen Challenge: Building a Blueprint for Nitrogen Use Efficiency and Food Security* (ed. C.M.d.S Cordovil), pp. 55–56. RAMIRAN – Network on Recycling of Agricultural, Municipal and Industrial Residues in Agriculture, Lisbon, Portugal.	a,b
Cavalli, D., Cabassi, G., Borrelli, L., Geromel, G., Bechini, L., Degano, L. *et al*. 2016. Nitrogen fertilizer replacement value of undigested liquid cattle manure and digestates. *European Journal of Agronomy*, **73**, 34–41.	a
Cavalli, D., Corti, M., Baronchelli, D., Bechini, L. & Marino Gallina, P. 2017. CO_2 emissions and mineral nitrogen dynamics following application to soil of undigested liquid cattle manure and digestates. *Geoderma*, **308**, 26–35.	a,b
Chadwick, D.R., John, F., Pain, B.F., Chambers, B.J. & Williams, J. 2000. Plant uptake of nitrogen from the organic nitrogen fraction of animal manures: a laboratory experiment. *Journal of Agricultural Science*, **134**, 159–168.	a
Delin, S., Stenberg, B., Nyberg, A. & Brohede, L. 2012. Potential methods for estimating nitrogen fertilizer value of organic residues. *Soil Use and Management*, **28**, 283–291.	b
Fuccella, R., Cabassi, G. & Marino, P. 2012. Determination of nitrogen concentration in pig slurries using NIR spectroscopy. In: *Innovations for Sustainable Use of Nitrogen Resources* (eds K.G. Richards, O. Fenton & C.J. Watson), pp. 299–300. 17th International Nitrogen Workshop, Wexford, Ireland.	a
Izaurralde, R.C., Williams, J.R., McGill, W.B., Rosenberg, N.J. & Quiroga Jakas, M.C. 2006. Simulating soil C dynamics with EPIC: model description and testing against long-term data. *Ecological Modelling*, **192**, 362–84.	a
Kirchmann, H. 1991. Carbon and nitrogen mineralization of fresh, aerobic and anaerobic animal manures during incubation with soil. *Swedish Journal of Agricultural Research*, **21**, 165–173.	b
Kirchmann, H. & Lundvall, A. 1993. Relationship between N immobilization and volatile fatty acids in soil after application of pig and cattle slurry. *Biology and Fertility of Soils*, **15**, 161–164.	a,b
Kyvsgaard, P., Sørensen, P., Møller, E. & Magid, J. 2000. Nitrogen mineralization from sheep faeces can be predicted from the apparent digestibility of the feed. *Nutrient Cycling in Agroecosystem*, **57**, 207–214.	a,b
Manzoni, S., Taylor, P., Richter, A., Porporato, A. & Ågren, G.I. 2012. Environmental and stoichiometric controls on microbial carbon-use efficiency in soils. *New Phytology*, **196**, 79–91.	a

Reference	Note[a]
Marino, P., De Ferrari, G. & Bechini, L. 2008. Description of a sample of liquid dairy manures and relationships between analytical variables. *Biosystems Engineering*, **100**, 256–265.	a
Morvan, T., Nicolardot, B. & Péan, L. 2006. Biochemical composition and kinetics of C and N mineralization of animal wastes: a typological approach. *Biology and Fertility of Soils*, **42**, 513–522.	a
Morvan, T. & Nicolardot, B. 2009. Role of organic fractions on C decomposition and N mineralization of animal waste in soil. *Biology and Fertility of Soils*, **45**, 477–486.	a,b
Peters, K. & Jensen, L.S. 2011. Biochemical characteristics of solid fractions from animal slurry separation and their effects on C and N mineralization in soil. *Biology and Fertility of Soils*, **47**, 447–455.	a,b
Petersen, B.M., Berntsen, S., Hansen, S., Jensen, L.S. 2005a. CN-SIM: a model for the turnover of soil organic matter. I. Long-term carbon and radiocarbon development. *Soil Biology & Biochemistry*, **37**, 359–374.	a
Petersen, B.M., Jensen, L.S., Hansen, S., Pedersen, A., Henriksen, T.M., Sørensen, P. *et al*. 2005b. CN-SIM: a model for the turnover of soil organic matter. II. Short-term carbon and nitrogen development. *Soil Biology & Biochemistry*, **37**, 375–393.	a
Powell, J.M., Wattiaux, M.A., Broderick, G.A., Moreira, V.R. & Casler, M.D. 2006. Dairy diet impacts on fecal chemical properties and nitrogen cycling in soils. *Soil Science Society of America Journal*, **70**, 786–794.	a
Probert, M.E., Dimes, J.P., Keating, B.A., Dalal, R.C. & Strong, W.M. 1998. APSIM's water and nitrogen modules and simulation of the dynamics of water and nitrogen in fallow systems. *Agricultural Systems*, **56**, l–28.	a
Reeves III, J.B. & Van Kessel, J.A.S. 2002. Influence of ash on the fiber composition of dried dairy manures. *Environmental Pollution*, **120**, 239–244.	a
Sørensen, P. 1998. Effects of storage time and straw content of cattle slurry on the mineralization of nitrogen and carbon in soil. *Biology and Fertility of Soils*, **27**, 85–91.	a
Sørensen, P. & Fernández, J.A. 2003. Dietary effects on the composition of pig slurry and on the plant utilization of pig slurry nitrogen. *Journal of Agricultural Science*, **140**, 343–55.	a,b
Sørensen, P., Weisbjerg, M.R. & Lund, P. 2003. Dietary effects on the composition and plant utilization of nitrogen in dairy cattle manure. *Journal of Agricultural Science*, **141**, 79–91.	a,b
Thomsen, I.K. & Olesen, J.E. 2000. C and N mineralization of composted and anaerobically stored ruminant manure in differently textured soils. *Journal of Agricultural Sciences*, **135**, 151–159.	b
Thomsen, I.K., Schjønning, P., Olesen, J.E. & Christensen, B.T. 2003. C and N turnover in structurally intact soils of different texture. *Soil Biology & Biochemistry*, **35**, 765–774.	b
Thomsen, I.K., Olesen, J.E., Møller, H.B., Sørensen, P. & Christensen, B.T. 2013. Carbon dynamics and retention in soil after anaerobic digestion of dairy cattle feed and feces. *Soil Biology & Biochemistry*, **58**, 82–87.	b
Triolo, J.M., Sommer, S.G., Møller, H.B., Weisbjerg, M.R. & Jiang, X.Y. 2011. A new algorithm to characterize biodegradability of biomass during anaerobic digestion: influence of lignin concentration on methane production potential. *Bioresource Technology*, **102**, 9395–9402.	a
Xu, X., Thornton, P.E. & Post, W.M. 2013. A global analysis of soil microbial biomass carbon, nitrogen and phosphorus in terrestrial ecosystems. *Global Ecology and Biogeography*, **22**, 737–749.	a

[a]Papers used to define distributions of model parameters (Table 1) are identified by 'a'; papers that were used to obtain net CO_2 and net N mineralization measurements (Figure S2) are identified by 'b'. Some papers were used for both purposes (a,b).

Table S4. Relative root mean squared errors between frequencies of measured and simulated net CO_2 emissions (mg C 100 mg manure C^{-1}) and net N mineralization (mg N 100 mg manure C^{-1}) prior and after parameters calibration.

Variable	Day	Errors prior calibration				Errors after calibration			
		MOD1	MOD2	MOD3	MOD4	MOD1	MOD2	MOD3	MOD4
Net CO_2 Emissions	3	11	13	27	18	24	5	5	5
	7	15	7	13	17	8	10	9	10
	14	15	10	27	12	14	5	6	6
	28	18	6	18	13	5	4	5	4
	42	20	8	12	16	8	5	6	4
	84	18	7	9	16	14	5	5	8
	120	17	7	6	20	15	6	5	9
	180	12	8	9	18	11	5	6	16
Net N Mineralization	3	25	15	13	25	6	22	20	22
	7	15	18	24	17	22	15	16	17
	14	26	25	15	26	20	21	21	23
	28	26	22	19	21	19	17	17	19
	42	25	24	18	19	18	15	15	16
	84	28	34	26	26	25	22	22	26
	120	30	40	30	20	26	23	20	20
	180	36	43	41	20	34	34	32	22

Main procedure (OMNIOPT genetic algorithm)

Initial parent population P:

- create n (48÷80) individuals, each with a vector **x** of size d (=number of μ, 2–4).
- initialize **x** according to Latin hypercube sampling.
- divide P into s (=16) groups of v individuals ($v=d+1$ and $n=s\times v$).
- **Call Procedure 1**.
- update P and calculate fitness (rank-based).

At each generation g (1–4):

- create an offspring population C of size n from P.
- divide C into s groups of v individuals.
- **Call Procedure 1**.
- update C and create a mixed population $M=P+C$.
- calculate fitness and select best n individuals as new P.

Procedure 1 (Nelder-Mead algorithm)

Initial s (=16) simplexes:

- for each simplex, create v vertexes, each with a vector **x** of size d.
- initialize **x** with values provided by the genetic algorithm.
- evaluate vertexes of each simplex (**call Procedure 2**).

At each iteration i (1–15):

- evaluate new vertexes (**call Procedure 2**).
- stop if simplex collapsed or maximum number of iteration was reached.

Procedure 2 (Objective function evaluation)

At each function evaluation:

- create 4 vectors **x**, **y**, **l** and **u** of size d for distributions' parameters μ, σ (=0.25μ), lower and upper limits (=$\mu\pm3\sigma$), respectively.
- estimate simulated net CO_2 and NNM uncertainty at each date (**call Procedure 3**).
- calculate errors (RMSE) between simulated and observed frequencies of net CO_2 and NNM for the 8 dates.
- the function value is the average of all RMSEs.

Procedure 3 (Model outputs uncertainty)

For each iteration j (1–2048):

- initialize a vector **z** of size d with values uniformly distributed in the range 0–1 (Sobol' sequence generator).
- initialize a vector **z'** of model parameters normally distributed (μ, σ) using inverse cdf.
- run the model with generated parameters **z'**.

Figure S1. Schematic procedure used to calibrate parameters of models.

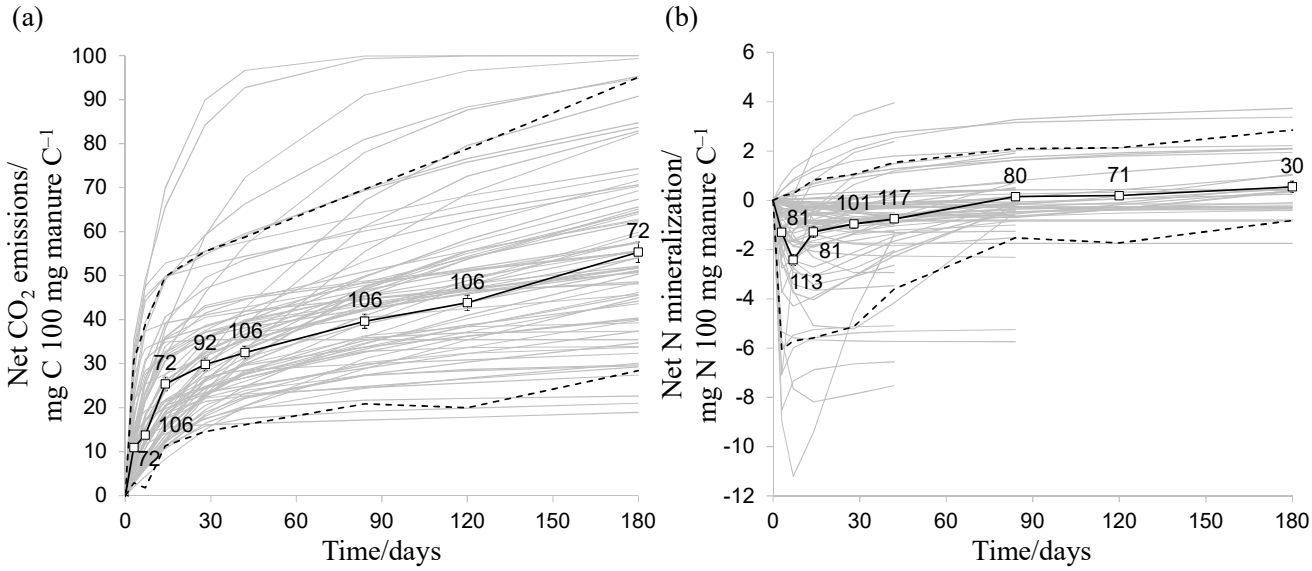


Figure S2. (a) Reference datasets of net CO_2 emissions and net (b) N mineralization measured in laboratory incubation experiments from manure-amended soils. Continuous black line and symbols indicate the average of all treatments (labels indicate the number of data used to estimate means); dashed black lines indicate 5th and 95th percentiles; continuous grey lines indicate individual treatments (taken from the literature sources reported in Table S3); error bars indicate standard error of the mean.

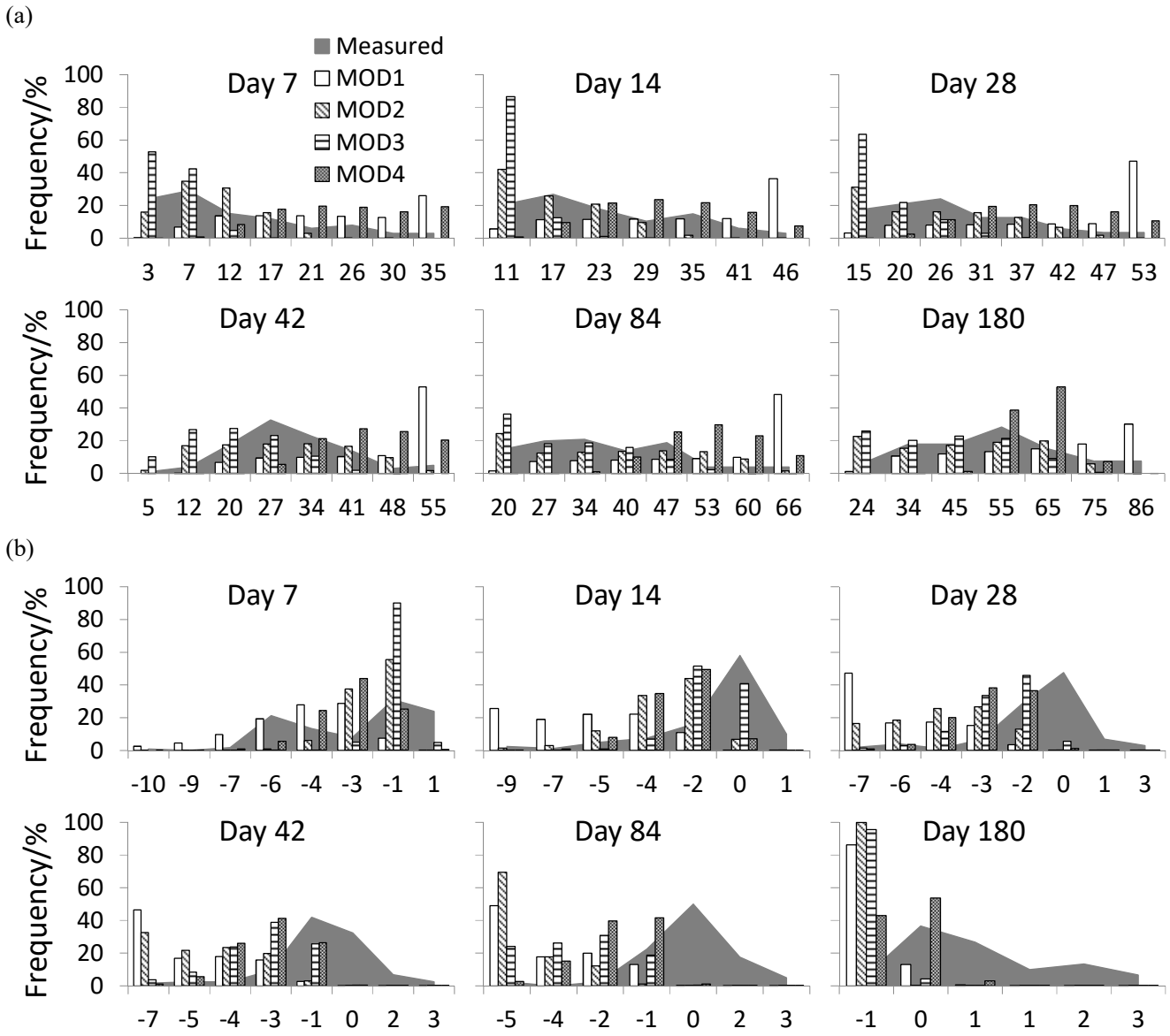
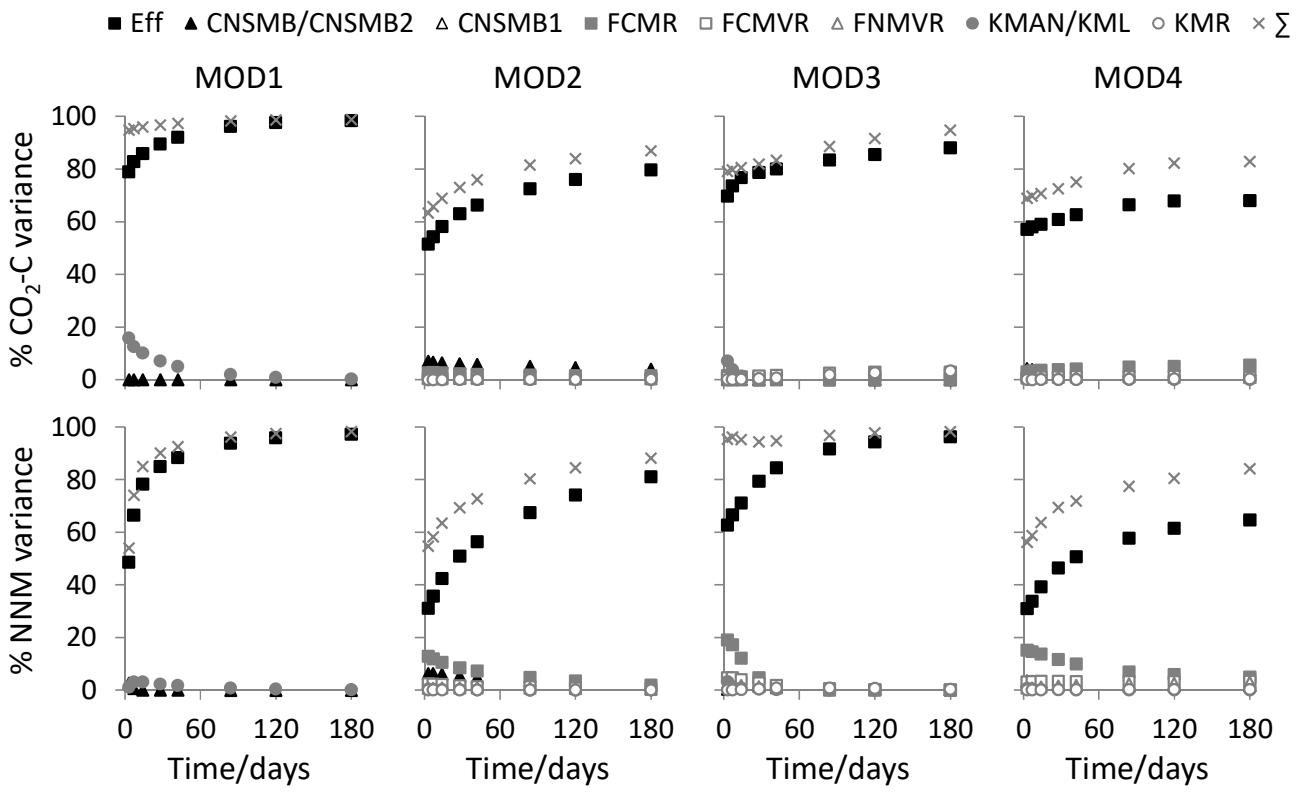

(a)
Measured
MOD1
MOD2
MOD3
MOD4
Day 7
Day 14
Day 28
Day 42
Day 84
Day 180
Frequency/%
100
80
60
40
20
0
3 7 12 17 21 26 30 35
11 17 23 29 35 41 46
15 20 26 31 37 42 47 53
5 12 20 27 34 41 48 55
20 27 34 40 47 53 60 66
24 34 45 55 65 75 86
(b)
Day 7
Day 14
Day 28
Day 42
Day 84
Day 180
-10 -9 -7 -6 -4 -3 -1 1
-9 -7 -5 -4 -2 0 1
-7 -6 -4 -3 -2 0 1 3
-7 -5 -4 -3 -1 0 2 3
-5 -4 -2 -1 0 2 3
-1 0 1 1 2 3

Figure S3. (a) Uncertainty of net CO_2 emissions (mg C 100 mg manure C^{-1}) and net (b) N mineralization (mg N 100 mg manure C^{-1}) prior calibration of parameters. On the x-axis the central value of each class is reported.

(a)


Eff
CNSMB/CNSMB2
CNSMB1
FCMR
FCMVR
FNMVR
KMAN/KML
KMR
∑
MOD1
MOD2
MOD3
MOD4
% CO2-C variance
% NNM variance
100
80
60
40
20
0
0
60
120
180
Time/days

(b)

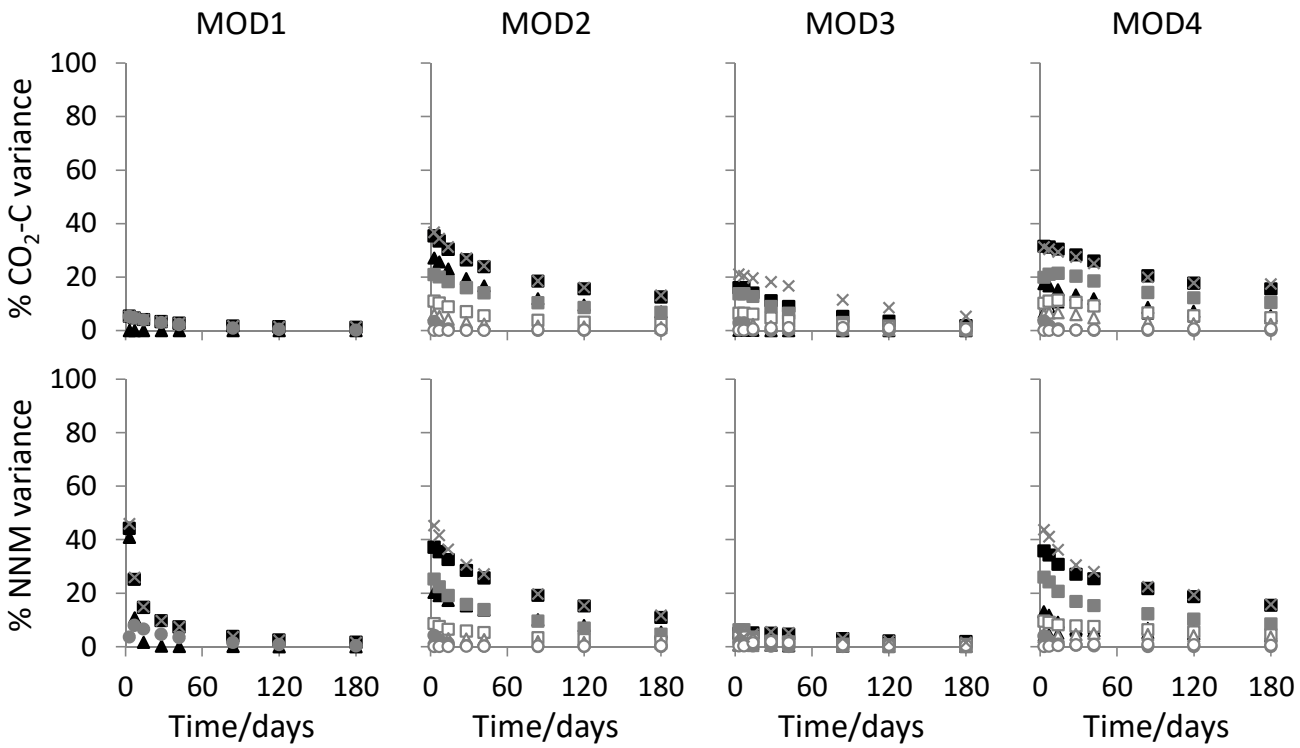


Figure S4. Sobol first-order sensitivity indices and (b) interaction terms for net CO_2 emissions (mg C 100 mg manure C^{-1}) and net N mineralization (NNM; mg N 100 mg manure C^{-1}) calculated for eight dates over the period days 3–180 with models MOD1–4. Results refer to small initial soil mineral N concentration and manure C to organic N ratio equal to 34. Only model parameters with at least one first-order index or interaction term >10% are shown. The symbol Σ indicates the sum of first-order sensitivity indices. See Figure 2 for names of the pools and Table 1 for a description of model parameters.

29